

RECENT MECHANISTIC AND EXPLORATORY ORGANIC PHOTOCHEMISTRY

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Abstract - Our photochemical research has taken two directions. One of these has been a search for new photochemical reactions and phenomena. The other has been the utilization of new methods of studying organic photochemistry. However, these really have a common aim, namely a better understanding of factors controlling excited state transformations and the development of photochemical theory.

INTRODUCTION

The chemistry discussed here includes some new photochemical reactions and some mechanistic studies. The mechanistic studies make use of single photon counting with simulated deconvolution as one very powerful tool to obtain rates of excited state transformations. Another tool is the independent generation of species thought to lie on an excited state hypersurface of interest. Comparison is then made with the known photochemistry. Such exploratory and mechanistic studies then allow development of photochemical theory.

SINGLE PHOTON COUNTING WITH SIMULATED DECONVOLUTION

Previously (Ref. 1, 2 & 3), we have reported the use of single photon counting utilizing an on-line minicomputer to act as a multichannel analyzer for accepting data and also to do a simulated deconvolution. The resolution of such a method has been determined as 14 picoseconds (Ref. 3).

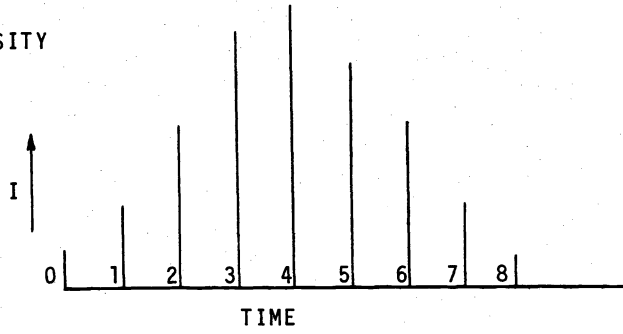
To understand the problems involved in such an approach we note Figure 1. Here Figure 1A gives the lamp intensity profile versus time, time zero being the beginning of the lamp flash. The data consists of a series of intensity spikes rather than a continuous function, since a computer stores data as a series of numbers; one can get more resolution by taking smaller time intervals between intensities stored. In any case a multichannel analyzer serves the same function.

Figure 1B shows the intensity of excited state emission versus time. Here we have dissected each vertical spike into components due to excited state formation at the different time delays; each component (0 through 8) is labeled. Thus, the emission at (e.g.) time delay 3 derives from excited states formed at time 0, time 1, time 2 and time 3.

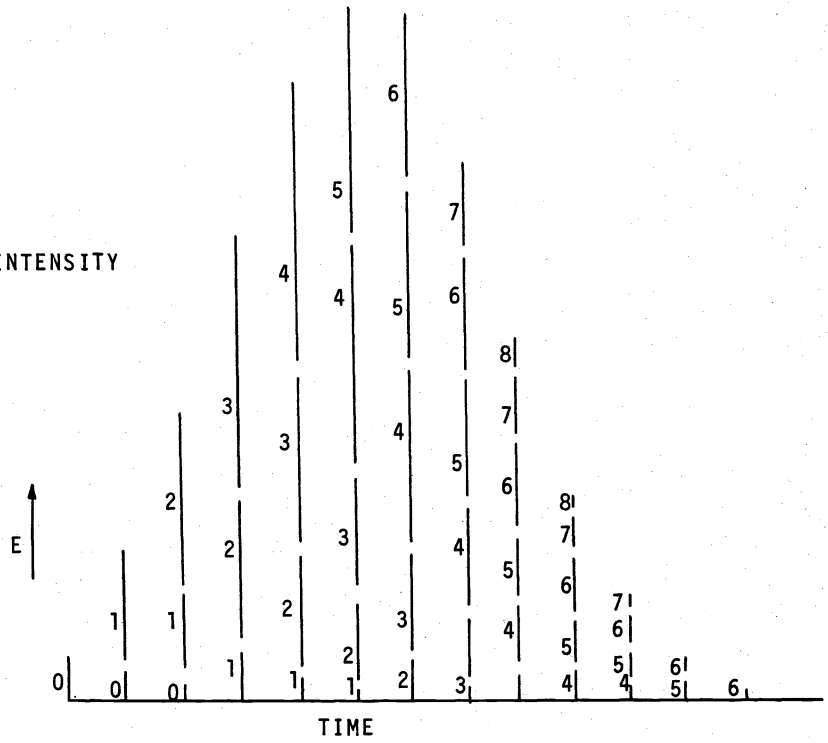
The problem is to utilize the information in Figures 1A and 1B to give the intensity of excited state emission versus time which one would observe if absorption occurred at only one interval (e.g. 3). Figure 1C shows the decay of those states generated by absorption at time 3 as an example. Such a dissection of information is termed deconvolution. Note Ref. 4.

One can state the same information in matrix equation 1.

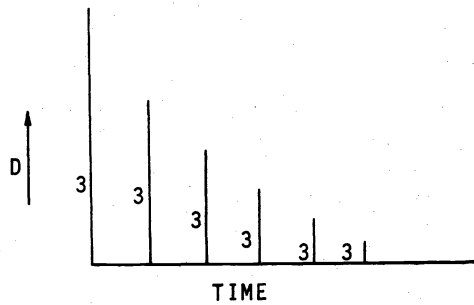
LAMP INTENSITY
FIGURE 1A



EMISSION INTENSITY
FIGURE 1B



EMISSION INTENSITY
DUE TO EXCITATION
AT ONE TIME DELAY
(HERE 3)
FIGURE 1C



$$\begin{bmatrix} E_0 \\ E_1 \\ E_2 \\ E_3 \\ \vdots \\ \vdots \end{bmatrix} = \begin{bmatrix} I_0 & 0 & 0 & 0 & \dots \\ I_1 & I_0 & 0 & 0 & \dots \\ I_2 & I_1 & I_0 & 0 & \dots \\ I_3 & I_2 & I_1 & I_0 & \dots \\ \vdots & \vdots & \vdots & \vdots & \vdots \\ \vdots & \vdots & \vdots & \vdots & \vdots \end{bmatrix} \begin{bmatrix} D_0 \\ D_1 \\ D_2 \\ D_3 \\ \vdots \\ \vdots \end{bmatrix} = \begin{bmatrix} D_0 & 0 & 0 & \dots \\ D_1 & D_0 & 0 & \dots \\ D_2 & D_1 & D_0 & \dots \\ D_3 & D_2 & D_1 & D_0 & \dots \\ \vdots & \vdots & \vdots & \vdots & \vdots \\ \vdots & \vdots & \vdots & \vdots & \vdots \end{bmatrix} \begin{bmatrix} I_0 \\ I_1 \\ I_2 \\ I_3 \\ \vdots \\ \vdots \end{bmatrix} \quad (1a)$$

$$\text{or } \bar{E} = \bar{I} \bar{D} = \bar{D} \bar{I} \quad (1b)$$

Where the I's are lamp intensities, the E's are emission intensities at the different time delays, and the D's are the values of the decay function at times zero, one, two, etc. This merely restates what we have said in words. For example, the emission at time zero, E_0 , comes from just one source, excitation at time zero and equals $I_0 E_0$. $E_1 = I_0 D_1 + I_1 D_0$ and thus comes from two sources, excitation at time zero and time one. Similarly $E_2 = I_0 D_2 + I_1 D_1 + I_2 D_0$, and derives from excited states formed at three times.

One might think that he could merely solve equation 1 by inverting the \bar{I} matrix and thus obtain the \bar{D} vector which gives the decay function at varying time delays. However, the \bar{I} matrix is nearly singular, since the diagonal elements represent the lamp intensity at time zero, and one cannot directly invert it.

Our approach to the problem has involved a reiterative convolution in which one assumes that the decay function is the sum of one or more negative exponentials. Then, with the lamp flash curve known, one determines the expected emission curve (i.e. E). The method determines the deviation of the calculated E from the experimental E. It also determines the optimum values of the preexponential terms and the exponential rate constants to be used for the next iteration. The process is repeated until convergence is obtained.

Thus, the method uses the minicomputer as an on-line multichannel analyzer. The computer also decides which data are real and which constitute noise. During the data collection process decay curves are displayed on an X-Y oscilloscope. Then the computer calculates the desired rate constants. Rates of 10^{10} sec^{-1} are obtained in this way.

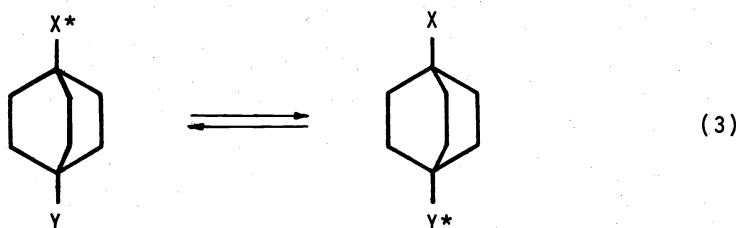
For still faster rate constants for decay a method was developed (ref. 1) which depends on the observation that as the temperature is lowered, the lifetimes of many excited singlets are lengthened. The relationship in equation 2 is used:

$$k_{dt}^{rt} = (\phi_f^{77} / \phi_f^{rt}) k_{dt}^{77} \quad (2)$$

This makes use of a "magic multiplier", the quantity in parenthesis; this is the ratio of fluorescence efficiencies at two temperatures (e.g.) 77°K and room temperature; since this is a ratio, absolute quantum yields are not needed, rather just the ratio of emission intensities. The derivation of equation 2 requires that the natural rate of fluorescence, k_f , remain constant. In most cases this will be true, especially where the molecule is relatively rigid and the excited state geometry is not too distorted. In the cases we have investigated, this assumption has proven valid.

Thus, equation 2 allows one to obtain the total rate of decay of an excited singlet at room temperature, a rate which may be too rapid to measure directly by single photon counting, in terms of the slower lower temperature (e.g. 77°K) rate k_{dt}^{77} . This extends the method's capabilities about 200-fold and allows one to obtain rates as fast as 10^{12} sec^{-1} .

One intriguing application of single photon counting deals with the oscillation of excitation energy between two chromophores attached to distant bridgehead positions of a bicyclo[2.2.2]octane unit. Note equation 3.



Here the excited moiety is designated with an asterisk. Table I gives the systems studied along with the results. One particularly fascinating question is whether the excited state lifetime of a system with two identical chromophores (i.e. $X = Y$ in equation 3) would be the same as that in which excitation was limited to one (i.e. where $X = \text{Naphthyl}$ and $Y = \text{H}$). The question is whether the reversible energy transfer process is inefficient.

This question was approached by the use of the two β -naphthyl groups as X and Y . As is seen in Table I, the lifetime was 64.2 nsec. A comparison case is entry two in Table I where there is just one β -naphthyl group, and this model compound has a singlet lifetime of 64.2 nsec, also. Thus, to the extent that isoenergetic excitation transfer occurs, it does not diminish the excited state lifetime.

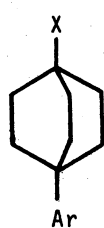


TABLE I. Intramolecular energy exchange rates (ref.5)

Ar	X	SINGLET LIFETIME ^a	λ EMISSION
α -Naphthyl	H	65.1 nsec	335 nm
β -Naphthyl	H	64.2 nsec	332 nm
β -Naphthyl	β -Naphthyl	64.2 nsec	332 nm
α -Naphthyl	Cis-Propenyl	64.7 nsec	335 nm
α -Naphthyl	Acetyl	1.84 nsec	320-335 nm
		4.39 nsec	390-405 nm
β -Naphthyl	Acetyl	0.28* nsec	330 nm
		3.68 nsec	400 nm
α -Naphthyl	Benzoyl	0.23 nsec	331 nm
β -Naphthyl	Benzoyl	0.10 nsec	331 nm

*0.16 nsec when excited at 265 nm; 0.36 nsec when excited at 285 nm.

^aExcitation at 275 nm except where noted.

TABLE II. Singlet lifetimes with variation of excitation wavelength (ref. 5)

Ar	X	EXCITATION	SINGLET LIFETIME
β -Naphthyl	Acetyl	265 nm	0.16 nsec
		275 nm	0.23 nsec
		285 nm	0.36 nsec
α -Naphthyl	Cyclohexane-carbonyl	270 nm	0.56 nsec
		280 nm	0.62 nsec
		290 nm	1.1 nsec

Another question was whether the presence of a group potentially capable of reaction (here cis-trans isomerization) would affect the singlet lifetime. In the fourth entry in Table I, we see that the very high energy cis-propenyl group does not diminish the lifetime; of course, we recognize that vertical energy transfer to isopropenyl would not occur since it would be endothermic.

A last question led to more positive results. This dealt with the effect on the singlet lifetime of a low energy acceptor as the other bridgehead group. As the donor we used α - and β -naphthyl and as acceptors we utilized acetyl, benzoyl and cyclohexanecarbonyl groups. It can be seen that all of these dramatically diminish the excited state lifetime. Thus, note the 1.84 nsec lifetime of the α -naphthyl acetyl compound listed as entry 5 of Table I; this lifetime was that measured by emission at 330 nm where naphthyl groups emit. The same short lifetimes are found for similar compounds with acyl groups as Y.

Related to this is the observation that emission at circa 400 nm, ascribable to ketonic fluorescence, could be observed as well. Thus, energy transfer was occurring.

Additionally there is the intriguing point that with the shorter lifetime and lower energy benzoyl group, a shorter naphthyl lifetime was observed in all cases. Thus, energy transfer occurs from naphthyl with greater facility in these cases. Since the ketonic decay was slower than that observed for the naphthyl groups, it seems likely that the dominant factor is energetic.

Also, a most interesting effect is seen in the consistently shorter lifetime for the β -naphthyl compounds bearing a ketonic acceptor relative to the α -naphthyl analogs. If one recognizes that the L_a and L_b excited states are close lying and that the carbonyl group singlet is polarized along the C-O axis as a result of magnetic dipole coupling, then it is seen that in the β -compounds the transition dipoles have a parallel arrangement in one molecular conformation for the L_a transition while such a possibility does not exist for the α -isomers. Note Figure 2.

Finally, it is observed that excitation of the lowest naphthalenic transition at shorter wavelengths leads to shorter lifetimes; note Table II. This has as one explanation the utilization of higher vibronic levels with increased rates of energy transfer to the carbonyl group.

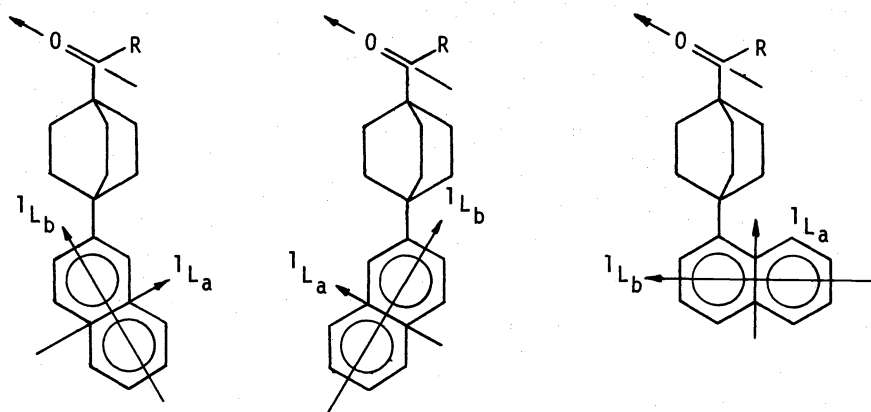
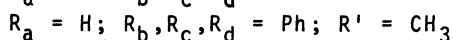
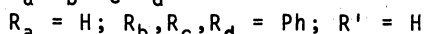
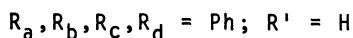
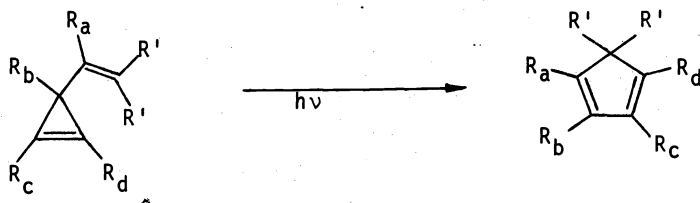


Figure 2. Some possible conformations and relationships between the transition dipoles of naphthyl and acyl groups

SOME EXPLORATORY ORGANIC PHOTOCHEMISTRY

A new cyclopentadiene synthesis.

One intriguing reaction we uncovered (see ref. 6) involves the direct photolysis of vinyl substituted cyclopropenes. This leads to cyclopentadienes as shown in equation 4.



$$\phi = .049$$

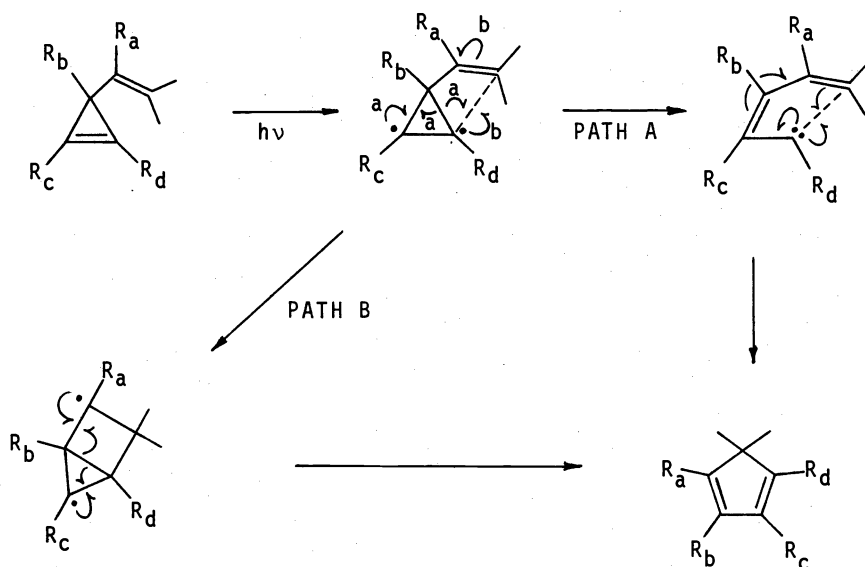
$$\phi = .027$$

$$\phi = .010$$

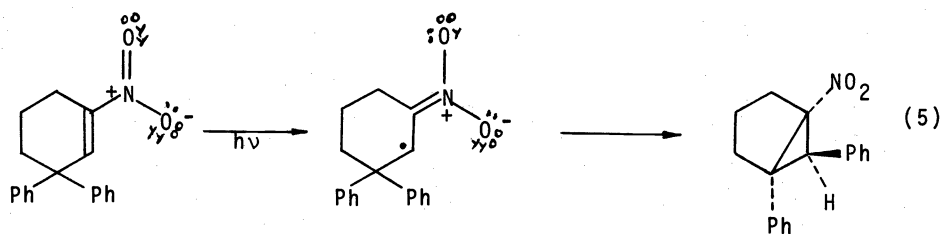
The quantum yields were found to be a function of substitution as shown. Interestingly, the efficiency was increased with phenyl substitution as R_a . Terminal methyl substitution on the vinyl group (*i.e.* as R') diminished the efficiency.

Two mechanisms are shown in Chart 1. One mechanism involves excited state bridging between the two ethylenic chromophores; this is labeled PATH B. The second mechanism begins with carbene formation followed by five ring formation; this is labeled PATH A. While clear evidence is not yet available to distinguish these mechanisms, the pattern of effect of substitution on efficiency suggests that PATH B is the correct one. Thus, phenyl substitution as R_a would stabilize odd electron density in the bicyclo[2.1.0]biradical formed by bridging. The carbene mechanism does not offer a similar source of this substituent effect. Also the decrease of efficiency with terminal methyl substitution would make sense in MECHANISM B as a steric effect; and a parallel rationale does not derive nicely from MECHANISM A since ring closure would occur only after the high energy carbene intermediate had already been formed.

CHART 1. Two mechanisms for the cyclopropene to cyclopentadiene rearrangement

Phenyl migration in nitroalkene rearrangements.

Another interesting reaction encountered is that of 3,3-diphenyl-1-nitrocyclohexene which rearranges to the bicyclic nitro compound as in eqn. 5 (note ref. 7). This rearrangement is parallel to the unsaturated ketone rearrangements reported by us many years ago; note reference 8 for example.



$$\phi \text{ (direct)} = 3.05 \times 10^{-4}; \phi \text{ (sens; acetophenone)} = 4.52 \times 10^{-4}$$

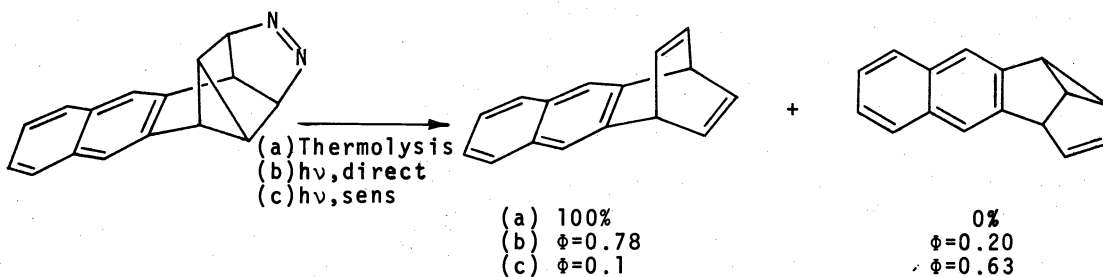
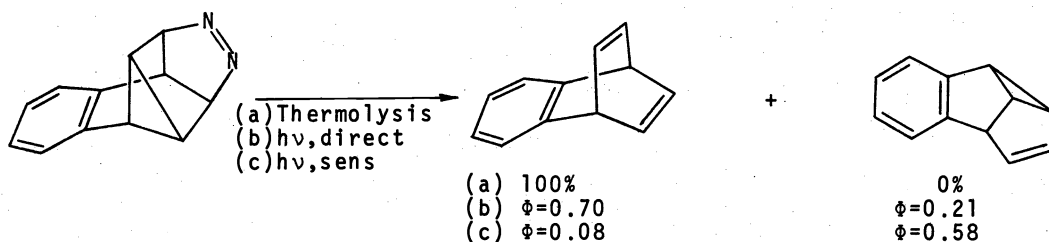
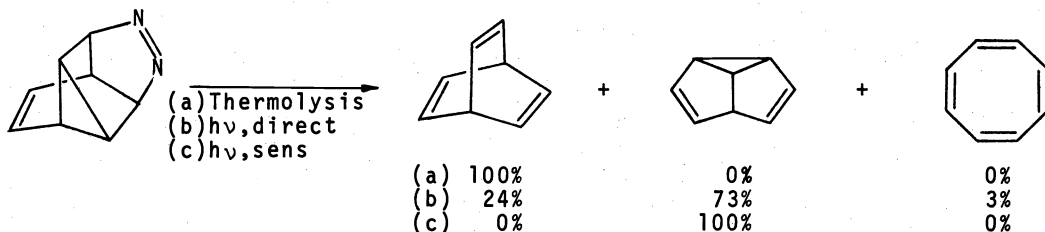
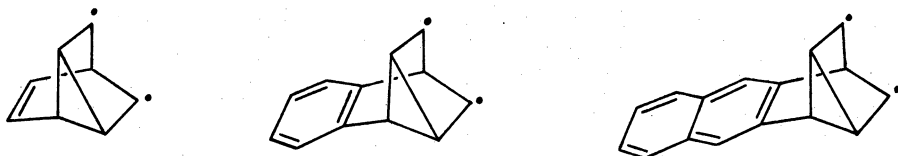
Two facets of nitroalkene photochemistry are of special interest. One is that the reaction goes with a sensitized quantum yield which is not too much greater than the direct efficiency. This shows that the triplet is capable of rearranging and suggests, but does not prove, that even in the direct irradiations the triplet is utilized. The second point is the very low reaction efficiency compared with comparable enone rearrangements (ref. 8). This suggests an efficient excited state decay mode such as reversible oxygen - carbon bonding.

Use of azo precursors for generation of di- π -methane type biradicals.

The three azo compounds shown below (Chart 2) were used to generate the corresponding diradicals. These diradicals have been postulated by us as involved in the di- π -methane rearrangement (ref. 9) of barrelene derivatives.

Chart 2 (ref. 10) describes the behavior of the azo compounds under thermal, direct photolytic and sensitized photolytic conditions. The most important observation is that thermally the azo compounds revert to the barrelene

CHART 2. Three diradicals involved in di- π -methane rearrangements and behavior of related azo compounds.



relatives while on irradiation semibullvalenes, observed in barrelene photochemistry, are among the products. From the sensitized runs, the semibullvalene products are major. This is in agreement with the photochemistry of barrelenes where it is the triplet which rearranges.

Although the azo chemistry may involve nitrogen in the transition state, especially in the case of the ground state process which is most likely a simple electrocyclic reverse Diels-Alder, the diradicals and species (e.g. transition states) incorporating nitrogen are electronically similar and should prove analogous in behavior. This is shown to be the case by Chart 2.

The cyclopropyldicarbonyl diradical; Some theoretical aspects.

The cyclopropyldicarbonyl species discussed in context of triplet, bicyclic photochemistry is of general interest. Thus, it occurs in acyclic and singlet di- π -methane photochemistry also. It is therefore of considerable interest to inspect the electronics of such a species. Using the basis set shown in Chart 3 both Hückel-level and SCF calculations come to the conclusion that in S_1 orbitals 1 and 5 are electron rich. The carbon bearing

CHART 3. The cyclopropyldicarbonyl species in truncated form.



orbitals 3 and 7 is electron deficient, this being the "methane carbon". The results do depend on resonance integrals of the type $(p|H|sp^2)$ being smaller than those of the $(p|H|p)$ type, but calculation based on geometry confirms this. Note reference 11. Also configuration interaction calculations place the triplet slightly below ground state.

Such a calculation is truncated from the cyclic array commonly assumed; however, this does simplify discussion and does seem to come close to reality.

CONCLUSION

It is clear that photochemistry is an ever broadening field. The number of new reactions is increasing exponentially. The utility of those reactions found is increasing as the generality of a given process becomes really clear. The development of methods for studying photochemical mechanisms is a similar challenge. The field is unique in giving research students particularly broad training. The paper presented here merely reflects the author's enthusiasm with these views in mind.

ACKNOWLEDGMENT

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