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Part I. Intramolecular energy transfer across an ester bridge: A study of the sphere of quenching model. Part II. The stereochemistry of 4-benzoyl-2,3-diazabicyclo[2.2.2]oct-2-ene

Waller, Andrew Stuart, M.A.

Rice University, 1986
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Part I
Intramolecular Energy Transfer across an Ester Bridge: A Study of the Sphere of Quenching Model

Part II
The Stereochemistry of 4-benzoyl-2,3-diazabicyclo[2.2.2]oct-2-ene

by

ANDREW S. WALLER

A THESIS SUBMITTED
IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE

MASTER OF ARTS

APPROVED, THESIS COMMITTEE:

Paul S. Engel, Professor of Chemistry
Chairman

W. E. Billups, Professor of Chemistry

F. Barry Dunning, Professor of Space Physics

HOUSTON, TEXAS

August 8, 1986
ABSTRACT

Part I
Intramolecular Energy Transfer across an Ester Bridge: A Study of the Sphere of Quenching Model

Part II
The Stereochemistry of 4-benzoyl-2,3-diazabicyclo[2.2.2]oct-2-ene
by
Andrew S. Waller

Part I

A series of bichromophoric molecules linked by an ester bridge is synthesized, and their photochemical and intramolecular energy transfer properties are examined. If benzophenone and naphthalene are held approximately 10 Å apart by this ester bridge rather than by an alkyl chain, intramolecular energy transfer is only 93% to 97% complete in a frozen glass, rather than 100% complete. This value shows the previous critical radius of 13 Å from the sphere of quenching model to be too long. The reason and rationalization for this loss of energy transfer efficiency is explored. Several irradiation experiments are also conducted, studying both intramolecular and intermolecular energy transfer along competing pathways.
Part II

The stereochemistry of 4-benzoyl-2,3-diazabicyclo[2.2.2]oct-2-ene is studied using various two-dimensional NMR techniques.
to Mom and Dad

for much careful nurturing
Acknowledgements

I would like to thank Dr. Paul S. Engel for his many helpful ideas and suggestions over the past two years. His immense patience and knowledge made this research both enjoyable and educational and contributed greatly to my understanding of photochemistry.

Thanks also go to my labmates Greg Bodager, Yan-Qui Chen, Gregor Marschke, and last but not least, John Scholz. Their assistance and continued good humor were most appreciated.

A special thanks goes to my dear wife, Hilary, for her willingness to become involved in the maelstrom at the last minute.
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PART I

Intramolecular Energy Transfer

across an Ester Bridge:

A Study of the Sphere of Quenching Model
INTRODUCTION

Electronic triplet energy transfer (ET), the ability of a molecule in an excited triplet state to transfer its energy to a nearby acceptor molecule with a lower triplet energy, has been a topic that has fascinated photochemists for the past several decades. Although the exact mechanism for ET is unknown, this phenomenon has been readily observed in a number of photochemical experiments. Generally, the two compounds are held rigidly in a frozen glass and irradiated to excite the donor molecule, which then transfers its energy to a nearby acceptor.

An early study was conducted by V. L. Ermolaev using benzophenone and naphthalene as the donor and acceptor, respectively. These two compounds were dissolved in a 2:1 mixture of ethyl alcohol and diethyl ether, frozen to a glass at liquid nitrogen temperatures (77°K), and irradiated at 365 nm, so as to excite only the benzophenone molecules present in the sample. Despite the fact that the naphthalene had no absorption in this region, naphthalene phosphorescence emission was observed. The explanation for this result involved intermolecular ET from the benzophenone to the naphthalene. The benzophenone was excited from
its ground state to its first singlet state by the 365 nm light, underwent intersystem crossing to the triplet state, and finally transferred its triplet energy to the naphthalene. As seen in Figure 1, naphthalene and benzophenone are ideally suited for an ET study, since the triplet energy, or $\Delta E_{S_0 \rightarrow T_1}$, for benzophenone is greater than that of naphthalene, and benzophenone is known to have an intersystem crossing (ISC) efficiency of 1.0. 3

![Energy Diagram for Benzophenone and Naphthalene](image)

Figure 1. Energy Diagram for Benzophenone and Naphthalene
Ermolaev found through this study that the principal requirements for successful energy transfer in a rigid solution were that the triplet state of the acceptor lie lower than that of the donor, and that the acceptor be in sufficiently large concentration to allow a high probability of an acceptor being near in space to an excited donor.

This experiment clearly illustrated a well known theory in photochemistry created by F. Perrin, known as the sphere of quenching model. Briefly, this theory states that if an excited donor has an acceptor molecule within a given volume defined by a critical radius, $R_C$, ET is 100% efficient and instantaneous. If there is no acceptor within this radius, then no energy transfer takes place and the donor emits with a normal lifetime, see Figure 2. Probability calculations gave an $R_C$ of ≈13 Å for most excited molecules. Since phosphorescence experiments are carried out in rigid media, there is no chance for an acceptor to move into or out of the $R_C$ of an excited triplet donor during its lifetime. Consequently, only those acceptors within $R_C$ at the moment of donor excitation will be able to engage in ET. This model makes the synthesis of bichromophoric molecules extremely interesting to a photochemist. If the donor and acceptor are linked with a chain of some known distance, an acceptor is guaranteed to fall within the $R_C$ of the donor regardless of concentration.
At first glance, it hardly seems reasonable to assume that ET is an all-or-nothing process, as most through-space interactions are gradients. However, a number of studies conducted over the past several years have reinforced this model. One such study of bichromophoric molecules examined ET between benzophenone and naphthalene linked by an alkyl chain of one to three methylenes, 1–3. 6
When 1, 2, or 3 was dissolved in 5:5:2 diethyl ether, isopentane, and ethyl alcohol (EPA), frozen at 77 °K and irradiated at 366 nm, the phosphorescence emission was found to contain bands due only to naphthalene. No benzophenone phosphorescence emission was seen. Since no naphthalene was excited by the light, all of the benzophenone triplet energy must have been transferred to the naphthalene with perfect efficiency. This result supported the sphere of quenching model quite well, as the distance between the chromophores varied from 9–10 Å, well within the $R_c$ of 13 Å. It should also be noted that the compound was at a concentration of 0.005 M, well below the level at which intermolecular ET would take place. The only other available deactivation pathways present for the benzophenone would be quite slow compared to ET to the naphthalene group. When piperylene was used as a triplet quencher for a solution phase study of 1, 2, and 3, the rate of energy transfer ($k_{ET}$) between the chromophores for all of these molecules was estimated to be in excess of
$1 \times 10^{10}$ sec$^{-1}$.

Another study that also supported the sphere of quenching model was conducted by Cowan and Baum using a benzoyl group linked to a trans-$\beta$-methylstyril group via an alkyl bridge, 4-7.  

![Chemical structure](image)

4 $n = 1$
5 $n = 2$
6 $n = 3$
7 $n = 4$

When 0.022 M solutions of 4-7 were irradiated, the triplet energy was transferred from the acetophenone group to the styryl group, resulting in a cis-trans isomerization of the double bond. In the case of compounds 5, 6, and 7, the $k_{et}$'s were estimated to be $7.2 \times 10^{10}$ sec$^{-1}$, $1.0 \times 10^{10}$ sec$^{-1}$, and $3.3 \times 10^9$ sec$^{-1}$, respectively. These values are similar in magnitude to those found for 1, 2, and 3, again demonstrating the tremendous efficiency of ET if the donor and acceptor are within $R_C$. It should be noted that compound 4 was not included in this study, since UV absorption studies showed a strong interaction between the chromophores.

Despite the fact that the current work in the field of intramolecular
energy transfer greatly supports the sphere of quenching model, recent work done by Dr. Paul S. Engel and Douglas W. Horsey of Rice University indicate that the 13 Å radius may be too long. They investigated bichromophoric molecules 8 and 9, known as 4BB-Py and 2BB-Py, respectively.

Previous studies of bichromophoric molecules had not used an ester bridge, but in this case the ester linkage was chosen due to ease of synthesis. Irradiation of the benzophenone moiety in a frozen glass of methylcyclohexane only gave an emission characteristic of benzophenone. The lifetime of this emission was identical to that of a model compound containing only the benzophenone moiety, but the intensity of the emission from 8 and 9 was decreased by a factor of 10 to 200. No phosphorescence was observed from the azo group whatsoever. This result is similar to the case noted in the sphere of quenching model, where some donors had an acceptor within $R_C$ and underwent ET, whereas others did not and emitted with a normal lifetime. However, in 8 and 9 every donor had an acceptor
within the 13 Å radius stipulated by the sphere of quenching model. Thus either this critical radius of 13 Å was too long for azo compounds, or ET in this particular molecule was inhibited by some unknown factor. It was conceivable that ET in 8 and 9 was intermolecular rather than intramolecular, but the concentration of the compound in the glass-forming solvent was far below the level normally required for bimolecular quenching. An argument may be made for aggregates forming in the glass, since unaggregated molecules would emit with a normal lifetime, but no turbidity was observed in the sample.

Solution phase Stern-Volmer quenching studies of 8 and 9 also revealed very poor ET. Compounds 8 and 9 were irradiated separately in solution in the presence of a quencher. In the case of 8, the small amount of ET that did take place could be completely accounted for using intermolecular ET, or energy transfer between two nearby molecules (bimolecular ET), rather than intramolecular ET. An estimate of $k_{ET}$ was obtained by assuming that no intramolecular ET took place. Employing a value for $k$ of bimolecular quenching, or $k_{BT}$, from a previous study, Engel and Horsey obtained $k_{ET}$'s for 8 and 9 as $3.4 \times 10^7$ s$^{-1}$ and $7.2 \times 10^8$ s$^{-1}$, respectively. It should be noted that these values are probably too high because the approximation made for $k_{BT}$ was probably too large.

This poor ET in 8 and 9 seemed to be due either to the small size of the azo chromophore or to the conformational rigidity of the linking ester.
bridge. Since most of the previous studies had used large aromatic systems for acceptors, the physically small size of the azo chromophore may well render it a difficult "target" for efficient ET. On the other hand, the ester bridge was considerably less flexible than the alkyl chains used by previous studies and may well hold the chromophores apart in an unfavorable conformation for ET. Since these two factors presumably operate separately, it was decided to investigate the ester bridge's influence on ET. The best method of determining this influence seemed to lie in the synthesis and testing of a series of model compounds linking two chromophores that had previously exhibited good ET via an alkyl linkage.

The chromophores chosen for this study were benzophenone and naphthalene, since Lamola's study had shown that ET was very efficient and rapid for these chromophores. We linked the benzophenone moiety and the 1-naphthyl moiety with an ester group and an alkyl chain of 1 to 2 methylene groups. These compounds were designated as 4BB-NaM, 10, and 4BB-NaE, 11. Phosphorescence emission experiments would be used to determine qualitatively the amount of transfer across the ester bridge.
In addition to these emission experiments, two other irradiation experiments were attempted. If the rate of intramolecular ET in 10 and 11 were slow, it might be possible to determine this rate by intercepting the benzophenone triplet using a quencher with a triplet energy between that of benzophenone and naphthalene. A suitable quencher for this experiment was 3,3,5,5-tetramethylpyrazoline (TMP), 12, whose triplet energy of 64 kcal lies exactly midway between the triplet energy of benzophenone and naphthalene. The triplet state of 12 is known to lose nitrogen if triplet energy is transferred to it.

![Chemical Structure](attachment:image.png)

12

If a mixture of 10 and 12 was irradiated at 366 nm to excite the benzophenone moiety, measuring the amount of nitrogen evolved during the irradiation would indicate the amount of triplet energy transferred from the benzophenone group to 12. The results could give a good indication of whether intermolecular ET to 12 was preferred to intramolecular ET to the naphthalene moiety.

This question of intermolecular versus intramolecular ET was also considered in another irradiation experiment. If a quencher could be synthesized that was distinguishable from 4BB-Py but retained the
1-pyrazoline moiety, a mixture of these two compounds could be irradiated and the products examined by NMR to determine which 1-pyrazoline moiety had received the benzophenone triplet energy. This experiment would effectively set up a competition between the intermolecular and intramolecular pathways for ET to the same chromophore. If intramolecular ET was as slow as the prior results had suggested, a large number of quencher molecules would react, as there would be ample time for them to diffuse up to the excited benzophenone moiety of the 4BB-Py.

![Chemical Structure](image)

13

The molecule chosen for this project was 13, known as CH-Py. Ideally, the azo would be linked to a chromophore with identical size and steric hindrance, but ease of synthesis and availability of starting materials made 13 a more feasible molecule for this study. Although 4BB-Py and 13 contain the same azo moiety, the products given by each molecule could be distinguished by the NMR shift of the methylene group next to the ester, thus allowing us to monitor the rate of product formation. These products are as follows:
The concentration of 13 could be varied to give an idea of the preference for intermolecular versus intramolecular ET. Even if no quantitative data were obtained, a qualitative answer would be useful in current research.
RESULTS AND CONCLUSIONS

1. Synthesis of Bichromophoric Molecules

The syntheses for 10 and 11 were modified from earlier work on ester linked molecules by Douglas W. Horsey.\textsuperscript{15} The starting materials in this present case were 4-benzoylbenzoic acid, 1-naphthalene methanol 15, and 1-naphthalene ethanol 16. The acid was treated with thionyl chloride and a catalytic amount of pyridine to form the acid chloride 14, followed by removal of the excess thionyl chloride and reaction with the 1-naphthalene methanol or 1-naphthalene ethanol in the presence of a catalytic amount of pyridine. The yield after workup was 30\% for 10 and 23\% for 11.

\[
\text{SOCl}_2, \text{pyridine} \xrightarrow{\text{reflux, 1 hr}} \quad \text{14} \quad 99\% \text{ yield}
\]

\[
\text{15} \quad \text{pyridine} \xrightarrow{60^\circ\text{C}, 48 \text{ hrs}} \quad \text{10} \quad 30\% \text{ yield}
\]
The final product was purified through a preparative HPLC silica gel column and recrystallization from 100% ethanol. Since these products were previously unreported in the literature, they were characterized by NMR and melting point (in the case of 4BB-NaM).

Due to the somewhat poor yields of unpurified product obtained by this method, another attempt at 10 and 11 was made using dicyclohexyl carbodiimide, DCC.\textsuperscript{16} Despite the reagent's well-known ability to link hindered acids and alcohols,\textsuperscript{17} all attempts to synthesize either 10 or 11 using this reagent failed. The DCC performed well in a test reaction linking 4-benzoylbenzoic acid with ethanol, but apparently the added steric hindrance of the naphthalene group overcrowded the transition state. Another explanation for this result may be the insolubility of an intermediate adduct between the acid and the DCC. In light of these failures, the synthesis was abandoned and the previous method was used to make 10 and 11.

The synthesis of compound 13 (CH-Py) was accomplished using several previously published methods.\textsuperscript{18,19} The azo portion of this molecule was created by first synthesizing acetone hydrazone, 17.

\[
\begin{align*}
\text{CH}_3\text{COCCH}_3 & \xrightarrow{\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}} (\text{CH}_3)_2\text{C}=\text{NN}=\text{C}(\text{CH}_3)_2 & \xrightarrow{\text{N}_2\text{H}_4} (\text{CH}_3)_2\text{C}=\text{NNH}_2 \\
17 & & 17
\end{align*}
\]
\[
(CH_3)_2C=NNH_2 \xrightarrow{\text{MnO}_2 (\text{active}) \quad \text{KOH}} (CH_3)_2CN_2
\]

18

However, two changes were made to the published method for 2-diazopropane, 18,\textsuperscript{19} that seemed to greatly improve yield and ease of handling. Tetrahydrofuran was used rather than diethyl ether for the solvent in the oxidation of the hydrazone, since it was a higher boiling solvent. Thus less solvent was needed for the co-distillation of 18. In addition, manganese dioxide was found to be a far better oxidizing agent than mercury oxide for this reaction.\textsuperscript{20} Use of manganese oxide also eliminated the problem of mercury toxicity and disposal.

\[
(CH_3)_2CN_2 + CH_2=CH(C(CH_3)COOCH_3 \longrightarrow \quad \text{CH}_3-\text{O-}
\]

19

After distillation from the manganese dioxide, 18 was then titrated with several small aliquots of freshly distilled methyl methacrylate until the characteristic orange color of 18 faded. 18 underwent a room temperature [4+2] Diels-Alder addition to make the pyrazoline ester 19. This ester was distilled, dried over magnesium sulfate, and reduced to 22 using lithium aluminum hydride. Final workup with water and potassium
hydroxide followed by distillation gave 22 in 20% yield based on the starting amount of hydrazone.

The other starting material for the synthesis of 13 was cyclohexane carboxylic acid, 20. This acid was converted to the acid chloride 21 via reaction with thionyl chloride and pyridine at room temperature.

\[
\text{C}_{10}H_{16}O \quad + \quad \text{SOCl}_2 \quad \xrightarrow{\text{pyridine}} \quad \text{C}_{10}H_{16}O\text{Cl}
\]

With the individual starting materials made, the two moieties were joined together in the same way as 10 and 11 to yield 13. In this case, however, no heat was applied. Once again, the product was identified using NMR.

\[
\text{C}_{10}H_{16}O\text{Cl} \quad + \quad \text{H-O-} \quad \xrightarrow{} \quad \text{C}_{10}H_{16}O\text{Cl}
\]
2. Ultraviolet Absorption Studies

Before any emission studies could be made, an appropriate solvent had to be found. The irradiation solvents that were selected formed a glass at 77 °K and showed no absorption in the region between 350 nm and 600 nm. After several trials using a mixture of isopentane, ether, and ethyl alcohol (EPA), the solvent previously used by Ermolaev, the 2:1 ethyl alcohol and diethyl ether, was chosen as the most suitable for the experiments. In addition, both solvents were easy to purify and dissolved 10 and 11 quite readily.

To check for any interaction between the individual chromophores in 10 and 11, absorption spectra were determined at two different concentrations for each compound. The higher concentration, $2.3 \times 10^{-3} M$, was used to look at the absorption of the benzophenone moiety and the more dilute concentration, $2.3 \times 10^{-4} M$, the naphthalene moiety. The absorption spectrum of 10 (see Figure 3) showed a peak at 338 nm ($\epsilon = 152$) and a shoulder at 315 nm from the stronger absorption at 300 nm. These absorption peaks correspond to a superimposed benzophenone and naphthalene absorption.
The absence of new bands indicated that there is no significant interaction between the individual chromophores in the molecule. The UV absorption peaks in 11 were similar to those of 10, appearing at 335 nm ($\epsilon = 252$) and the inner shoulder at 315 nm (see Figure 4).

3. Emission Studies

The solutions for the phosphorescence spectra were taken directly from the UV cells and were placed in cleaned and annealed phosphorescence tubes. These solutions were then frozen to a glass in liquid nitrogen and placed in the phosphorimeter. It should be noted that the concentrations of these samples were sufficiently low to remove any chance of intermolecular ET.

To obtain the best phosphorescence emission spectrum, 10 and 11 were excited at 346 nm, a wavelength that would only excite the benzophenone moiety. In both cases, ET did take place, as emission bands were seen from the naphthalene moiety. However, contrary to the results observed by Lamola$^7$, ET was not 100% efficient despite the chromophores being within 13 Å. A comparison of the emission observed from 10 with a pure benzophenone and naphthalene emission clearly shows emission from the sensitizer moiety (see Figure 5). Similar results were seen in the case of 11 (see Figure 6).
Figure 5

Emission of 346 nm Excitation
4BB-DaM in ER (0.0023 M)
Figure 6
Emission of 346 nm Excitation
4BB-NaE in EB (0.0023 M)
In order to measure the emission intensity for benzophenone and naphthalene, and thus the amount of energy transfer, the spectrum peaks were carefully cut into benzophenone and naphthalene regions and weighed (for an example, see Figure 10). The benzophenone portion that lay under the naphthalene emission was assumed to look like the phosphorescence of benzophenone alone. The weight of the area under the curves was then divided by the appropriate phosphorescence quanum yields and the corrected naphthalene peak weight was divided by the corrected total peak weight to yield an efficiency rating for intramolecular ET in a glass.

\[
\text{peak weight} = \text{corrected weight} / \text{quantum yield}
\]

\[
\text{corrected weight of naphthalene} = \text{ET efficiency} \times \text{total corrected weight}
\]

Using this method, ET was found to be 97% ± 2% complete in 10 and 93% ± 2% complete in 11. Apparently, an additional methylene group in the linking bridge drops the ET efficiency by 4%. This additional methylene increases interchromophoric distance by 0.9 Å based on molecular models in an extended conformation, but it enhances the flexibility of the linking bridge. The drop in ET, if examined using the sphere of quenching model, would seem to indicate that fewer naphthalene chromophores are within the sphere of quenching for this system.
Excitation spectra were determined for the principal emission bands for each compound. The excitation spectrum for the 544 nm emission of 11, a purely naphthalene emission, clearly showed that this emission was due to excitation of the benzophenone moiety (Figure 7). Likewise, the excitation spectrum of the 455 nm emission, a purely benzophenone emission, showed that the benzophenone emission was caused by benzophenone excitation (Figure 8). These results were identical for compound 10.

A deviation from ideal benzophenone emission bands was noticed in 11 (see Figure 6 and 9). The benzophenone bands (400-460 nm) of 11 were shifted toward longer wavelengths than those of 10 or benzophenone. This shift can be partly explained by consideration of the emission bands from a model compound called 4BB-Me, 23, previously made by Douglas W. Horsey.

![Chemical structure](image)

23

The emission bands for this compound appear at 424 nm, 456 nm, and 492 nm, all of which are at longer wavelength than pure benzophenone.
Figure 7
Excitation of 544 nm Emission
4BB-NaE in EA (0.0023 M)

WAVELENGTH, NM

INTENSITY

Benzophenone Excitation
of 413 nm Emission
Figure 8
Excitation of 455 nm Emission
4BB-NaE in ER (0.0023 M)

INTENSITY

WAVELENGTH, NM

Benzophenone Excitation of 440 nm Emission
Figure 9
4BB-Na III vs. 4BB-Na E
Emission of 346 nm Excitation
Since 23 is the more appropriate model compound, the emission bands of 10, which happened to match those of benzophenone quite closely, are clearly shifted to a lower wavelength as compared to the model compound. This shift was thoroughly investigated using a different solvent and sample concentration and was found to be a real shift, not an artifact of a particular solvent or the phosphorimeter.

The emission and excitation spectra of 10 and 11 were also run using the more dilute solution of 2.3 × 10⁻⁴ M in EA to investigate any possible changes in ET. This change in concentration did not seriously affect the amount of energy transfer, as ET efficiency was 98% ± 2% based on the previous method for Figures 5 and 6 (see Figure 10). The shaded region of the Figure 10 belonged to benzophenone emission. It was interesting to note that ET increased upon dilution. If the observed ET was due to intermolecular ET, this value would have been expected to decrease. As in the previous study, there was no turbidity evident in the sample.

These experiments were also repeated using a different glass forming solvent, 2-methyl tetrahydrofuran or 2-Me THF. The emission spectra and ET efficiencies in this solvent were similar to those seen in 2:1 EA. (Figure 11) One interesting phenomenon to note, however, is the shift of the emission to longer wavelengths for the benzophenone portion of the spectrum (410–465 nm). Although a shift to longer wavelengths (red shift) is often seen for n,π* absorption in a non-polar solvent, there seems to be no previous evidence for this shift for n,π* emissions.¹
Figure 10
Emission of 346 nm Excitation
4BE-DeF in EA (0.00024 M)
Figure 11
Emission of 340 nm Excitation
4BB-NaE in 2-MeTHF (0.0023 M)
4. Conclusions from Emission Study

This work and earlier work done in this laboratory\textsuperscript{8} present a challenge to the 13 Å critical radius for a benzophenone and naphthalene pair. In the case of 10 and 11, ET was seen to be distance dependent similar to a gradient, rather than an all-or-nothing process. If the distance between the chromophores was increased, ET decreased, but no critical radius was observed. The distance between chromophores in 10 and 11 with the esters in the extended conformation was 9.75 Å and 10.65 Å, respectively, based on molecular models. These radii were well within the critical radius calculated by Ermolaev using Perrin's model.\textsuperscript{2} Since the maximum possible interchromophoric distance for 11 is 10.65 Å, $R_0$ must be less than the previously determined 13 Å calculated for this pair by Ermolaev.

The only other published case of partial ET was a study performed by Keller and Dolby where a benzophenone and naphthalene moiety were rigidly linked by a steroid bridge at a distance of 15 Å.\textsuperscript{24} The ET efficiency was only 40%, but since the bridge was longer, less transfer would be expected.
The reason for partial transfer in 10 and 11 is unclear. In addition to the concept of a gradient, it is possible that there are two conformations of the molecule—one that favors ET and one that forbids it. If 3% of the molecules of 10 were in the unfavorable conformation, then the partial ET could be explained. A possible explanation for incomplete ET may be poor orientation of the chromophores with respect to one another. Several studies have shown that triplet-triplet transfer from benzophenone has an optimum transfer geometry.25,26 These studies indicate that the C-O axis in the carbonyl of benzophenone must be parallel to the molecular plane of the acceptor (in this case naphthalene), in order for efficient ET to take place. Thus, it is possible that 3% of the molecules of 10 exist in a conformer where this specific orientation is not met, whereas the remaining molecules have the correct orientation. This factor did not affect Lamola's study when the chromophores were linked by an alkyl chain. Therefore, further discussion is needed into the nature of the ester bridge itself.

Studies of ester model compounds confirm that the ester bridge prefers to be in the extended or anti conformation, rather than the syn conformation.27,28
Although both the syn and anti ester conformations exist in these model compounds, the energy difference between them is 5 kcal at room temperature, allowing only 0.03% of the syn conformer to exist in the starting solution. Of course, even fewer syn conformers exist at low temperatures. In addition, force field calculations indicate that the barrier to rotation about the C-O bond, or the barrier to interconversion from anti to syn conformer, is at least 10 kcal. However, 10 and 11 have such large R and R' groups, that this barrier may be even higher, removing any possibility of interconversion from the anti to the syn conformer at 77 °K.

Dr. Jack Saltiel of Florida State University suggested that the rate of freezing could affect the population of each conformer for 10 and 11, since a fast freezing time might trap an unfavorable conformer of a given molecule. An experiment was conducted using a thermocouple to determine the rate of sample freezing in the glass forming solvent when plunged into liquid nitrogen, but the fastest freezing rate that could be achieved was ~20 °K/sec. This rate, according to a simple treatment with the Arrhenius equation, would freeze out a barrier of 10 kcal or greater. However, the syn conformer is the conformer that favors ET, and thus it cannot be responsible for a lack of ET in this molecule.

In contrast to the ester group, the barrier to rotation about the alkyl chain is only 1.0 kcal at room temperature, and it is possible that conformers caused by rotation about this chain could be in equilibrium. These conformers could be very close to one another in energy and exist in a
ratio of 97 to 3. An improper orientation caused by rotation about a C-C bond could explain the partial transfer in 10 and 11. However, this idea is not supported by Lamola's study.

An obvious cause for this difference is the lack of flexibility of the ester group in comparison to the alkyl chain. Winnick and Wagner have studied alkyl chain flexibility in solution$^{31,32,33}$ and have found that an alkyl chain has a tendency to twist and turn randomly, instead of assuming an all anti conformation. Thus it is quite possible that the distance measured by Lamola for 1, 2, and 3, based on molecular models, was in fact greater than the true distance. If molecular models of Lamola's compounds are examined, the chains are seen to be sufficiently long and flexible to allow the benzophenone and naphthalene to stack with an interchromophoric distance of little more than 2 Å. Although no work has been done to show the conformation of 1, 2, or 3, it is highly possible that some sort of complexation between the benzophenone and naphthalene moiety occurred. If this were the case, it would explain the 100% efficient transfer seen in that study, since the interchromophoric distance would have been only 2 Å, and the chromophores could assume the most favorable orientation for ET. A similar complexation in 10 and 11 would be inhibited by the tendency of the ester linkage to remain anti. Despite the flexibility of the alkyl chain, the chromophores in 10 and 11 cannot approach closely.

It should be noted that ET in 10 and 11, although not complete, is still quite good. ET in this case would appear to be a statistical process
controlled by two factors--distance and orientation. At a given distance or orientation, there is a finite probability of ET taking place. This probability increases with decreasing interchromophoric distance and the presence of favorable conformers, until it finally reaches 100%. The poor amount of transfer seen in the case of 8 and 9 cannot be accounted for solely by the rigidity of the ester bridge. Some fault must lie either with the orientation of the azo moiety or the azo group itself, and more work will be needed to solve this puzzle completely.

5. Irradiation Results and Kinetics

Benzophenone, Naphthalene, and TMP systems

A mixture of 10 and 12 (cf. p. 11) was irradiated so as to excite only the benzophenone moiety. The amount of nitrogen given off by 12 during the irradiation was measured to gauge the amount of triplet energy transferred from the benzophenone group to 12. This experiment was not a great success due to the peculiar nature of the kinetics, but the large amount of nitrogen evolved indicated that intermolecular ET to 12 was a very favorable process relative to intramolecular ET to the naphthalene moiety.
**Kinetics**

B = benzophenone moiety of 10

N = Naphthalene moiety of 10

A = TMP (triplet energy acceptor)

\[
\begin{align*}
B-N & \quad \rightarrow \quad B^{\ast 3}-N & 1 (\Phi_{isc} \text{ for benzophenone is } 1) \\
B^{\ast 3}-N & \quad \rightarrow \quad B-N^{\ast 3} & k_{ET} \\
B^{\ast 3}-N + B-N & \quad \rightarrow \quad B-N + B-N^{\ast 3} & k_{BT} \\
B^{\ast 3}-N + A & \quad \rightarrow \quad B-N + A^{\ast 3} & k_Q \\
A^{\ast 3} & \quad \rightarrow \quad N_2 & k_R \\
A^{\ast 3} & \quad \rightarrow \quad A & k_{dA} \\
B^{\ast 3}-N & \quad \rightarrow \quad B-N & k_{dS}
\end{align*}
\]

\[
\Phi_R = \frac{k_Q [A]}{k_{ET} + k_{dS} + k_{BT} [B-N] + k_Q [A]} \cdot \frac{k_R}{k_R + k_{dA}}
\]

\[
\frac{1}{\Phi_R} = \left[ 1 + \frac{(k_{ET} + k_{dS} + k_{BT} [B-N])}{k_Q [A]} \right] \cdot \frac{1 + k_{dA}}{k_R} \frac{k_R}{F}
\]

Plot $1/\Phi_R$ versus $1/[A]$

then slope/intercept = $\left( k_{ET} + k_{dS} + k_{BT} [B-N] \right)/k_Q$
Under the experimental conditions, $k_q$ would be equal to $10^{10}$ sec$^{-1}$, since quenching would be diffusion controlled in solution. If the concentration of A, the quencher, were varied for a given concentration of 10, one might imagine that the value of the slope/intercept would give information regarding $k_{ET}$, the rate of intramolecular ET. Unfortunately, while $k_{ds}$ can be estimated from previous work on benzophenone, $k_{BT}$ [B-N] can only be estimated. Since $k_{ET}$ is so small relative to $k_{BT}$, [B-N] would have to be greatly decreased to observe $k_{ET}$. However this drop in concentration would cause experimental difficulties and errors. Despite this problem, some qualitative information regarding ET was obtained by this experiment, due to the large amounts of triplet energy transferred to 12.

This experiment illustrated one important point. Since intermolecular ET did take place, there does not seem to be any difficulty in ET from a benzophenone moiety to a tetramethylpyrazoline moiety as there was in the case of 8 and 9. It would seem as though the ester bridge in these two compounds is not just holding the chromophores rigidly apart, but is also holding the chromophores in an orientation that is unfavorable for ET.

Compound 10 was dissolved in benzene with a 5 fold excess of TMP and degassed by a freeze-thaw technique. In contrast to the emission
experiments, it is important to note that the concentration of 10 is sufficient to allow bimolecular ET. The tube was then sealed with a torch, irradiated in a merrygoround using a medium pressure mercury lamp, and attached to a Toeplar pump for nitrogen measurements.

A total of 0.138 mmol of nitrogen was found, corresponding to a $\Phi_{\text{nitrogen}}$ of 0.185 for this experiment. When one considers that the maximum possible value would only be 0.23 based on earlier work, 10 clearly prefers to transfer its energy to an external molecule of TMP rather than to the internal naphthalene moiety. Although intramolecular ET was a favorable process for 10 in a frozen glass due to lack of other modes of deactivation, intermolecular ET seem to predominate in solution. Due to the slow rate of benzophenone decay in solution, 35 it is presumed that the remaining benzophenone triplets that did not transfer to 12 transferred their energy to naphthalenes, but it is not known whether or not this ET was intramolecular or intermolecular.

**4BB-Py and Cyclohexyl-Py Systems**

The second irradiation experiment investigated the effect of intramolecular versus intermolecular transfer to an azo moiety in a pyrazoline ester. The compounds used in this study were 4BB-Py, 8, and CH-Py, 13. The benzophenone moiety was irradiated using a high-pressure mercury lamp, and the amount of ET to each compound was measured by monitoring the disappearance of reactants by NMR. All of the reactants and
products in this irradiation have a single methylene α to the ester group (cf. p. 12, 13). The shift of the AB quartet formed by each methylene is slightly different, and thus the methylenes could be distinguished (see Figure 12). Since there were four distinct compounds, two reactants and two products, a total of 12 peaks were seen between 3.5–5.0 ppm (4 peaks overlapped). Unfortunately, since proton integration from the 90 MHz NMR was unable to distinguish between these peaks, peak height was measured using a ruler.

Although this experiment seemed very good on paper, a sample kinetics calculation revealed that the experimental accuracy needed to observe an effect due to $k_{ET}$ was much higher than could be achieved using the 90 MHz NMR.

**Kinetics**

B = Benzophenone moiety

Py = Pyrazoline moiety

CH = Cyclohexyl group

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate Constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>B-Py --&gt; B**3-Py</td>
<td>$k_{ET}$</td>
</tr>
<tr>
<td>B<strong>3-Py --&gt; B-Py</strong>3</td>
<td>$k_{BT}$</td>
</tr>
<tr>
<td>B<strong>3-Py + B-Py --&gt; B-Py + B-Py</strong>3</td>
<td>$k_X$</td>
</tr>
<tr>
<td>B<strong>3-Py + CH-Py --&gt; B-N + CH-Py</strong>3</td>
<td>$kP_1$</td>
</tr>
<tr>
<td>B-Py**3 --&gt; N$_2$</td>
<td>$kP_2$</td>
</tr>
<tr>
<td>CH-Py**3 --&gt; N$_2$</td>
<td></td>
</tr>
<tr>
<td>B**3-Py --&gt; B-Py</td>
<td>$k_{dS}$</td>
</tr>
</tbody>
</table>

$(\Phi_{isc} \text{ for benzophenone is } 1)$
\[
\Phi_{\text{CH-Py}} = \frac{k_{ET} [\text{CHPy}]}{k_{ET} + k_{BS} + k_{BT} [\text{BPy}] + k_{X} [\text{CHPy}]} \cdot \frac{k_{P2}}{k_{P2} + k_{dX}} \cdot \frac{k_{P1}}{k_{P1} + k_{dP}}
\]

\[
\Phi_{\text{B-Py}} = \frac{k_{ET} + k_{BT} [\text{BPy}]}{k_{ET} + k_{BS} + k_{BT} [\text{BPy}] + k_{X} [\text{CHPy}]}
\]

If we assume that \( F2/F1 = 1 \) and plot \( \Phi_{\text{CH-Py}}/\Phi_{\text{B-Py}} \) versus the concentration of CH-Py, then the reciprocal of the slope would be: \( k_{ET}/k_{X} + (k_{BT}/k_{X})[\text{B-Py}] \). A plot of this reciprocal versus [B-Py] will then have a slope of \( (k_{BT}/k_{X}) \) and an intercept of \( k_{ET}/k_{X} \). The estimated values for \( k_{X} \) and \( k_{BT} \) were \( 5 \times 10^9 \text{ sec}^{-1} \) and \( 5 \times 10^9 \text{ sec}^{-1} \), respectively, based on earlier work. The sample calculation for the reciprocal of the slope was as follows:
Figure 12. Irradiation of 4BB-Py and CH-Py

Before Irradiation
Black = 4BB-Py
White = CH-Py

After 15 minutes Irradiation
White = 4BB-Py Product
Black = CH-Py Product

After 30 minutes Irradiation
White = 4BB-Py Product
Black = CH-Py Product

J for all AB quartets is 12 Hz
\[ [\text{B-Py}] = 0.02 \ \text{M} \]

reciprocal of the slope \( = \frac{k_{ET}}{k_X} + \left(\frac{k_{BT}}{k_X}\right)[\text{B-Py}] \)

\[ = \frac{k_{ET}}{5 \times 10^9} + 0.02 \]

If \( k_{ET} = 1 \times 10^6 \ \text{sec}^{-1} \), then the reciprocal of the slope = 0.0202. The contribution to this value by \( k_{ET} \) is only 0.0002. If the estimated rate constants are accurate, then an experimental accuracy of four decimal places would be needed to observe \( k_{ET} \). The concentration of 4BB-Py could be lowered, but this would lead to experimental difficulties and errors. The accuracy of the integration measurement needs to be increased without lowering 4BB-Py concentration.

A 300 MHz NMR spectrum of CH-Py showed much greater peak separation in the 4.0–5.0 ppm region (see NMR spectra). Although time constraints precluded further work, this enhanced peak separation may well provide the means for more accurate measurement of the four AB quartets and enable \( k_{ET} \) to be seen experimentally.
EXPERIMENTAL

1. Equipment and Materials

Phosphorescence spectra were obtained at 77°K using a Perkin-Elmer MPF-2A fluorescence spectrophotometer with a phosphorescence attachment. These spectra were digitized using an HP-7225A plotter and displayed on an HP-2648A graphics terminal. The UV spectra were run on a Cary 17 UV-Vis spectrophotometer. NMR spectra were obtained in CDCl₃ with TMS as a standard, using a JEOL FX-90Q 90 MHz FT NMR spectrometer.

All analytical and preparative high-performance liquid chromatography was performed using a Beckmann HPLC system consisting of a Beckman 420 Controller, two 112 solvent delivery modules and a 165 variable wavelength UV-Vis detector. A Beckman 4.5 mm internal diameter ODS 600-SI ultrasphere silica gel column provided separation for analytical work, and a 10mm ODS ultrasphere silica gel column was used for preparative work. Unless noted, 10% EtOAc in hexane was used as the preparative and analytical solvent. UV absorptions of the individual components were graphed on an Omniscribe recorder and an HP 7005B X-Y recorder. All melting points were performed in a capillary tube on a Mel-Temp apparatus and are uncorrected.
The two lamps used for the irradiation experiments were a Hanovia 450 W medium-pressure mercury lamp for the experiment involving 10 and 12, and an Oriel 500 W high-pressure mercury lamp for the irradiation of 8 and 13. A 2,7-dimethyl-3,6-diazacyclohepta-1,6-diene perchlorate (diaza) filter and a sample water bath were used to screen out all unwanted radiation.

The solvents and reagents used in this study were purified according to methods found in "Purification of Laboratory Chemicals." Specific purifications were as follows: The Fisher reagent grade pyridine used for the syntheses of 10 and 11 was dried over dry 4 Å molecular sieves for one day, followed by distillation through a glass helices packed column. Tetrahydrofuran was J. T. Baker reagent grade, distilled from sodium and benzophenone through a glass helices packed column. Ethanol used in the phosphorescence solvent glass was 200 proof ethanol, distilled from sodium and the ether was a fresh bottle of J. T. Baker anhydrous diethyl ether that had been purged with argon. J. T. Baker HPLC grade benzene was used without special treatment for the irradiation experiments. Unless noted, all solid starting materials for the syntheses were from Aldrich and were used without further purification.
2. **Syntheses**

**4-benzoyl benzoyl chloride, 14**

In a single-neck round-bottom flask fitted with a stir bar, water condenser, and nitrogen inlet was placed 0.4845 g (2.01 mmol) of 4-benzoyl benzoic acid, 2.0 ml thionyl chloride, and 2 drops of pyridine from a dispo-pipet. This reaction mixture was then vigorously refluxed for one hour and allowed to cool, before the excess thionyl chloride was removed by vacuum distillation and gentle heating. The reaction gave 14 in quantitative yield and the product was characterized by IR spectrophotometry and melting point. mp 86 °C.

**4-naphthylmethoxycarbonyl benzophenone (4BB-NaM) 10**

In a single-neck round-bottom flask equipped with a stir bar, water condenser and nitrogen inlet was placed 0.5607 g of 14 (2.29 mmol) and 2 ml of distilled pyridine. The acid chloride was then slurried in the pyridine, and 0.2282 g (1.44 mmol) of 1-naphthyl methanol, 15, was added directly to the flask. The reaction mixture was heated in an oil bath maintained at 60 °C and allowed to stir for 48 hours. The reaction was followed by NMR to insure that the maximum amount of alcohol had reacted, as the reaction did not go to completion. Workup consisted of adding distilled water to the crude product, extracting with methylene chloride, and washing the organic
layer with 1N HCl. The methylene chloride was then removed by rotovapping and pumping.

The crude product yield was above 100%, but this included some unreacted starting alcohol. This material was then brought up in ethyl acetate and filtered through a small silica gel column in a dispo-pipet, rotovapped, dissolved in ethanol, and decolorized with activated charcoal. The yield prior to HPLC preparative work was 30%. Final purification of 13 was achieved on a Beckman ODS silica gel preparative HPLC column, eluting with 10% EtOAc in hexane followed by two recrystallizations from 200 proof ethanol. The final purified product weight was 0.0822 g of 13 in 15% overall yield. This product exhibited a mp of 124-125 °C. 1H NMR & 5.85 (s, 2H); 7.20-8.30 (m, 16H).

4-naphthylethoxycarbonyl benzophenone (4BB-NaE), 11

The synthesis of 11 was essentially the same as that of 10 above. The major difference in the reaction was the amount of heat and the time of reaction. The weight of 14 used was 0.4286 g (1.89 mmol) and 0.2177 g (1.26 mmol) of 1-naphthalene ethanol. The reaction mixture was heated in a regulated oil bath at 65 °C and only stirred for 24 hours. Workup was identical to that for 10 except charcoal decolorization was not required. Overall yield of 0.0617 g, or 13%, was achieved. Despite several recrystallization attempts from EtOH and storage over dry ice in the freezer, the product remained a viscous oil and no melting point was
obtained. $^1$H NMR δ, 3.65 (t, 2H); 4.70 (t, 2H); 7.20–8.25 (m, 16 H).

3,5,5-trimethyl-3-hydroxymethyl pyrazoline 22

The literature preparation for acetone azine,$^{18}$ acetone hydrazone,$^{18}$ and 2-diazopropane$^{19}$ was used with the following exceptions for the 2-diazopropane synthesis: Tetrahydrofuran was used as the solvent, as opposed to ether, and a 25% excess of MnO$_2$ was employed rather than HgO. Final yield was 0.158 mols or a 54% yield based on starting acetone azine. 2-diazopropane was identified by its characteristic apricot color and the appearance of a 350 nm UV absorption band.

The 2-diazopropane was immediately titrated with 11.2 ml of methyl methacrylate contained in a buret. The contents of the flask were dried over MgSO$_4$ and distilled under vacuum to remove the excess THF and methyl methacrylate. The product ester was then distilled, bp 68–73 °C / 1.5 mm. The yield was approximately 15.5 g (0.098 mol) or 14% based on acetone azine.

The product ester was dissolved in ether and added to a slurry of 4 g LAH in ether in an ice water bath. The mixture was allowed to come to room temperature and stirred for 30 minutes. The workup used was found in Fieser and Fieser; for n g of LAH, n ml of water were added, followed by n ml of 15% NaOH solution and 3n ml of water.$^{21}$ The alcohol was distilled under vacuum, bp 88–90 °C / 1.2 mm with a final yield of 12% based on
starting acetone azine. ¹H NMR ð, 1.4 (s, 3H); 1.5 (s, 3H); 1.7 (s, 3H); 1.7 (s, 1H); 1.8 (AB, 2H, J = 12 Hz); 3.8 (s, 2H). Special thanks go to Gregor Marschke for his assistance in preparing the 2-diazopropane and the workup of the finished product.

**Cyclohexanecarbonyl Chloride 21**

Into a 100 ml single-necked flask equipped with a water condenser, nitrogen inlet, and stir bar was placed 12.7 g of cyclohexanecarboxylic acid, 1 ml pyridine, and 30 ml of thionyl chloride. The thionyl chloride was added slowly, as it reacted immediately with the acid. The reaction mixture was stirred for 20 minutes until the fizzing had stopped, and the excess thionyl chloride was removed by vacuum distillation. The final product was distilled in a micro distillation apparatus, bp 50.5-51.0 °C / 6mm. NMR was used to check the reaction by verifying the absence of the acid proton.

**(3,5,5-trimethyl-1-pyrazolin-3-yl) methyl cyclohexanecarboxylate**

(13)

Into a 100 ml single-necked round-bottom flask equipped with a 10 ml dropping funnel, nitrogen inlet, and a stir bar was placed 0.6695 g (4.71 mmol) of 22 and 5 ml of pyridine. After stirring to dissolve the starting alcohol, the acid chloride, 21, was placed in the dropping funnel and added dropwise. The reaction mixture was then stirred for 3 hours with no heating.
The crude product was worked up by addition of water, extraction with methylene chloride, acidification of the organic layer, separation, and removal of the solvent via a rotovap and vacuum pump. Distillation of the product ester gave 0.4796 g, a 40% yield, bp 135°C /0.1 mm. $^1$H NMR $\delta$, 1.2 (s, 3H); 1.4 (s, 3H); 1.8 (s, 3H); 1.0–2.0 (br m, 11 H); 4.3 (AB, 2 H, J = 12 Hz).

3. Nitrogen Quantum Yield Measurements

The proper amounts of 10 (0.0198 M) and 12 (0.1033 M) were first dissolved in UV grade benzene and placed into a round pyrex sample tube with two sealing constrictions. A diffusion pump operating at a pressure of $10^{-7}$ torr removed any dissolved gases in the sample by a freeze-pump-thaw degas method. After four cycles, the tube was sealed at the upper constriction and irradiated in a merrygoround at 366 nm using a Hanovia 450 W medium pressure mercury lamp with an intensity of 0.744 me/hr and a diaza filter. During the irradiation, the carousel and sample tube were continuously turning to minimize any deviations in the tube or the irradiating light. The actinometer used to measure the lamp intensity was a mixture of 0.02 M benzophenone and 0.02 M DBH.

The volume of gas evolved upon irradiation was measured by connecting the sample tube to a vacuum line equipped with a mercury manometer and a Toepler pump. When the system had been evacuated, the lower constriction in the tube was broken, and the nitrogen was forced into
the manometer through the pump. The moles of nitrogen evolved were calculated from the manometer reading, the volume of the gas buret, and the ideal gas law.

4. Irradiation Experiments

Irradiations for the study of bimolecular energy transfer were made at 313 nm using an Oriel 500 W high pressure mercury lamp and diaza filter. An NMR tube containing 0.3 ml of 0.0142 M 4BB-Py in deuterated benzene and 0.3 ml of 0.0305 M CH-Py in deuterated benzene was placed in a ring stand clamp and immersed in a water bath, with the diaza filter cell between the lamp and the sample. The sample was irradiated in 15 minute increments. During the periods between irradiations, the sample was kept in the refrigerator.

90 Mhz $^1$H NMR was then used to measure the peak ratio of products and reactants after each irradiation. Since the peaks were too close together for accurate integration, peak height was used to estimate peak area for a qualitative result. Unfortunately, for these initial experiments, no internal NMR standard was used, so an exact analysis of the rate of product formation was difficult, as the peak height varied depending on the NMR parameters.
NMR SPECTRA
References


11. Reference 8, p. 15.

12. Reference 9, p. 84-85.

13. Reference 8, p. 17.

15. Reference 9, p. 118.


30. This suggestion was provided by Dr. Jack Saltiel of Florida State University. His help and interest are gratefully appreciated.


PART II

The Stereochemistry of

4-benzoyl-2,3-diazabicyclo [2.2.2] oct-2-ene
INTRODUCTION

Douglas W. Horsey at Rice University had earlier prepared a compound known as 4-benzoyl-2,3-diazabicyclo[2.2.2]oct-2-ene or AP-DBO, 24.\(^1\) While 24 had been characterised by NMR, the exact stereochemistry at the carbon \(\alpha\) to the carbonyl, endo or exo, was not known.

The nature of the synthesis, as well as a sharp melting point, indicated that only one epimer was present, but the exact epimer was unknown. The molecule was synthesized by Douglas W. Horsey using the following steps:\(^2\)

\[
\begin{align*}
\text{phenylacetic acid} & \xrightarrow{\text{Na} / \text{NH}_3} \text{phenylacetic acid} & \xrightarrow{\text{KOH} / \text{H}_2\text{O}} \text{phenylacetic acid}
\end{align*}
\]
The stereochemistry of 24 was determined by the catalytic hydrogenation performed midway through the synthesis. We decided that the most effective probe of the stereochemistry at the carbon \( \alpha \) to the carbonyl would be NMR. A study of nuclear Overhauser effects, NOE, could be used to determine the proximity of the hydrogen in question, \( H_a \), to other hydrogens on non-adjacent carbons.
If the benzoyl group were in the endo configuration, the hydrogens on the unsubstituted bridge should show some interaction with $H_a$, whereas if it were in the exo configuration, (structure shown above) no such interaction would be observed. The only difficulty with such an experiment would be judging the significance of the observed NOE effects, since only one epimer of the molecule was available. If both epimers were available, the NOE experiment should clearly indicate the stereochemistry at the desired carbon center. The attempts to determine the stereochemistry of AP-DBO can be divided into two main areas: attempts to synthesize the epimer and 300 MHz studies of the original sample synthesized by Douglas W. Horsey.
RESULTS

An NMR sample of AP-DBO that had been sent to California for 300 MHz NMR analysis decomposed during the trip. It appears that impurities or carbenes in the chloroform attacked the AP-DBO. A TLC of the decomposed sample showed two spots and an impurity streak at the origin. The spot closest to the origin was identified as AP-DBO, giving rise to the possibility that the other spot was the epimer. The contents of the NMR tube were finally separated by HPLC into five components. The five peaks corresponded to three contaminants and two fractions containing an azo and benzoyl group, based on UV spectroscopy. The slowest-moving component was identified by NMR as the original AP-DBO sample. It was hoped that the other non-contaminant fraction would prove to be the epimer, but insufficient amounts of the material were purified and collected.

In an attempt to duplicate the earlier decomposition, AP-DBO was refluxed with chloroform for 10 days, but insufficient amounts of the supposed epimer could be collected by HPLC. AP-DBO was also treated with a number of reagents in an effort to remove $\text{H}_2$. These reagents, primarily bases, were as follows: $\text{K}_2\text{CO}_3$, NaOD, or $\text{D}_3\text{PO}_4$. All of these substances failed to remove the desired proton. In addition, several unsuccessful attempts were made to grow a crystal of AP-DBO suitable for x-ray
crystallography. The diffusion method of crystal growing\textsuperscript{3} using chloroform and cyclohexane as solvents, gave no suitable crystals and only destroyed the original starting material.

The only method found for successful epimerization was treatment with lithium diisopropylamide, LDA, followed by workup with either water or D\textsubscript{2}O. The LDA removed the hydrogen $\alpha$ to the carbonyl, forming the presumably planar anion. Following a workup with D\textsubscript{2}O, $^1$H NMR showed no evidence of H\textsubscript{a}, implying that the hydrogen was replaced by a deuterium. Unfortunately, due to the small amount of starting materials that were available, this epimerization had to be run in very small batches, making it difficult to purify a large amount of the epimer. Finally, close to 7 mg of D-epimer made using LDA was collected via preparative HPLC using a Beckman 10mm i.d. ODS silica gel column and 60\% EtOAc in hexane as eluent. This sample gave too weak a signal for effective NOE measurements. Since H\textsubscript{a} was replaced by a deuterium, any chance for NOE to an adjacent hydrogen was destroyed, but this experiment might have given the relative orientation of the geminal hydrogens $\alpha$ to H\textsubscript{a}.

In an effort to obtain more material with similar stereochemistry, the intermediate acid, 25, was reacted with diazomethane to synthesize 26, DB00Me.
Although this synthesis gave more usable compound, the sample of 26 was impure. Preparative gas chromatography was tentatively chosen as the best method for purification, but lack of time precluded any attempt to study the feasibility of purifying 26 via GC.

The NMR spectra were run on a Bruker 300 MHz NMR by Dr. Alan Kook of Rice University. All samples were dissolved in CDCl₃ and used TMS as a reference. The 5 mm NMR sample tubes used for these experiments were either Wilmad PS precision grade or Norell 508-UP ultra precision grade.

Unfortunately, little information could be gained through the use of 300 MHz NMR experiments. Originally, several two-dimensional J-correlated (COSY) and one-dimensional and two-dimensional nuclear Overhauser effect (NOESY) experiments were performed on the sample from Douglas W. Horsey's work, but no clear information about the stereochemistry at the indicated carbon center was obtained. The most useful information was the correlation of C-13 and ¹H NMR spectrum (HETCOR) (Figure 1) and a two dimensional COSY experiment that clearly indicated the hydrogens attached to the carbons. A COSY of the region from
1.0 to 6.0 ppm (Figure 2), showed coupling between all the bridging hydrogens and the bridgehead hydrogens and confirmed the assignment of the bridgehead hydrogens, see Figure 3 in the text. The bridging hydrogens were divided into two groups: the two hydrogens hanging over the azo group appearing at 1.34 ppm, and the two hydrogens toward the benzoyl group appearing at 1.62 ppm. This spectrum likewise identified the bridgehead hydrogen at 5.51 ppm to be the bridgehead position between the azo and the benzoyl group. This assignment relegates the remaining bridgehead hydrogen to the peak at 5.34 ppm.

Unfortunately, since the group of peaks at 2.0 ppm could not be properly resolved, none of these experiments provided any information about the coupling of the adjacent hydrogens to $H_a$.

![Diagram](image)

Figure 3. Proton and $^{13}C$ assignments for AP-DBO

Although slight NOE effects were seen between $H_a$ and other hydrogens, the peaks at 2.0 ppm for the geminal hydrogens adjacent to $H_a$,
$H_{g1}$ and $H_{g2}$ could not be distinguished (Figure 4). This region was particularly important, as $H_a$ must either point up or down, and must therefore be closer to the adjacent hydrogen pointing in the same direction (either $H_{g1}$ or $H_{g2}$) than to the other geminal hydrogen. The stereochemistry of $H_{g1}$ or $H_{g2}$ could in theory be determined by NOE to the bridging methylene hydrogens. Once the direction in space of $H_{g1}$ and $H_{g2}$ was known, the appearance of greater NOE to $H_a$ by one of these hydrogens would confirm the stereochemistry at the desired carbon center. Although these two hydrogens seemed to appear at different frequencies, namely 1.90 and 2.00 ppm, their proximity to the bridging hydrogens cannot be accurately determined. An interesting fact to note in this spectrum is the lack of any NOE to the bridgehead hydrogens by any nearby hydrogens. The one-dimensional NOE experiments likewise failed to give any useful information.

The $^1$H NMR spectrum of 26 was similar to that of 24, except for the absence of aromatic peaks and the appearance of the new sharp singlet of the isolated methyl group at 3.75 ppm. As was the case earlier, the NOE to $H_a$ could not be determined. An NOESY of 26, including a blow-up of the region from 0.2 to 1.5 ppm (Figure 5 and 6), seemed to separate the signals of $H_{g1}$ and $H_{g2}$, but the signal was too weak to establish accurate NOE assignments.
FIGURE 5
ROESY of 26, 0.2 - 1.5 ppm
The key to the successful assignment of the stereochemistry of AP-DBO is the synthesis of pure starting material coupled with probes by high resolution NMR. It is regrettable that this problem was not solved during this period of work, but some new information was gained, even though this information was not decisive.
References


2. Reference 1, p. 38.

APPENDIX I

Modifications to Laser Flash Photolysis Apparatus
During the period from November 1985 to February 1986, several changes were made in the group laser flash photolysis apparatus in an attempt to upgrade and improve the system from the previous 100 MHz transient digitizer to a new 200 MHz transient digitizer. The following is a brief summary of those changes and the appropriate programs and subroutines:

1. A new, lighter weight analyzing light shutter and two new lenses were installed in the analyzing light path to improve the focus. Changes to the software were made to drive the shutter.

2. The Bi-Ra ADC voltage range and numerical representation were changed to offset binary to match the DAC. The offset binary encoding gave a range of +5 V to -5 V corresponding to the following octal values:

   -5 V   0  
   0 V    2048
   +5 V   4096

3. A new subroutine was written to read and write to the OR-3 output register and the Bi-Ra known as SUREAD. Two additional subroutines,
OREAD1 and OFFCH1, were written to change the offset of the 200 MHz transient digitizer.

4. A new nulling subroutine to remove the effect of the "light-on" voltage was written. The subroutine is entitled NULLDE and incorporates the new routines OREAD1, OFFCH1, and SUREAD.

5. A shutter for the laser was installed to aid in the removal of background noise. Previously the background was obtained by simply not firing the laser. Since the laser generates a great deal of Rf noise on firing, this previous method was not overly effective. Using the new method, one shot would be used to irradiate the sample with the shutter open. The next shot would be a background subtraction shot with the shutter closed. The subtraction would take place during the calculation portion in the program, thereby removing the oscillations caused by the laser firing.

6. A moveable platform was mounted for the laser shutter to allow the shutter to be moved out of the laser firing path. This permitted other laser irradiation experiments to be made without destroying the alignment of the shutter.

7. A number of changes were made to YAC100, the previous program for
running the laser flash photolysis apparatus. Most of these changes affected calculations with the 200 MHz transient digitizer, timing for the laser and analyzing light shutters, and background noise subtraction. In addition, the entire program, including the new material and all new subroutines, was documented. This new program was then called YAC200.

8. The testing program for the flash photolysis apparatus SAC100 was also changed to account for the hardware improvements. The new program was called SAC200.

9. A new library was created to run both YAC200 and YAC100, incorporating the new subroutines and older routines. The library is known as ASWLIB.

10. YAC200 was finally linked to a plotting program known as HARDCO created by John N. Scholz. Several modifications had to be made to the reading and writing statements in the program and in YAC200. The principal change was to create a variable known as YPLOT which contains the decay time information. In addition, a new heading subroutine was created, called HEADZ. The new plotting program was renamed YACPLT.
11. A final program, known as TAC200, was written for the laser to examine the data points, background points, and corrected data points as separate columns within a file. Its purpose was to aid in analyzing and correcting any background noise. Plotting of these files cannot be done using the YAC200 graph command, but must be done with the HP autoplot function.
SUBROUTINE SUREAD (ICHAN, RLYFLG, STPFLG, IVOLT) ! P.S. ENGEL 12/12/85

C READS BI-RA VOLTAGE USING CHOPPED LIGHT. ICHAN IS 3 FOR OP AMP,
C ! FOR PMT OUTPUT. OP AMP RELAY CLOSED IF RLYFLG=1.
C STEPPER PWR ON IF STPFLG=1.
C NOTE: BOTH DAC AND BIRA ADC ARE IN OFFSET BINARY
COMMON/SUBCOM/ADADR, OR3AD, ! COMMON WITH CALLING PROGR.
       ADADR, OR3AD
       INTEGER ADADR, OR3AD
       LOGICAL OR3AD, RLYFLG, STPFLG
       IDAT = 102 ! ASSUME RELAY OPEN, STEP PWR OFF
       IF (.NOT.RLYFLG.EQ.1 .AND. STPFLG.EQ.0) IDAT = 122
       IF (.NOT.RLYFLG.EQ.1 .AND. STPFLG.EQ.1) IDAT = 142
       IF (.NOT.RLYFLG.EQ.0 .AND. STPFLG.EQ.0) IDAT = 142
       CALL CC3A(16, ADADR, ICHAN, 0) ! SET BI-RA TO DESIRED CHANNEL
       CALL CC3A(16, OR3AD, IDAT, 0) ! SET START CONVERT FLIP FLOP
       CALL CC3A(21, OR3AD, "100", 0) ! RESET FLIP FLOP
       CALL CC3A(0, ADADR, IVOLT, 0) ! TRY TO READ BI-RA
       IF (.NOT.0) GO TO 1 ! CYCLE UNTIL CHOPPER ALIGNED
       VOLT = (FLOAT(IVOLT - 240))/409.6
WRITE (5, 3) ICHAN, VOLT
3 FORMAT (' CH.', I2, ',=', F6.3)
RETURN
END
SUBROUTINE READ(I0FRA)
! READS LECROY OFFSET
MODIFIED FROM OFREAD 1/85, UPDATED 12/16/85 BY ASW
COMMON/MODCOM/DACAD,TDADR,CRA DR
INTEGER=2 DACAD,TDADR,CRA DR
LOGICAL=1 Q
CALL CSSA(1,TDADR,I0FFDA,Q) ! READS OFFSET INTO HIGH BITS (9-16)
WRITE(5,07) TDADR,Q
87 FORMAT(' TDADR=','07,2X,' Q=',12)
WRITE(5,06) I0FFDA
86 FORMAT(' I0FFDA=',7)
C THE FOLLOWING LINE CONVERTS THE HIGH BITS (9-16) INTO LOW
C BITS (1-8) SO THEY CAN BE PROPERLY READ
I0FFD=(I0FFDA,AND,'177400)/256
C THE NEXT LINE REMOVES ANY EXTRAENED VALUES IN REGISTER 9-16
I0FFR=(I0FFR,AND,'3777)
WRITE(5,1008) I0FFR,I0FFR
1008 FORMAT(' OFFSET=',7,16)
RETURN
END
SUBROUTINE OFFCH1
! CHANGES LECROY LOWER VOLTAGE
C
NEW VERSION OF OFFCHG, FIRST WRITTEN 1/85, MODIFIED 12/17/85
COMMON/MODCON/DACAD,TDADR,CRADR
INTEGER+2 DACAD,TDADR,CRADR
LOGICAL+1,9
120 WRITE(5,2032)
2032 FORMAT(' ENTER NEW LOWER VOLTAGE LIMIT (BETWEEN -511 AND 0)'>$)
READ(5,9,m) IOFF
IF(IOFF.LE.-512) GO TO 111
GO TO 113
111 WRITE(5,112)
112 FORMAT(' LOWER LIMIT EXCEEDED')
GO TO 120
113 WRITE=('\((IOFF+511)/2\)'\$)
\&CONVERTS LOWER LIMIT TO OFFSET VALUE
CALL CISSA(9,TDADR,WRITE,0) \&WRITE OFFSET TO TD
WRITE(5,91) \&WRITE
91 FORMAT(' WRITE=\(07\)
\&WRITE(5,2030) WRITE,IOFF,IOFF+511,9
2030 FORMAT(X,15, WRITE TO TD. RANGE=\(,14, TO \',14, NV,\) G=\(,12\)
RETURN
END
SUBROUTINE NULDE(STPFLG)
! TESTS THE NULLING FUNCTION FOR LIGHT ON
C
! BOTH DAC AND BIRA ADC ARE IN OFFSET BINARY
COMMON/ADAC,ADAD,DRAD
COMMON/MODCOM/DACAD,TDACR,CRACR ! COMMON WITH MAIN
INTEGER+2 ADAC,ADAD,DRAD,CREG
LOGICAL+1 QT,STPFLG,RVFLG
ADAC=CREG(1+.5,0)
ADAD=CREG(1+.5,0)
CALL CSSA(16,ADAC,248,0) ! SET DAC TO -2V OUTPUT
CALL CSSA(26,ADAD,0,0) ! SET BIRA TO RUN MODE
CALL SREAD(11,1,STPFLG,IPHOT) ! READ PMT OUTPUT INTO IPHOT
IDAC=IPHOT ! INITIALIZE VALUE FOR DAC
CALL CSSA(16,ADAC,0,0) ! WRITES OFFSET V INTO DAC
CALL SREAD(3,1,STPFLG,IPOUT) ! READ OPAMP OUTPUT
DO 10 I=0,1
10 IDAC=(IPOUT-2658) ! CALCULATE OFFSET VOLTAGE
IDAC=IDAC-IDACJ ! CALCULATE NEW DAC VOLTAGE
CALL CSSA(16,ADAC,0,0) ! WRITE NEW VOLTAGE TO DAC
CALL SREAD(3,1,STPFLG,IPOUT) ! READ OPAMP OUTPUT
IF(IPOUT.LE.2058.AND.IPOUT.GE.2038) GO TO 5
C END OF LOOP
5 RETURN
END
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YACO3A FOR P.S. ENGEL 6-JAN-86
PROGRAM TO ACQUIRE AND ANALYSE TRANSIENT ABSORPTIONS. BE SURE
1MHz THE DELAY BETWEEN STOP TRIGGER AND LASER FIRING IS SET
PROPERLY. (THREE POSITIONS SWITCH ON TIMING BOX). SET PAM POWER
SUPPLY FOR "INTERNAL".

BACKGROUND WILL NORMALLY BE SUBTRACTED (IBKGFL), POINTS
AVERAGED IN GROUPS OF 3 (XSCALE), UNFORMATTED DATA FILES
WRITTEN TO DISK

BACKGROUND SUBTRACTION AND AUTOMATIC PLOTTING ADDED 2/4/84
MODIFIED TO PLOT USING HARDCO 1/7/86
1ST VERSION FOR 200 MHZ LECROY.

COMMON/SCOM/ADADR,ORDRD ! COMMON WITH SREAD
COMMON/SCOM/ADADR,ORDRD,CRADR ! COMMON WITH PEREAD, ETC.
COMMON/FNAME/FILEM ! COMMON WITH TGDFMA
COMMON/RANDAT/XKEEPY(342),YKMIN,YKMAX ! COMMON WITH SBUYI
COMMON/ONEFIT/ONEPAR(16),ISAMP,YARR(342) ! WITH LEGUA

THE VARIOUS ARRAYS IN THE PROGRAM ARE THE FOLLOWING:
XKEEPY CONTAINS THE SIGNAL AVERAGED POINTS IN GROUPS OF THREE
YARR IS LOG(ABSORBANCE) FOR LEAST SQUARES FIT

YPLLOT CONTAINS THE POINTS FOR PLOTTING THE FITTED DECAY CURVE
YCALC IS USED FOR CONSTRUCTING A FIRST ORDER PLOT

IBKG CONTAINS THE BACKGROUND POINTS FROM THE LASER FIRING
IDATOT CONTAINS THE SUMMATION OF THE RAW DATA FROM EACH SHOT
DATA CONTAINS THE DIGITIZED DATA FROM EACH INDIVIDUAL SHOT

DIMENSION YCALC(342),IBKG(1024),YPLLOT(342)

INTEGER*2 DACAD,ADADR,ORDRD,TDADR,CDREG,CRADR,IDATOT(1024)
INTEGER*2 CBI(5) ! FOR CSUBC COMMAND
INTEGER*2 FF(5),AA(5),CB(5),DBKG(5),DDATA(S) ! FOR CSA
INTEGER*2 BUF(512),CFLAG

EQUIVALENCE(IBUF,DATA) ! BOTH INTO SAME MEMORY SPACE
BYTE ANG(2),IDATA(1024),FILEM,ESC,IDATE(9),CTIME(8),C(14)
BYTE ID(60) ! IDENTIFIES FILES TO BE WRITTEN
LOGICAL*1 Q,2Q(5)

DATA FF/16,16,16,16,21/ ! ARRAY FOR CSA
DATA AFG/240,320,330/ ! FOR CSA
DATA XSCL/3.0/ ! FOR CSA
DATA XADC/0.1,0.1/ ! FOR CSA
DATA TADC/0.1,0.1/ ! FOR CSA
DATA CDREG/1.5,10.0/ ! FOR CSA
DATA CRADR/1.5,10.0/ ! FOR CSA
DATA AA(1)=0.120 ! FOR CSA
DATA AA(2)=0.00 ! FOR CSA
DATA AA(4)=0.00 ! FOR CSA
DATA AA(11)=0.00 ! FOR CSA
DATA AA(12)=0.00 ! FOR CSA
DATA AA(13)=0.00 ! FOR CSA
DATA AA(14)=0.00 ! FOR CSA
DATA C(11)=512 ! FOR CSA
DATA C(12)=5 ! FOR CSA
DATA C(9)=512 ! FOR CSA

CALL SETERR(4,225) ! KILL "GO TO" ERROR MESSAGE
CALL ERRANS ! CLEAR THE ERROR BUFFERS
ORDRD=CDREG(1,5,11,0) ! OFF ADDRESS
DACAD=CDREG(1,5,10,0) ! DA/12 ADDRESS IN SLOT 12
TDADR=CDREG(1,5,16,0) ! LECROY TO IN SLOT 17
CRADR=CDREG(1,5,0,0) ! CRATE ADDRESS
AA(1)=ADADR ! ARRAY OF ADDRESSES FOR CSA
AA(2)=0.00 ! FOR CSA
AA(3)=0.00 ! FOR CSA
AA(4)=0.00 ! FOR CSA
AA(11)=0.00 ! FOR CSA
AA(12)=0.00 ! FOR CSA
AA(13)=0.00 ! FOR CSA
AA(14)=0.00 ! FOR CSA
DATA C(11)=512 ! FOR CSA
DATA C(12)=5 ! FOR CSA
DATA C(9)=512 ! FOR CSA
DATA C(8)=5 ! FOR CSA

CALL APADE ! CLEAR ALPHANUMERICS
*E*-ENTER SAMPLE PERIOD

1006 WRITE(5,448)0,ESC

448 FORMAT(2A1,'dD')

CALL PERCH

CALL PERCH(ISAMP)

WRITE(5,669)ISAMP

669 FORMAT('PERIOD WAS SET TO',I4,' NS')

CALL DREAD1(IOFFSET)

WRITE(5,6146)

6146 FORMAT('TYPICAL OFFSET IS 3. HIT "S" TO CHANGE IT.')

CALL RCRDL0

WRITE(5,136)

136 FORMAT(1X,'FLASH','S')

WRITE PROMPT

READ(5,709,END=5)ANS(1)

709 FORMAT(1A1)

C

NEXT STATEMENT WORKS IN RT-11 BUT NOT IN IAC

GO TO (1000,1001,1002,1003,1004,1005,1006,1007,1008,1009,
  1010,1011,1012,1013),INDEX(C,ANS(1))

WRITE(5,711)

711 FORMAT('ILLEGAL COMMAND. REENTER')

GO TO 3

C

"H"-HELP FILE OF ALLOWED COMMANDS

1800 WRITE(5,448)0,ESC

WRITE(5,723)

723 FORMAT(1X,'The commands available are:','/'
  5X,'A'-' Abort the program'/
  5X,'B'-' Background minimum-maximum determination'/
  5X,'C'-' Calculate decay time of transient'/
  5X,'D'-' Enter transient digitizer parameters'/
  5X,'F'-' First order plot to be displayed'/
  5X,'G'-' Graph decay curve on screen'/
  5X,'H'-' Help file (this text) typed to screen'/
  5X,'I'-' Integrate over one or more shots'/
  5X,'O'-' Overwrite scattered laser light points'/
  5X,'P'-' Print output data on local printer'/
  5X,'R'-' Read data from a previously written file'/
  5X,'S'-' Special parameter settings desired'/
  5X,'U'-' Type out raw summed data and background'/
  5X,'W'-' Write 341 XKEEPY points to a file'/

GO TO 3

C

"S"-SPECIAL PARAMETER SETTINGS

1812 WRITE(5,448)0,ESC

WRITE(5,491)

491 FORMAT('DEFAULT SETTING FOR THE FOLLOWING QUESTIONS IS "N".')

WRITE(5,423)

423 FORMAT('DO YOU WISH TO OMIT BACKGROUND CORRECTION?')

READ(5,709)ANS(1)

IF(ANS(1).EQ.'Y')IBKFL=0

IF(ANS(1).NE.'Y')IBKFL=1

TYPE 423

434 FORMAT('DO YOU WISH TO OMIT AVERAGING IN GROUPS OF 32?')

READ(5,709)ANS(1)

IF(ANS(1).EQ.'Y')XSCALE=1.0

IF(ANS(1).NE.'Y')XSCALE=3.0

WRITE(5,425)

435 FORMAT('DO YOU WISH TO WRITE FORMATTED FILES?')

READ(5,709)ANS(1)

IF(ANS(1).EQ.'Y')IFILFL=1

IF(ANS(1).NE.'Y')IFILFL=0

CALL OFFCOM

WRITE(5,425)
GO TO 3

"I" - INTEGRATE OVER SEVERAL SHOTS

WRITE(5,448) 0,ESC ! TURN OFF GRAPHICS

WRITE(5,426) ! TURN OFF GRAPHICS

READ(5,49)NSHOTS

IF(NSHOTS.LE.0) GO TO 799

CALL CSBA(16,ORIAD,",2,0) ! OPEN SHUTTER

CALL WAIT(0,0,5) ! ALLOW TIME TO SETTLE

WRITE(5,2020)

FORMAT( ' WAIT PASSED' )

CALL NULLDE(0) ! NULL OUT LIGHT-ON VOLTAGE

PULTOT=0.0

PULMAX=0.0

PULMIN=0.12

WRITE(5,779)

DO 199 I=1,1024 ! SET ARRAYS TO ZERO

IBK(I)=0

CALL SUREAD(3,1,0,1,OUT) ! READ GPAMP OUTPUT

GPAMP1=(FLOAT(OUT-2048))/409.6 ! CALC DC VOLTAGE FOR OFFSET BINARY

CALL SUREAD(1,1,0,IPHT) ! READ PHT OUTPUT

PHOT1=(FLOAT(IPHT-2048))/409.6 ! CALC DC VOLTAGE FOR OFFSET BINARY

C

C

DO 399 J=1,NSHOTS ! START ACQUISITION OF DECAYS

C

THE FOLLOWING CSBA COMMAND SETS THE BI-RA TO CH. 2 (PULSE ENERGY),

C

RESETS THE SATED INTEGRATOR, AND FIRES THE LASER TO ACQUIRE BACKGROUND.

C

C

FINALLY, THE SHUTTER IS OPENED.

C

CALL CSBA(9,TAADR,D,0) ! START DIGITIZING

CALL CSBA(0,AADDI,IBUKI,0,0,0) ! READ DATA TO INTEGER=2 ARRAY

CALL CSBA(17,TAADR,D,0) ! LOAD STARTING ADDRESS

IF(.NOT.D) GO TO 249

WRITE(5,719) ! THIS IS IMPORTANT

GO TO 249

IF(.NOT.D) GO TO 719

C

C

DO 209 I=1,1024 ! SUMMATION OF DECAYS

IF(IDATA(I))=222,222,225 ! HANDLES 2'S COMPLEMENT OUTPUT

GO TO 209

C

C

THE FOLLOWING CSBA COMMAND SETS THE BI-RA TO CH. 2, RESETS THE SATED

C

INTEGRATOR, AND FIRES THE LASER TO ACQUIRE DATA WITH THE SHUTTER

C

C

OPEN.

C

CALL CSBA(9,TAADR,D,0) ! START DIGITIZING

CALL CSBA(0,AADDI,IPULS,D,0) ! READ OUT PULSE ENERGY (CH.2)

CALL CSBA(27,TAADR,D,0) ! CHECK IF LEGRO CYCLE FINISHED

IF(.NOT.D) GO TO 716

C

C

DO 405 I=1,1024 ! SUMMATION OF DECAYS

IF(IDATA(I))=332,332,332 ! HANDLES 2'S COMPLEMENT OUTPUT

GO TO 405
CALL CSSA(16,OR3AD,",2,2")   ! OPEN SHUTTER
CALL WAIT(0,0,5)            ! ALLOW TIME TO SETTLE
CALL NULLDE                ! NULL LIGHT-ON VOLTAGE
CALL CSSA(9,TD3AR,0,0)     ! START DIGITIZING
CALL CSSA(8,AD3AR,1DBN,0)  ! GET BACKGROUND
248 IF(.NOT.0) GO TO 248
718 IF(.NOT.0) GO TO 718     ! THIS IS IMPORTANT
CALL CSSA(27,TD3AR,0,0)    ! LOAD STARTING ADDRESS
CALL CSSA(17,TD3AR,0,0)    ! READ DATA TO INTEGER+2 ARRAY
IDMAX=300
IDMIN=300
DO 143 L=17:1024            ! FIND MAX. AND MIN. OF BKGND
   IF(IDATA(L))=IDATA(L)+"200"
      GO TO 144
143 WRITE(5,1111) IDMAX,IDMIN ! MAX FAILS ON BYTE VARIABLE
1111 FORMAT(5,"MINIMUM",14,2X,"MINIMUM",14) ! FOR BACKGROUND, MAXMIN=14,2X, MINIMUM=14
CALL CSSA(9,OR3AD,0,0)     ! CLOSE SHUTTER
CALL CSSA(24,AD3AR,0,0)    ! INHIBIT BI-RA'S RUN MODE
GO TO 3
C
"C"-GRAPH THE DATA ON THE SCREEN
C
1013 TBASE=FLOAT(ISAMP)/1000.0 ! TIME BASE IN MICROSEC./CH.
   TYPE 5,TBASE
5 FORMAT(1,'TIME BASE=',15,F8.3,'MICROSEC./CHANNEL')
XINC=50.0 ! X INCREMENT FOR GRAPH LABELS
YINC=(YMAX-YMIN)/5.0 ! Y INCREMENT FOR GRAPH LABELS
C
CLEAR GRAPICS MEMORY AND TURN OFF ZOOM
   TYPE 18,0,ESC
10 FORMAT(2'A1,'d h a')
C
FILL IN AUTOPLLOT MENU AND DRAW AXES. AVOID "RECORD TOO LONG" ERROR.
   TYPE 11,0,ESC,(YMIN-YMAX),
   XINC,XINC/2.0
11 FORMAT(2'A1,,'d h 2i 1i 2j 9k 8l 342m',F12.4,'n 0
   a',F10.2,",',F10.2,",'2Z")
   TYPE 19,0,ESC,YINC,YINC/2.0,112
19 FORMAT(2'A1,,'d h 3i',F10.2,",',F10.2,",'8S',',14,",s 8v 8w 8z")
   TYPE 12,0,ESC,ESC,ESC
   ! SKIPS A PAGE AND 2 LINES
12 FORMAT(2'A1,,'d h 3i'
   TYPE 13,0,ESC
13 FORMAT(2'A1,,'d h 3i'
   CALL WAIT(0,2,0)     ! WAIT WHILE AXES ARE DRAWN
   DO 87 I=1,325,12
      Y1=XKEYEP(1)-YMAX
      Y2=XKEYEP(1)+YMAX
      Y3=XKEYEP(1)+YMAX
      Y4=XKEYEP(1)+YMAX
      WRITE(5,14) I,Y1,1+3,Y2,1+6,Y3,1+9,Y4
   IF((ITITRN()=.EQ."32") GO TO 88
   WRITE(5,887) '*','ESC
87   FORMAT(2'A1,,'d h a')
14 FORMAT(4'16,x,F12.4')   ! SEND 4 PAIRS AT A TIME
88 WRITE(5,881) 0,ESC,ESC,ESC
   ! SKIP A PAGE AND 2 LINES
   WRITE(5,888) '+','ESC
888 FORMAT(2'A1,,'d h 3i'
   ! FOR SCREEN LOCATION OF STANDARD
   ICALL 8
C CALL SREAD(1,1,0,IPHT)  READ PMT OUTPUT
PHOT:=FLOAT(IPHT/2048))/409.6  CALC DC VOLTAGE FOR OFFSET BINARY
CALL SREAD(1,1,0,OUUT)  READ GPAMP OUTPUT
DPAMP:=FLOAT(OUUT/2048))/409.6  CALC DC VOLTAGE FOR OFFSET BINARY
THE "O" AND "U" ARE NECESSARY DUMMY VARIABLES IN WHAT FOLLOWS
CALL CCFLG(1,DPAMP,OUUT)  CLOSE SHUTTER, RESET OR I
CALL CBUFF(24,HAUH,1,0,0)  INHIBITS BIRA'S RUN MODE
PHOT:=PHOT+PHOT(1)/2.0
DPAMP:=DPAMP+DPAMP(1)*2.0
PULS:=PULS+PULS(1)*2.0
CONTINUE  LOOP BACK TO STMT 298

C

C FLOWT(IDATOT) := IDATO(1)-IBK(1)  SUBTRACTS BACKGROUND
C
C CALL SREAD(1,1,0,IPHT)  READ PMT OUTPUT
PHOT:=FLOAT(IPHT/2048))/409.6  CALC DC VOLTAGE FOR OFFSET BINARY
CALL SREAD(1,1,0,OUUT)  READ GPAMP OUTPUT
DPAMP:=FLOAT(OUUT/2048))/409.6  CALC DC VOLTAGE FOR OFFSET BINARY
THE "O" AND "U" ARE NECESSARY DUMMY VARIABLES IN WHAT FOLLOWS
CALL CCFLG(1,DPAMP,OUUT)  CLOSE SHUTTER, RESET OR I
CALL CBUFF(24,HAUH,1,0,0)  INHIBITS BIRA'S RUN MODE
PHOT:=PHOT+PHOT(1)/2.0
DPAMP:=DPAMP+DPAMP(1)*2.0
PULS:=PULS+PULS(1)*2.0
CONTINUE  LOOP BACK TO STMT 298

C

C

C

C
GO TO 3

CALL SUBSLE(1 BASEX, BASEY)  'GETS PRE-FLASH BASELINE
C= NEXT, OVERWRITE ALL KKEEPY POINTS WHICH ARE TOO POSITIVE
WRITE(5,087) C

TYPE 359
FORMAT('ENTER A WHEN YOU HAVE DONE SO. ') RETURNS POSITION IN DATASET UNITS
IXOVRM=IXOVRM-FIX(1000)
DO 8857 I=IBASEX,IXOVRM
   KKEEPY=IBASEY
   ICOUNT=ICOUNT-IBASEX
   WRITE(5,0859) ICOUNT
8857 FORMAT(11,14)  'OVERWRITE POINTS AS BASELINE
   WRITE(5,0859) ICOUNT
6 FORMAT(11,14)  'KKEEPY POINTS WERE OVERWRITTEN. HIT "G" TO
   REPOINT. )
   GO TO 8850
   WILL FIND NEW KMIN AND KMAX

C= "C=CALCULATE DECAY TIME"

CALL SUBSLE(IBASEX,BASEY)  'GETS PRE-FLASH BASELINE
IBASEX=IBASEX
IF FE 1a,BASEX,BASEY
   FORMAT(IN DATASET UNITS, X=",F7.1, \(",F9.2)"
C= ABDORANCE CALCULATING ROUTINE FOLLOWS
VR=1000.0,MPHAT
   ERROR VOLTAGE IN MV
C= KMIN COMES FROM KKEEPY IN THE "I" PORTION OF THE PROGRAM
SIGMA-BASE=KMIN
   SIGNAL MAGNITUDE IN MV
ABSMAX=ALOG10(VR/(1-SIGMA))
   CALL STEX1(SIGMA,VR,ABSMAX)
   WRITE(5,8850) '+',ESC
   MOVE CURSOR NEAR LEFT LIMIT
8850 FORMAT(2A1, \"a \d \")
   TYPE 22
   FORMAT('PLACE CURSOR AT LEFT FITTING LIMIT. ')
   TYPE 359
   CALL SUBPLOT(KLEIM,YLEIM)
   TYPE 1a,KLEIM,YLEIM
   TYPE 23
   FORMAT('PLACE CURSOR AT RIGHT FITTING LIMIT.')
   TYPE 359
   DO 516 I=1,11
      WRITE(5,516) I,ESC
   516 FORMAT(2A1, \"a \")
   WRITE(5,519) I,ESC
   'CURSOR POSITIONING
   CALL SUBPLOT(KRILIM,YRILIM)
   TYPE 1a,KRILIM,YRILIM
   C= NEXT, FIND INDEXES LLim AND Rlim FOR FITTING LIMITS
   DO 31 LIML=1,142
      DIFF=XLEIM-FLOAT(LIML)
   31 IF (DIFF.LE.0.010 TO 0)
   DO 33 LIMR=1,142
      DIFF=XRILIM-FLOAT(LIMR)
   33 IF (DIFF.LE.0.010 TO 0)
   C= NON SET UP V ARRAY TO BE FITTED. X ARRAY IS IN SUBROUTINE LLSQUR.
   CALL SETERR(15,255)  'SUFFRRESS SYS. CONTROL FOR LOG 0
   DO 28 IF (LIML.LIMR
      TEMP=BASEX-KKEEPY(I)
      'SIGNAL MAGNITUDE IN MV
      IF (TEMP.LE.0.052 TO 75) \(\"REMEMBER 1 FOR FIRST BAD POINT
      \"TEMP=(ZERO)I"
   28 C= IN THE FOLLOWING EQUATION, ALOG10(TEMP) IS THE ABSORBANCE, THE
   C= NATURAL LOG IS THEN USED FOR THE FIRST ORDER PLOT
   YARR(I)=ALOG(ALOG10(TEMP))
   CALL EARSNS(I,IR.IU)
30 IF (IR<50.15) GO TO 277
275 WRITE (5,276) I,LIMR
276 FORMAT (" POINT NO.,14,' WAS BELOW BASELINE. FITTING WILL STOP" + ,/,' HERE INSTEAD OF REQUESTED POINT NO.,',14)
277 LIMR=1
! RESET LIMR NOT TO EXCEED 1
278 NFIT=1,LIMR,LIML+1
! NO. OF POINTS TO FIT
C ISCALE SCALES SQUARE DEPENDING ON WHETHER POINTS WERE IN THREE'S CALL LSQUARE(ISCALE,NFIT,LIML,LIMR)
C TYPE 35,LIML,LIMR,NFIT
35 FORMAT (" LEFT LIMIT='",I3,'X',RIGHT LIMIT='",I3,'X',+)
+ ' NO. POINTS FIT='",I3)
30
SDFA=ONEPAR(2)/ONEPAR(1)**2)*0.081
IYVAL=178-30*IYCAL
! SCREEN LOCATION OF OUTPUT
C NEXT CALL IS TO TYPE OUTPUT PARAMETERS TO GRAPHICS SCREEN
500 CALL GTEXT2(YCAL,ONEPAR(5),ONEPAR(6),SDFA)
ICALL=ICALL+1
! MOVE DATA OUTPUT LOCATION DOWN
C NEXT, CALCULATE AND PLOT THE FITTED CURVE
C TYPE 40, 0, ESC, NFIT/3
+ ! EVERY THIRD POINT WILL BE PLOTTED
40 FORMAT (2AI,'***1',15I,' U Z')
! START AUTOPLT AGAIN
DO 50 I=LIML,LIMR
XARR=SCALE+(FLOAT(I-1))/FLOAT(ISAMP)
YCALC(I)=ONEPAR(1)*XARR+ONEPAR(2)
YPLOT(I)=V1/(1.0+EXP(VCALC(I))))-V1+BASE
DO 877 I=LIML,LIMR
Y1=YPLOT(I)-YMAX
Y2=YPLOT(I+3)-YMAX
Y3=YPLOT(I+6)-YMAX
Y4=YPLOT(I+9)-YMAX
WRITE (5,877)'*',' ESC
! SKIP A PAGE AND 2 LINES
CPLN=1
GO TO 3
50
WRITE (5,8760)
8760 FORMAT (" ( LOG & ERROR OCCURRED DURING DATA PREPARATION.)")
CALL SETERR(15,1)
+ ! REINSERT PROGRAM CONTROL IF LOG & OCCURS
GO TO 3
C
C **F** FIRST ORDER PLOT
1011 TYPE 10, 0, ESC
+ ! CLEAR GRAPHICS AND TURN OFF ZOOM
C TYPE 12, 0, ESC AND FILL IN AUTOPLT MENU AND DRAW AXES
146 FORMAT (2AI,'*a 2H 11 2J 9K 01 342M -9.0N -3.8O S0 25a Z')
WRITE (5,147) 0, ESC,NFIT
147 FORMAT (2AI,'**1.5a 0T ,13,'U V W C Z')
TYPE 13, 0, ESC
+ ! SETS AUTOPLT TO ACCEPT DATA
CALL WAIT(0,2,0)
! WAIT FOR AXES TO BE DRAWN
DO 148 I=LIML,LIMR,12
WRITE (5,1441), YARR(I), I=5,YARR(I+3), I=6,YARR(I+6), I=9,YARR(I+9)
WRITE (5,887)'*',' ESC
! WRITE NEXT POINT IN SAME SPOT
WRITE (5,885)'*',' ESC
! SCROLL ONE LINE
WRITE (5,880)'*',' ESC
! TURN AUTOPLT OFF
C NEXT, PLOT THE FIRST ORDER "LINE" +
TYPE 48, 0, ESC,NFIT/3
START AUTOPLT
DO 149 I=LIML,LIMR,3
YARR=SCALE+(FLOAT(I-1))/FLOAT(ISAMP)
YCALC(I)=ONEPAR(1)*YARR+ONEPAR(2)
DO 150 I=LIML,LIMR,12
WRITE (5,1441), YCALC(I), I=3,YCALC(I+3), I=6,YCALC(I+6), I=9,YCALC(I+9)
WRITE (5,887)'*',' ESC
CALL GTEXT1(SIGMA,V1,ABSMAX)
CALL GTEXT2(YVAL,ONEPAR(5),ONEPAR(6),SDFA)
TYPE 12, 0, ESC, ESC, ESC
! SKIP PAGE AND 2 LINES
C GO TO 3
PRINT OUTPUT DATA ON EPSON FX-80 PRINTER

WRITE(5,9826)
9826 FORMAT(1X, "THE CURRENT ID IS: ")
WRITE(5,9829) ID(I), I=1,60
WRITE(5,9827)
9827 FORMAT(1X, "DO YOU WISH TO CHANGE IT? ")
READ(5,709) ANS(1)
IF(ANS(1).NE. 'Y') GO TO 9828
WRITE(5,661)
READ(5,6002) ID(I), I=1,60
PRINT 544
544 FORMAT(1X, "ONE BLANK LINE SEPARATES DATA")
PRINT 589, (ID(I), I=1,60)
PRINT 590, TDAT,E, DTIME
PRINT 591, NSHOTS, PHOTAV
PRINT 529, IOFFST, ISAMP
PRINT 9821, LIML, LIMR, LBMFL, XSCALE
PRINT 9822, SGNV, ABSMAX, ICOUNT
PRINT 9823, ONEPAR(5), ONEPAR(6), SDATA
GO TO 3

"T"-TYPE OUT DATA POINTS

WRITE(5,44810,ESC) ! TURN OFF GRAPHICS
TYPE 540
540 FORMAT(1X, "ENTER MIN, MAX POINTS TO SEE. ("I TERMINATES")")
READ(5,437)
437 FORMAT(2X, "POINT NO. RAW TOTAL BACKGROUND")
DO 364 L=3,K,2
364 WRITE(5,489) L, IDATOT(L), LBMFL(L), L+1, IDATOT(L+1), LBMFL(L+1)
WRITE(5,499) X(L), X(L), X(L), X(L), X(L), X(L), X(L), X(L)
IF(ITITMR(L), EQ. "32") GO TO 3
GO TO 3

"W"-WRITE DATA TO A FILE

WRITE(5,1026) CFLAG, LIML, LIMR
1026 FORMAT(1X, CFLAG=' ', I2, ' ', LIML=' ', I4, ' ', LIMR=' ', I4)
IF(CFLAG.EQ.1) GO TO 660
ABSMAX=0.0
LIML=0
LIMR=0
ONEPAR(5)=0.0
ONEPAR(6)=0.0
SDATA=0.0
DO 659 I=1,1342
659 WRITE(5,1026) CFLAG, LIML, LIMR
660 CALL DATE(TDATE)
CALL TIME(TTIME)
WRITE(5,661)
661 FORMAT(1X, "ENTER <60 CHARACTER RUN DESCRIPTOR: ")
READ(5,4002) IFLAG, ID(I), I=1,60
4002 FORMAT(4X)
GO TO 1101
1029 CALL ERRMS (IERR, IUN)
! IN CASE FILE WON'T OPEN
WRITE(5,1027) IERR, IUN
1027 FORMAT(1X, "FILE OPEN ERROR. CODE=", I5.2X, "UNIT=", I4)
1101 IF(IFLAG.EQ.1) GO TO 3
! GETS FILE NAME
IF(IFLAG.EQ.1) GO TO 4187
THE FOLLOWING ARE THE COMMANDS FOR CREATING UNFORMATTED FILES
OPENUNIT=1, NAME=FILENAME, TYPE='OLD', READONLY, DISP='SAVE',
FORM='UNFORMATTED', CARRIAGECONTROL='NONE'.
BUFFERCOUNT=2, ERR=332
CLOSE UNIT=1, DISP='SAVE'
WRITE(5,1030)
1030 FORMAT('Overwriting existing file. ARE YOU SURE? 'S)
READ(5,709,END=3) ANS(1)
IF(ANS(1).NE.'Y') GO TO 1101
321 OPEN(UNIT=1, NAME=FILENAM, TYPE='NEW', FORM='UNFORMATTED', ERR=321)
WRITE(5,1029)
1029 FORMAT('OVERWRITING EXISTING FILE. ARE YOU SURE? 'S)
READ(5,709,END=3) ANS(1)
IF(ANS(1).NE.'Y') GO TO 1101
322 OPEN(UNIT=1, NAME=FILENAM, TYPE='NEW', DISP='SAVE', ERR=322)
WRITE(5,1029)
1047 FORMAT('OVERWRITING EXISTING FILE. ARE YOU SURE? 'S)
READ(5,709,END=3) ANS(1)
IF(ANS(1).NE.'Y') GO TO 1101
322 OPEN(UNIT=1, NAME=FILENAM, TYPE='NEW', DISP='SAVE', ERR=322)
WRITE(5,1029)
589 FORMAT(1X,6 eax)
WRITE(5,1590) TDATE,CTIME
590 FORMAT(1X,9a1,1X,6a1)
WRITE(5,1591) NSHOTS,PHOTAV
591 FORMAT('NO. SHOTS=',I4,3X,'AVG. PMT VOLTAGE=',F7.3)
WRITE(5,1529) IOFFST,ISAMP
529 FORMAT('OFFSET=',I4,2X, 'SAMPLE PERIOD=',I4)
WRITE(5,1550) YMIN,YMAX
530 FORMAT('MIN Y VALUE=',E12.3,2X,'MAX Y VALUE=',E12.3)
WRITE(5,1551) LIML,LIMH
531 FORMAT('LEFT LIMIT=',I4,2X,'RIGHT LIMIT=',I4)
DO 454 J=1,550
454 WRITE(1,1460) J,XKEEPY(J),YPLLOT(J)
160 FORMAT(1X,14,2E12.3)
CLOSE(UNIT=1, DISP='SAVE')
GO TO 3
4010 IF(FILENAM().LT.0) GO TO 3
1 GETS FILE NAME
IF(FILEL.ED.1) GO TO 4000
4 READING UNFORMATTED FILES
OPEN(UNIT=1, NAME=FILENAM, TYPE='OLD', READONLY, DISP='SAVE', ERR=321)
WRITE(5,311)
311 FORMAT('FILE READ ERROR')
GO TO 3
3 READING UNFORMATTED FILE
READ(1,END=36,ERR=36) ID
WRITE(5,598) (ID(I),I=1,60)
READ(1,END=36,ERR=36) TDATE,CTIME
READ(1,END=36,ERR=36) NSHOTS, PHOTAV
WRITE(5,591) NSHOTS, PHOTAV
READ(1,END=36,ERR=36) IOFFSET, ISAMP
WRITE(5,529) IOFFSET, ISAMP
READ(1,END=36,ERR=36) XKEEP, YPLOT
READ(1,END=36,ERR=36) LIML, LIMR, IBKGFL, ISCALE, YKMIN, YMAX
WRITE(5,9821) LIML, LIMR, IBKGFL, IScale, YKMIN, YMAX
9021 FORMAT(' LEFT LIMIT=',I4, ' RIGHT LIMIT=',I4, ' BKGND FLAG '
      ' (NORMALLY 1) = ',1I2, ' POINTS AVG IN GROUPS OF= ',F4.1, 
      ' YKMIN= ',E12.3, ' YMAX= ',E12.3)
READ(1,END=36,ERR=36) SIGM, ABMAX, ICOUNT
WRITE(5,9822) SIGM, ABMAX, ICOUNT
9022 FORMAT(' SIGNAL=',F8.2, ' AVG. ABMAX=',F8.5, '# PTS OVERWRITTEN '
    ' = ',1I2)
READ(1,END=36,ERR=36) ONEPAR(5), ONEPAR(6), SDTAU
WRITE(5,9823) ONEPAR(5), ONEPAR(6), SDTAU
9023 FORMAT(' CORR. COEFF.=',F9.6, ' TAU=',F8.3, ' MICROSEC. ', 
    ' STD DEV.=',F7.3)
CLOSE(UNIT=1, DISP='SAVE')
GO TO 8840
36 CALL ERRNS(IERR, IUNC)
WRITE(5,1027) IERR, IUNC
GO TO 3
C
C
C
4108 WRITE(5,4126)
4109 FORMAT(' TRYING TO READ FORMATTED FILE. ') 
    OPEN(UNIT=1, NAME=FILE, TYPE='OLD', REASON=DISP='SAVE', 
    ERR=229)
READ(1,1399) ID(1), I=1, 60
1399 FORMAT(6X4I1)
WRITE(5,509) ID(1), I=1, 60
READ(1,1390) TDATE, CTIME
1390 FORMAT(6X4I1, 1X, 9X, 4I1)
WRITE(5,599) TDATE, CTIME
READ(1,1391) NSHOTS, PHOTAV
1391 FORMAT(10X, I4, 20X, F7.3)
WRITE(5,591) NSHOTS, PHOTAV
READ(1,1329) IOFFSET, ISAMP
1329 FORMAT(7X, I4, 17X, I4)
WRITE(5,529) IOFFSET, ISAMP
READ(1,1330) YKMIN, YMAX
1330 FORMAT(12X, E12.3, 15X, E12.3)
WRITE(5,530) YKMIN, YMAX
READ(1,1331) LIML, LIMR
1331 FORMAT(11X, I4, 15X, I4)
WRITE(5,531) LIML, LIMR
DO 743 K=1, 342
READ(1,163) XKEEP(K), YPLOT(K)
743 IF(ITINIA.K. EQ. '2') GO TO 3
163 FORMAT(4X, 2E12.3)
WRITE(5,744) K=1
744 FORMAT(1X, ' POINTS HAVE BEEN READ. ')
CLOSE(UNIT=1, DISP='SAVE')
GO TO 8840 ! WILL FIND NEW MAX AND MIN
C
C "A"-ABORT THE PROGRAM
C
1808 WRITE(5,448) 0, ESC
STOP
END
PROGRAM SAC200
SAC200, FOR P.S. ENGEL 16-DEC-82
PROGRAM TO TEST TOTAL DATA ACQUISITION FROM LECDROY AND BI-RA.

IF AMP VOLTAGE IS AUTOMATICALLY COMPENSATED.
CONTROLS OF AMP OUTPUT RELAY. WORKS WITH CHOPPED LIGHT IF
SYNC SWITCH IS ON. FOURTH VERSION FOR 200 MHZ LECDROY
NOTE!!! BOTH IRCA AND IRAC ARE NOW OFFSET BINARY
COMMON/SUBCOM/ADADR, OR3AD
COMMON/MODECOM/DACAD, TDAAD, CRAD
COMMON/FNAME/FILNAM = COMMON WITH SUBROUTINE DGFIN
INTEGER# DACAD, ADADR, OR3AD, TDAAD, CREG, CRAD, IDATOT(1024)
INTEGER# CB1(5), AA(5), CB2(5), DLAS(5) = FOR CS3A COMMAND
INTEGER# IBUF(512), ITEST(512)
DIMENSION KKEEPY(342)
EQUIVALENCE(IBUF, IDATA)
BYTE ANS(2), IDATA(1024), FILNAM
LOGICAL# 0, IBUF(5)
DATA FF/16, 16, 21, 16, 21/
ADADR=CREG(1, 5, 11, 0) = 81-RA ADDRESS
OR3AD=CREG(1, 5, 13, 0) = OR3 ADDRESS
DACAD=CREG(1, 5, 10, 0) = DA/12 ADDRESS IN SLOT 10
TDAAD=CREG(1, 5, 16, 0) = LECDROY TO IN SLOT 16
CRAD=CREG(1, 5, 8, 0) = CRATE ADDRESS
CALL PERCHG
CALL PERREAD(ISAMP)
WRITE(1,44) ISAMP
66 FORMAT( 'PERIOD WAS SET TO ',14,' NS')
CALL CS3A(19, TDAAD, '3,0') = SET OFFSET FOR -50S TO 5 MV RANGE
CALL READ1(10FFR)
WRITE(5,67)
67 FORMAT( 'DO YOU WISH TO CHANGE OFFSET? Y,N)'
READ(15,78) ANS(1)
IF(ANS(1), NE, 'Y') GO TO 79
70 FORMAT(41)
CALL OFFCOM
CALL OREAD1(10FFR)
79 TYPE 1
1 FORMAT( 'ENTER NO. OF SHOTS DESIRED: ')
READ(5, #) NSHOTS
CALL CS3A(16, OR3AD, '2,0') = OPEN SHUTTER
CALL WAIT(0, 0, 0)
THE NEXT STEP NULLS THE "LIGHT ON" VOLTAGE
CALL CS3A(16, OR3AD, '22,0')
CALL WAIT(0, 0, 0)
CALL NULLDE
PHOT0=0, 0
OPT0=0, 0
FILNAM=0, 0
AA(1)=ADADR
AA(2)=OR3AD
AA(3)=OR3AD
AA(4)=OR3AD
AA(5)=OR3AD
CB1(1)=512
CB2(1)=0
PHOMAX=0, 0
PHOMIN=5, 12
OPMAX=0, 0
OPMIN=5, 12
PULMAX=0.0
PULMIN=5.12
WRITE(5,77)
77 FORMAT(‘ NULLING COMPLETE’)
DO 100 I=1,1024
100 IDATOT(1)=0
DO 3 J=1,NSHOTS
! START ACQUISITION OF DECAYS
CALL SREAD(1,1,0,PHTOT)
CALL SREAD(2,1,0.IOUT)
! READ OP AMP OUTPUT
CALL CSQA(9,TDADR,0)
! START DIGITIZING
CALL CSQA(9,TDADR,0)
! THE FOLLOWING CSQA COMMAND SETS THE BI-RA TO CH. 2 (PULSE ENERGY),
C ! SETS THE GATED INTEGRATOR, AND FIRES THE LASER ONCE.
CALL CSQA(0,ADADR,IPULS,0)
! READ OUT PULSE ENERGY (CH.2)
IF(NOT.0) GO TO 24
CALL CSQA(27,TDADR,D,0)
! CHECK IF LECROY CYCLE FINISHED
IF(NOT.0) GO TO 71
! THIS IS IMPORTANT
CALL CSQA(17,TDADR,D,0)
! LOAD STARTING ADDRESS
CALL CSUBC(2,TDADR,1BUF,CB1)
! READ DATA TO INTEGER*2 ARRAY
DO 1242 I=1,512
1242 ITEST(I)=1BUF(I)
! SUMMATION OF DECAYS
IF(IDATA(I)) 222,222,225
! HANDLES 2'S COMPLEMENT OUTPUT
IDATA(I)=IDATA(I)+200
GO TO 224
222 IDATA(I)=IDATA(I)+177
224 CONTINUE
10 IDATOT(1)=IDATOT(1)+IDATA(I)
! CALC. DC VOLTAGE FOR OFFSET BINARY
OPOUT=(FLOAT(IDOUT-2048))/409.6
! CALC. DC VOLTAGE FOR OFFSET BINARY
PULM=(FLOAT(IPULS-2048))/409.6
C ! THE NEXT ROUTINE STORES MINIMUM AND MAXIMUM VALUES OF THE READ
C PHT VOLTAGE, OP AMP OUTPUT, AND PULSE ENERGY.
PHOT=PHTOT
IF(PHOT.PT.PHOMAX) PHOMAX=PHOT
IF(PHOT.LT.PHOMIN) PHOMIN=PHOT
OPTION=OPOUT
IF(OPTION.LT.OPMAX) OPMAX=OPTION
IF(OPTION.LT.OPMIN) OPMIN=OPTION
PULM=PULEN
IF(PULM.LT.PULMAX) PULMAX=PULM
IF(PULM.LT.PULMIN) PULMIN=PULM
PHOT=PHTOT+PHOT
! SUM PHT OUTPUT OF ALL SHOTS
OP7=OP7+OPOUT
PUL7=PUL7+PULM
C ! THE "D" AND "Q" ARE NECESSARY DUMMY VARIABLES IN WHAT FOLLOWS
CALL CSQA(9,DRAD,0)
CALL CSQA(24,ADADR,0)
! INHIBITS BI-RA'S RUN MODE
PHOT=PHTOT/FLOAT(NSHOTS)
! CALCULATE AVG PHT OUTPUT
OP7=OP7/FLOAT(NSHOTS)
PUL7=PUL7/FLOAT(NSHOTS)
WRITE(5,33)
WRITE(5,34) PHOMAX,OPMAX,PULMAX
WRITE(5,35) PHOTAV,OPAV,PULAV
WRITE(5,36) PHOMIN,OPMIN,PULMIN
WRITE(5,223) CB1(2)
! TELL US THE TALLY
223 FORMAT(‘ TALLY’=,15)
50 TYPE 5
5 FORMAT(‘ ENTER MIN,MAX POINTS YOU WISH TO SEE.
* (I TERMINATES; 0.0 CONTINUES,>)’)
READ(5,*) J,K
IF(K.EQ.0) GO TO 11
DO 27 L=1,K,2
WRITE(5,40) L,IDATOT(L),IDATOT(L),L+1,IDATOT(L+1),IDATOT(L+1)
  ,IDATA(L),IDATA(L)
40 FORMAT(1X,1X,2X,15,2X,07,4X,14,2X,16,2X,07,4X,16,2X,07)
37 IF(ITTIN(.EQ.,'32'))GO TO 50
GO TO 50
11 WRITE(5,43)
43 FORMAT(1X,'DO YOU WANT TO CREATE A FILE?','$')
READ(5,70) ANS(1)
IF(ANS(1).NE.,'Y')GO TO 12
IF(AGFAM().LT.,0)GO TO 11 ! GETS FILE NAME
C NEXT ROUTINE CALCULATES AVERAGE OF POINTS IN GROUPS OF 3.
6665 K=(I+2)/3
   XKEEPY(K)=FLOAT(IDATOT(I)+IDATOT(I+1)+IDATOT(I+2))/
   (3.0+FLOAT(NSHOTS))
   CONTINUE
6665 XKEEPX(K)=FLOAT(IDATOT(1024)+NAMES) ! LAST POINT
   OPEN(UNIT=1,NAME=FLNAME,TYPE='NEW',DISP='SAVE',ERR=50)
   WRITE(1,5001)
   5001 FORMAT(1X,'JUNK')
   WRITE(1,5001)
   WRITE(1,5001) ISAMP
   6000 FORMAT(1X,1X)
   DO 454 J=1,1000,2
   454 WRITE(1,160) J,TEST(J),IBUF(J),IDATA(J),J+1,ITEST(J+1),IBUF(J+1),
   IDATA(J+1)
   160 FORMAT(14,2X,07,2X,07,2X,16,6X,14,2X,07,2X,07,2X,16)
   CLOSE(UNIT=1,DISP='SAVE')
   GO TO 12
30 WRITE(5,31)
31 FORMAT(1X,'FILE READ ERROR')
12 TYPE 17
17 FORMAT(1X,'DO YOU WANT TO RUN AGAIN?','$')
READ(5,70) ANS(1)
   IF(ANS(1).EQ.,'Y')GO TO 16
STOP
END
PROGRAM YACPLOT

*PROGRAMMED BY JOHN N. SCHOLZ   SUMMER 1984
*MODIFIED BY ANDREW WALLER WINTER 1986 FOR USE WITH YAC200

HARDCO WILL PRINT A GRAPH OF A DATA FILE WRITTEN WITH
CALCULATED VALUES FROM YAC200. A DRIVER ALLOWS 3 FILES TO
BE PRINTED CONSECUTIVELY WITHOUT USER INTERVENTION

LINKS WITH YACOR AND PLOT
BYTE ID(64), TDATE(9), CTIME(8), FILNAM(16)
BYTE FILNM(16),FILEM(16),FLNM(16),FLNM(16),FLNM(16)
DIMENSION ONEPAR(6), YPLOT(342), BFY(336)
COMMON /FNAME/FILNM
COMMON /A/TDATE, ID
COMMON /B/LIM, LIMR, XSCALE, SIGMV, ABMAX, SDTAV, PHQAV
COMMON /C/ONEPAR
COMMON /D/IFILFL, IBKGFL, ICOUNT, NSHTS, IFFST, ISAMP, YKMIN, YKMAX
CALL DATE(TDATE)
CALL TIME(CTIME)
DIMENSION XKEEPY(342), Y(336), IB(2,16)
DIMENSION IPENS(7)
DATA IPENS/192,0,40,0,12,0,3/
DIMENSION IMICRO(12)
DATA IMICRO/63,120,2,0,2,0,0,63,0,0,0,0,0,0,0,0,
DIMENSION ININE(5)
DATA ININE/27,94,0,12,0,
DIMENSION ISEG(4)
DATA ISEG/243,229,227,255,
DIMENSION ITIME(5)
DATA ITIME/32,212,235,237,229,
DATA ISEG/33/

2121 WRITE(5,446) 0, IESC
446 FORMAT(2A1,'U')
WRITE(5,449)
449 FORMAT(' YACPLOT PLOTS DATA COLLECTED BY YAC200.'/
1X,'MAKE SURE THE PRINTER IS READY AND SET TO TOP OF FORM.'/
IX,'DO NOT TRY TO PLOT DATA FILES COLLECTED BY A/'
1X,'DIFFERENT PROGRAM. INITIATE ONE FORM FEED'/
1X,'BEFORE PLOTTING YOUR DATA FILES.')

READS A DECAY FILE AND GENERATES A HARD COPY
GRAPH ON THE FX-88 EPSON PRINTER

*R*—READ DATA FROM A FILE
IFILFL = 0

THIS PROGRAM WILL ONLY READ UNFORMATTED FILES
TO READ FORMATTED FILES, COMMENT OVER THE PREVIOUS
ASSIGNMENT TO IC STATEMENTS.

CONTINUE : FOR RETURNS OF GOTO

535 FORMAT(1X, 'ENTER 0 TO READ UNFORMATTED FILES; 1 FOR FORMATTED; ')
2735 READ(5,2736) IFILFL
2736 FORMAT(12)
C DRIVER DETERMINES NUMBER OF FILES TO BE READ
C
134 WRITE(5,135)
135 FORMAT(' HOW MANY DATA FILES DO YOU WANT TO PLOT? (1 TO 5) '9)
READ(5,136)NOFIL
136 FORMAT(12I)
IF (NOFIL.LT.1 .OR. NOFIL.GT.5) GOTO 124
'DO 1000 KFIL=1, NOFIL
1010 IF (IFNAME(KFIL,LT.D)) GO TO 3
'GETS FILE NAME
GOTO(1001,1002,1003,1004,1005),KFIL
1001 DO 1101 M=1,16
1101 FILM(M)=FILNAM(M)
GOTO 1000
1002 DO 1102 M=1,16
1102 FILM2(M)=FILNAM(M)
GOTO 1000
1003 DO 1103 M=1,16
1103 FILM3(M)=FILNAM(M)
GOTO 1000
1004 DO 1104 M=1,16
1104 FILM4(M)=FILNAM(M)
GOTO 1000
1005 DO 1105 M=1,16
1105 FILM5(M)=FILNAM(M)
1000 CONTINUE
KFIL=1
1999 IF (.NOT.FILG.NOFIL) GOTO 740
GOTO(1011,1012,1013,1014,1015),KFIL
1011 DO 1201 M=1,16
1201 FILNAM(M)=FILNM1(M)
GOTO 1111
1012 DO 1202 M=1,16
1202 FILNAM(M)=FILNM2(M)
GOTO 1111
1013 DO 1203 M=1,16
1203 FILNAM(M)=FILNM3(M)
GOTO 1111
1014 DO 1204 M=1,16
1204 FILNAM(M)=FILNM4(M)
GOTO 1111
1015 DO 1205 M=1,16
1205 FILNAM(M)=FILNM5(M)
C C READS THE DATA FILE, TAKEN FROM YAC280, HAS BEEN MODIFIED FOR YPLOT
C
1111 IF (.NOT.FILFL.ED.,.) GO TO 4100
  OPEN(UNIT=M,NAME=FILNAM,TYP='OLD',REASONLY,DISP='SAVE',
* FORM='UNFORMATTED',CARRIAGECONTROL='NONE',ERR=3099
  GO TO 310
309 WRITE(5,311)
311 FORMAT(' FILE READ ERROR')
GO TO 3
310 READ(1,END=36,ERR=35)ID
WRITE(5,589)ID(1),I=1,600
READ(1,END=36,ERR=35)TDATE,CTIME
WRITE(5,590)TDATE,CTIME
READ(1,END=36,ERR=35)HSHTS,PHOTAV
WRITE(5,591)HSHTS,PHOTAV
591 FORMAT(' NO. SHOTS=',14,2X,'AVG. PHT VULGAGE=',F7.3)
WRITE(5,529)IDSOFT,ISAMP
WRITE(5,529)IDSOFT,ISAMP
529 FORMAT(' OFFSET=',14,2X,'SAMPLE PERIOD=',14)
READ(1,END=36,ERR=35)XKEEP,YPLOT
WRITE(5,7821)LIML,LIMR,IDSOFT,XSCALE,YMIN,YMAX
`FORMAT(' LEFT LIMIT= ',1A, ' RIGHT LIMIT= ',1A, ' USEND FLAG
* (NORMALLY I) = II., POINTS AVG IN GROUPS OF= ',F4.1,
* ' MIN Y VALUE= ',E12.3,2X, ' MAX Y VALUE= ',E12.3)
READ(1,END=36,ERR=36) SIGNAL, ABSMAX, ICOUNT
WRITE(5,9022) SIGNAL, ABSMAX, ICOUNT
9022 FORMAT(' SIGNAL= ',F8.2, ' MV. ABSMAX= ',F8.5, ' * PTS OVERWRITTEN
* = .12)
READ(1,END=36,ERR=36) ONEPAR(5), ONEPAR(6), SDTAU
WRITE(5,9023) ONEPAR(5), ONEPAR(6), SDTAU
9023 FORMAT(' CORR. COEFF. = ',F9.6, ' TAU= ',F8.5, ' MICROSEC. ',
* STD DEV. = ',F7.3)
CLOSE(UNIT=1,DISP='SAVE')
GO TO 8860
36 CALL ERRNS(IERR,ION)
WRITE(5,1027) IERR, ION
1027 FORMAT(' FILE OPEN ERROR. CODE= ',I2,2X, 'UNIT= ',I2)
GO TO 3
C
C READING AND WRITING FORMATTED FILE
C
4100 OPEN(UNIT=1,NAME='FILENAME',TYPE='OLD'),READONLY,DISP='SAVE'.
* ERR=709
1399 READ(1,1399) (ID(I),I=1,60)
509 FORMAT(6A1)
WRITE(5,509) (ID(I),I=1,60)
590 FORMAT(11,A8)
READ(1,1290) (DATE(I),I=1,60)
570 FORMAT(9A1,1X,8A1)
WRITE(5,570) (DATE(I),I=1,60)
590 FORMAT(11,A8,1X,8A1)
READ(1,1291) (NEFITS, PHOTOAV)
1391 FORMAT(10X,I4,2X,F7.3)
WRITE(5,1391) (NEFITS, PHOTOAV)
1329 FORMAT(11,A8,1X,14)
WRITE(5,1329) (NEFITS, PHOTOAV)
READ(5,1230) VKMIN, VKMAX
1330 FORMAT(10X,14,15X,1E12.3)
WRITE(5,1330) VKMIN, VKMAX
520 FORMAT(' MIN Y VALUE= ',E12.3,2X, ' MAX Y VALUE= ',E12.3)
READ(5,1231) LIMLIM
531 FORMAT(' LEFT LIMIT= ',I4,2X, ' RIGHT LIMIT= ',I4)
DO 743 K=1,542
731 READ(1,140) XKEEPY(K), YPLOT(K)
140 FORMAT(4X,1E12.3)
743 IF (ITITNMN(.EQ.,'22)) GO TO 3
744 WRITE(5,744) K=1
C
C FIND MINIMUM AND MAXIMUM Y VALUES OF ARRAY XKEEPY
C
8860 CALL ASCII(27)
CALL ASCII(64)
WRITE(5,8860)
8002 FORMAT(' PLOTTING')
CALL HEAD2
CALL HORIZ
YMAX=60.
YMIN=0.
DO 8 L=1,542
YMAX=MAX(YMAX,YKEEPY(L),YMAX)
8 YMIN=MIN(YMIN,YKEEPY(L),YMIN)
IF (YMIN.LT.0) ANORM = ABS(YMIN) + 1.0
TF (YMIN,0,T,0) Rnorm = -ABS(YMIN) + 1.0
SCALE = 8000. / (YMAX - Rnorm)

C FORMAT PRINTING: Reverse array, junk first & points, scale to 8000PL

DO 97 I = 1, 326
   Y(I) = (XKEEP(I) + 1) * SCALE
   BFY(I) = (YPLOT(I) + 1) * SCALE
   IF (YPLOT(I) = 1.0 .EQ. 0) BFY(I) = YPLOT(I) + 1)
   CONTINUE

C INITIALIZE PRINT BUFFER AND BEGIN INTERNAL NON-KEYWORD LOOP

L = 1
K = 1
IW = 1
IX = 5
IY = 5
IZ = 12
SIEF = 12
JVERT = 1
SPCIN = 150. * FLOAT(ISAMP) / 1000.
IMIC = 0

DO 200 I = 1, 7, 2
   IB(1, I) = IFIX(W.5 + BFY(K))
   IB(1, I + 1) = IFIX(W.5 + Y(K))
   IB(2, I) = 2**7 - I
   IB(2, I + 1) = 2**7 - I
   K = K + 1
   LT = IB(1, I) = L.E., IB(1, I + 1)
   LR = IB(1, I) = L.E., IB(1, I + 1)
   IF (LT .AND. LR) IB(2, I) = 0

DO 4100 I = 1, 7, 2
   IF (IB(1, I) .EQ. 0) GOTO 4102
   DO 4101 J = 8, 9, 1
      KRUNCH = 1
      IB(1, J) = IB(1, I) = KRUNCH
      IB(2, J) = IPENS(I)
   CONTINUE

DO 4102
   DO 4103 J = 8, 9, 1
      IB(1, J) = IB(1, J + 1) = 0
   CONTINUE

DO 4105 J = 1
   IB(1, J + 1) = 1
   IB(2, J + 1) = 0

CONTINUE

C SORT THE BUFFER

DO 42 J = 1, 15
   DO 43 I = 1, 15
      IF (IB(I, J) .LT. IB(I, J + 1)) GOTO 45
      IBT = IB(I, J)
      IB2 = IB(I, J)
      IB(I, J + 1) = IB(I, J + 1)
      IB(I, J) = IBT
      IB2 = IB(I, J + 1)
   CONTINUE

CONTINUE

C PRINTING BEGINS HERE
TBMax = TB(1.16) + 125
CALL ENTER(1,IBMAX)
J=1
C
C SPACE OVER ONE INCH; 120 DOTS WHEN IN MODE 2
C
DO 2111 I = 1, 116
2111 CALL ASCII(0)
C
C PRINT THE VERTICAL AXIS SECTOR, MARK AT EVERY TENTH DATA POINT
C
IF ((K/4).EQ.IZ) GOTO 26
IVERT = 0
IF ((K/4).EQ.IX) GOTO 64
IF ((K/4).EQ.IY) GOTO 1
DO 4 J = 1, 8
CALL ASCII(0)
4 CONTINUE
GOTO 6
6 DO 21 N = 1, 4
21 CALL ASCII(0)
DO 22 N = 1, 4
22 CALL ASCII(16)
IX = IX + 5
GOTO 6
1 DO 23 N = 1, 4
23 CALL ASCII(0)
DO 24 N = 1, 4
24 CALL ASCII(1)
IY = IY + 5
GOTO 6
26 IVERT = 1
DO 25 N = 1, 8
25 IF (I2.EQ.IX) CALL ASCII(16)
IF (I2.EQ.IY) CALL ASCII(1)
IF (I2.EQ.IX) IX = IX + 5
IF (I2.EQ.IY) IY = IY + 5
IZ = IZ + ISTEP
IF (I4.EQ.1) ISTEP = 12
IF (I4.EQ.2) ISTEP = 12
IF (ISTEP.EQ.12) IY = 1
IF (ISTEP.EQ.13) IY = 2
CALL ASCII(255)
C
C PRINT BUFFER
C
DO 5 I = 1, IBMAX
KBOOM = 0
5 IF (I.NE.IB(1,J)) GOTO 207
KBOOM = KBOOM + IB(2, J)
J = J + 1
IF (J.LT.17) GOTO 206
207 CALL ASCII(KBOOM)
5 CONTINUE
IF (IVERT.EQ.1) GOTO 3101
GOTO 3200
3101 CALL ASCII(27)
CALL ASCII(64)
CALL ASCII(13)
SENT = FLOAT(IVERT) * SPACIN
IF (SENT.LT.0.) M = 6
IF (SENT.LT.10.) M = 5
IF (SENT.GT.10.) M = 4
IF (SENT.GT.100.) M = 3
3539 DO 3540 M2 = 1, M
3540 CALL ASCII(32)
IF (L.R.EQ.2) GOTO 635
CALL F1580(SENT. 2)
IF (LK.EQ.2) GOTO 636
LK = LK + 1
JVERT = JVERT + 1
CALL ASCII(13)
3202 IF (IMIC.NE.1) GOTO 3208
IMIC = 2
CALL ASCII(13)
CALL ASCII(32)
CALL ASCII(13)
DO 3205 I = 1, 5
3205 CALL ASCII(ININE(1))
DO 3206 I = 1, 12
3206 CALL ASCII(8)
CALL ASCII(INMICRO(1))
CALL ASCII(13)
CALL ASCII(32)
CALL ASCII(13)
DO 3202 I = 1, 4
3582 CALL ASCII(INSEC(1))
3208 IF (IX.NE.23) GOTO 3207
IF (IMIC.EQ.2) GOTO 3203
CALL ASCII(13)
DO 3204 I = 1, 5
3204 CALL ASCII(INTIME(1))
3205 IF (ITTIMR(1).EQ."32") GOTO 745
IF (K.LT.55) GOTO 209
C THIS MARKS THE END OF THE INTERNAL LOOP
C
C MASTER RESET PRINTER WHEN EXITING THE PROGRAM
C
CALL ASCII(18)
CALL ASCII(27)
CALL ASCII(64)
GOTO 745
635 CALL ASCII(27)
CALL ASCII(74)
CALL ASCII(13)
GOTO 637
636 CALL ASCII(27)
CALL ASCII(106)
CALL ASCII(12)
LK = 0
GOTO 639
745 DO 746 I = 1, 5
CALL ASCII(7)
746 CONTINUE
IFF = 10
IF (IFIFL.EQ.0) IFF = 5
DO 747 I = 1, IFF
CALL ASCII(12)
747 CALL ASCII(10)
IF (IFIFL.EQ.1) GOTO 748
CALL ASCII(27)
CALL ASCII(74)
CALL ASCII(113)
KFL = KFL + 1
GOTO 1999
'BACK TO DRIVER
748 WRITE(5,500)
500 FORMAT( ENTER 0 TO MAKE ANOTHER FLOT; ENTER 1 TO QUIT : )
READ(5,501) KIT
1  FORMAT(12)
   IF (K1T.EQ.0) GOTO 2121
   IF (K1T.EQ.1) GOTO 2119
   GOTO 748
2119  WRITE(5,448)0,IESC
   STOP
   END
TAC200.FOR ANDREW S. WALLER 2/6/86

THIS PROGRAM USES SOURCE CODE FROM YAC200

COMMON/SUBCOM,ADADR,ORDAD
COMMON/MODCOM,DACAD,TDADR,CRADR
COMMON/FNAME,FILENAME

DIMENSION BKG(1024), BKGAVE(1024)

INTEGER*2 DACAD,ADADR,ORDAD,TDADR,CRADR, IDATOT(1024)
INTEGER*2 CB1(5), RAWDAT(1024), RAWBKG(1024)
INTEGER*2 FF(5), AA(5), CB2(5), BSBKG(5), IDATA(5)

INTEGER*2 BUF(512)
BYTE ANS(2), IDATA(1024), FILENAME, TDATAE(9), CTIME(8), C(4)
EQUIVALENCE (IBUF, IDATA)
BYTE ID(60)
LOGICAL*1 Q, Q2(5)

DATA FF/16,16,21,16,21/
DATA ANS/240, ESC/"33/
DATA C/ A, I, E, H/
DATA BKG/"22,10,27,5/
DATA BKGAVE/"22,32,10,25,1/

CALL SETERR(4, 255)
CALL ERRNS
ADADR=CRADR(1, 5, 11, 0)
ORDAD=CRADR(1, 5, 12, 0)
DACAD=CRADR(1, 5, 10, 0)
TDADR=CRADR(1, 5, 16, 0)
CRADR=CRADR(1, 5, 8, 0)
AA(1)=ADADR
AA(2)=ORDAD
AA(3)=ORDAD
AA(4)=ORDAD
AA(5)=ORDAD
CB1(1)=512
CB2(1)=5
CALL APAGE

"E"=ENTER SAMPLE PERIOD

100n CALL PRCNG
CALL PERADC(ISAMP)
WRITE(5, 699) ISAMP

699 FORMAT (' PERIOD WAS SET TO ', A, ' NS')
CALL OREAD1 (OFFST)
WRITE(5, 126)

126 FORMAT (') DO YOU WISH TO CHANGE THE OFFSET?')
WRITE(5, 127)

127 FORMAT (')
READ(5, 709) ANS(1)
IF (ANS(1).EQ. N) GO TO 2
CALL OFFD1
CALL OREAD1 (OFFST)

2 CALL RCTRL
WRITE(5, 6146) 

6146 FORMAT (') FLASH ') S)
READ(5, 709, END=3) ANS(1)

709 FORMAT (A1)
GO TO (1000, 1005, 1006, 1008), INDEX(C, ANS(1))
GO TO 3

"H"=HELP COMMANDS

WRITE(5,723)

723 FORMAT(' THE AVAILABLE COMMANDS ARE:'//
SX,'A' = ABORT THE PROGRAM'//
SX,'E' = ENTER TRANSIENT DIGITIZER PARAMETERS'//
SX,'H' = HELP COMMANDS TYPED TO SCREEN'//
SX,'I' = INTEGRATE OVER ONE OR MORE SHOTS'//
GO TO 3

"I"=INTEGRATE OVER SEVERAL SHOTS

1005 TYPE 199

199 FORMAT(1,' ENTER NO. OF SHOTS DESIRED:'//)
READ(*,*)NSHOTS
IF(NSHOTS.LE.0) GO TO 1005
CALL CSSA(16,DRADR,'2.0')
CALL WAIT(0,0,5)
WRITE(5,2020)
2020 FORMAT(' WAIT PASSED')
CALL NULLCE(0)
WRITE(5,779)
779 FORMAT(' NULLING COMPLETE')
DO 109 IMM=1,1024
IMBKG(I)=0
IMDAT(I)=0
IMK(I)=0
109 I=1,1024
CALL SUREAD(2,1,0,1024)
CALL SUREAD(1,1,0,1024)

C

904 DO 399 J=1,NSHOTS
CALL CSSA(9,TDAOR,D,0)
CALL CSSA(FF,AA,BKGS,02,C82)
249 CALL CSSA(6,ADOR,10MB,0)
IF (.NOT.O) GO TO 249
719 CALL CSSA(27,TDAOR,D,0)
CALL CSSA(17,TDAOR,D,0)
CALL CSUBC(2,TDAOR,1BUF,CBI)
DO 910 IMM=1,1024
IF (IDATA(I)) IMM=1,1024
222 INTVAR=IDATA(I)**200
GO TO 929
225 INTVAR=IDATA(I)**200
999 IMBKG(I)=IMBKG(I)+INTVAR
910 IMK(I)=INTVAR
CALL CSSA(9,TDAOR,D,0)
CALL CSSA(FF,AA,IDATA,02,C82)
246 CALL CSSA(0,ADOR,1PULS,0)
IF (.NOT.O) GO TO 246
716 CALL CSSA(27,TDAOR,D,0)
CALL CSSA(17,TDAOR,D,0)
CALL CSUBC(2,TDAOR,1BUF,CBI)
DO 405 J=1,1024
IF (IDATA(I)) IMM=1,1024
322 IDATA(I)=IDATA(I)**200
GO TO 420
325 IDATA(I)=IDATA(I)**200
1002 INTVAR=IDATA(I)
1005 IMDAT(I)=IMDAT(I)+INTVAR
DO 403 I=1,1024
   IDATOT(I)=IDATOT(I)+IBKG(I)
403   CONTINUE

CALL CSSA(9,GR33D.D,2)
CALL CSSA(24,ADDR.D,2)
DO 609 I=1,1021,3
   K=(I+2)/3
   XKEEPY(K)=FLOAT(IDATOT(I)+IDATOT(I+1)+IDATOT(I+2))/
              (3.0*FLOAT(NSHOTS))
   DATAVE(K)=FLOAT(RAWDAT(I)+RAWDAT(I+1)+RAWDAT(I+2))/
              (3.0*FLOAT(NSHOTS))
   BKSAVE(K)=FLOAT(RAWBK(I)+RAWBK(I+1)+RAWBK(I+2))/
              (3.0*FLOAT(NSHOTS))
609   DO 621 I=1,342
      XKEEPY(I)=XKEEPY(I)+2.0*FLOAT(IOFFST)-255.0
      DATAVE(I)=DATAVE(I)+2.0*FLOAT(IOFFST)-255.0
      BKSAVE(I)=BKSAVE(I)+2.0*FLOAT(IOFFST)-255.0
621   
   FORMAT( / DO YOU WISH TO WRITE THE VALUES TO A FILE?/ )
   READ(5,709) ANS(1)
   IF(ANS(1).EQ.'N') GO TO 3
   CALL DATE(TDATE)
   CALL TIME(TTIME)
   WRITE(5,661)
   501   FORMAT(' ENTER A CHARACTER RUN DESCRIPTOR ')
   READ(5,5002)(ID(I),I=1,60)
5002   FORMAT(60A1)
   GO TO 1101
1028   CALL ERRNG(IERR, IUN)
   WRITE(5,1027) IERR, IUN
1027   FORMAT( /FILE OPEN ERROR, CODE='13,2X', UNIT=,'12C/)
   IF(IGFNM(1).LT.0) GO TO 3
322   OPEN(UNIT=1,NAMFILNM,TYPE='NEW',DISP='SAVE',ERR=1029)
   WRITE(5,600)
   600   FORMAT( / NOW WRITING FILE ')
   WRITE(1,599)(ID(I),I=1,60)
599   FORMAT(1X,60A1)
   WRITE(1,590) TDATE,TTIME
590   FORMAT(1X,9H41,2X,B9A1)
   WRITE(1,591) IOFFST,ISAMP,NSHOTS
591   FORMAT( 'OFFSET=' ,14,2X, 'SAMPLE PERIOD=' ,14,2X,
   1                 'NO. SHOTS=' ,14,2X) WRITE(5,601)
601   FORMAT( /NOW ENTERING THE LONG DATA LOOP, PLEASE WAIT/) DO 454 I=1,342
454   WRITE(1,592) I,DATAVE(I),BKSAVE(I),XKEEPY(I)
592   FORMAT(1X,14,2X,2E12.3,4X,1E12.3)
   CLOSE(UNIT=1,DISP='SAVE') GO TO 3
C
"A"--ABORT THE PROGRAM
C
1000   STOP
END