markedly intensified on charge transfer to iodine. There appears no doubt that sulfur is the donor site in the charge-transfer complexes of alkylthioureas with iodine.

Infrared Spectra of Metal Complexes of Alkylthioureas. Examination of the infrared spectra of the Cu(I), Pd(II), Cd(II), and Zn(II) complexes of N,N′-dimethylthiourea seem to show evidence for two different types of coordination, the Cu(I) and Pd(II) belonging to the first group and the other two belonging to the second group. The first group of complexes show a smaller increase (10–15 cm^{-1}) of the 1506-cm^{-1} band compared to the second group (25–37 cm^{-1}). The 1287-cm^{-1} band shows a marked increase in frequency and intensity in the second group of complexes. The out-of-plane δ(NH) frequency decreases in the first group and increases in the second group. The δ(NCS) frequency decreases while the 1568-cm^{-1} band frequency increases in all the complexes. The band at $\sim$760 cm^{-1} [ν(CS) + ν(CN) + ν(C′N)] is shifted to higher frequencies in the first group and to lower frequencies in the second group. These results clearly show that the metal complexes of N,N′-dimethylthiourea fall into two groups just as in the case of the N-methylthiourea complexes.[7] The results, however, are not as conclusive as in metal–urea complexes.[22] This is because the C=O stretching frequency in urea is considerably higher than the C–N stretching frequency, while the ν(CS) frequency is quite close to the latter.

The infrared spectra of the Pd(II), Cd(II), and Hg(II) complexes of tetramethylthiourea show an increase in the frequency of the 1500-cm^{-1} band and a decrease in the 1120-, 660-, and 490-cm^{-1} bands. The band at $\backsim$1000 cm^{-1} with appreciable contribution from ν(CS) is not affected greatly.[23]

From the preceding discussion it becomes clear that great care has to be exercised in the interpretation of the infrared spectra of metal complexes where the bands due to the ligands arise from mixed vibrations, and it often becomes difficult to establish the donor site or the nature of metal–ligand interaction on the basis of the shifts of infrared bands alone.

Experimental Section

All the dialkylthiourea derivatives were prepared by standard procedures reported in the literature.[24] Infrared absorption spectra were recorded (in solutions, mulls, pellets, or thin films) employing a Carl-Zeiss UR 10 spectrophotometer fitted with LiF, NaCl, and KBr prisms. The spectrophotometer was calibrated with indene.[3] Infrared spectra in the first N-H overtone region were recorded with a Cary 14-R spectrophotometer fitted with a variable-temperature cell compartment. Nmr spectra were recorded with Varian A-60 as well as HR-100 spectrometers. An IBM 1620 computer was employed in the calculations of normal vibrations.

Infrared spectra of the charge-transfer complexes of alkylthioureas with iodine were recorded in CCl$_4$ or CHCl$_3$ solutions in presence of a slight excess of iodine.

The metal complexes of alkylthioureas were prepared by mixing aqueous or alcoholic solutions of the corresponding salts with the solutions of the ligands. The Cu(I) complex of N,N′-dimethylthiourea was prepared according to the method described in the literature.[25] The complexes were purified and analyzed[26] before use. The infrared spectra of the metal complexes were recorded in Nujol mulls or KBr pellets.

Acknowledgment. The authors are thankful to the Council of Scientific and Industrial Research, India, for a research grant and to Dr. M. J. Janssen of The Netherlands for a gift sample of tetramethylthiourea.

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[22] R. B. Penland, S. Mizushima, C. Curran, and J. V. Quagliano, *J. Am. Chem. Soc.*, 79, 1575 (1957).

[23] After this work was completed a paper appeared [M. Schafer and C. Curran, *Inorg. Chem.*, 5, 265 (1966)] where the 1120-cm^{-1} band has been assigned to ν(CS) and the decrease in the frequency of this band in metal complexes has been ascribed to metal-sulfur bonding. The results of the present study based on the normal coordinate analysis of the ligand clearly shows that it is difficult to draw such unequivocal conclusions when bands arise from mixed vibrations.

[24] M. L. Moore and F. S. Crossley, "Organic Synthesis," Coll. Vol. III, E. C. Horning, Ed., John Wiley and Sons, Inc., New York, N. Y., 1955, pp 599, 617.

[25] W. G. Palmer, "Experimental Inorganic Chemistry," Cambridge University Press, London, 1959.

[26] The C, H, and N elemental analyses were carried out by the Microanalytical Laboratory of the University College of Science and Technology, Calcutta.

The Absorption, Emission, and Excitation Spectra of Diarylmethylenes

A. M. Trozzolo and W. A. Gibbons

Contribution from the Bell Telephone Laboratories, Inc.,
Murray Hill, New Jersey. Received August 15, 1966

Abstract: The absorption, emission, and excitation spectra of a series of substituted diphenylmethylenes have been observed in a variety of rigid organic matrices at 77°K. These triplet ground-state molecules were obtained by the low-temperature photolysis of the appropriate diazo compound. The emission is assigned to *fluorescence* from the lowest excited triplet level to the ground state. No phosphorescent emission was observed in the wavelength range studied. Esr spectroscopy was used to monitor the formation and disappearance of the triplet diphenylmethylenes. The absorption spectra were characteristic of odd-alternant radicals, showing a strong band near 300 mμ and a much weaker band in the visible range. These transitions are consistent with a π–π^* assignment.

The chemistry of methylenes, $R\ddot{C}R'$, has been interpreted in terms of two electronic configurations: (a) a singlet configuration (I) in which the unshared electrons are paired in an sp^2 orbital, leaving an empty p orbital; or (b) a triplet configuration (II) in which the two unshared electrons are unpaired, each in a p

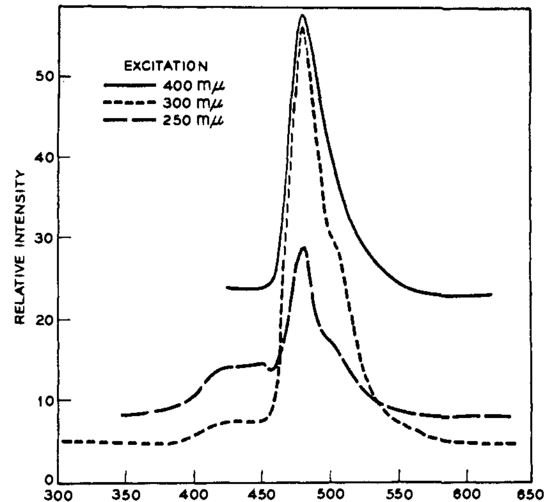
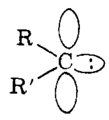


Figure 1. Luminescence of diphenylmethylene.

orbital and in which the R–C–R′ angle is more nearly linear than when the molecule is in configuration I.[1]



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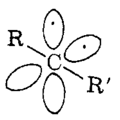
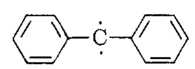


II

Recent electronic spin resonance (esr) studies of a number of methylene intermediates[2–4] resulted in the assignment of a triplet ground state to these species. The methylenes were obtained by the photolysis of the appropriate diazo compound in a rigid matrix. However, in order to apply the esr results in a program designed to study the reactivity of the methylenes, it became necessary to study the optical spectroscopy of these species. A preliminary report of the results recently has been published,[5] and this paper constitutes a more complete description of the work.

The electronic spectra of relatively few methylenes have been reported. Among these are included difluoromethylene, CF_2, which has been observed by a number of workers.[6] The most detailed study of methylene, CH_2, has been that of Herzberg and Shoosmith[7] who showed that CH_2 exhibits two absorption bands (one in the vacuum ultraviolet at approximately 140 mμ and the other in the visible region at 550–950 mμ) and that its ground state is probably a triplet with a linear geometry. The spectra of CHCl and of CDCl recently have been reported[8] by Merer and Travis. These workers also have observed CHF and CHCN,[9] and the latter molecule has been shown by esr studies[4a] to possess a triplet ground state. The optical spectrum of CNN has been obtained,[10] and this species also has a triplet ground state.[2g]

While all of the above methylenes except CNN were studied in the gas phase, attempts to study the optical spectrum of CH_2[11] or of substituted methylenes[12] in condensed phases had until recently led only to rather tentative spectral assignments. Almost simultaneously, three papers appeared describing the optical absorption of diphenylmethylene (III). Closs, Hutchison, and Kohler[13] reported the long-wavelength absorption band of III oriented in single crystals of 1,1-diphenylethylene. This technique also allowed the assignment of the polarization of the long-wavelength absorption. Esr measurements were used in an elegant fashion to monitor the polarization experiments. Moritani, *et al.*,[14] found two new absorption bands in photolyzed solutions of diphenyldiazomethane and 1-diazo-2,3,6,7-dibenzocycloheptatriene in rigid media. Since earlier esr studies[2,3] had detected the presence of III in similar photolysis experiments, the new absorption bands were assigned to the corresponding diarylmethylenes. By correlating esr studies, fluorescence, fluorescence excitation, and absorption spectroscopy, the present authors[5] previously reported the luminescence, excitation, and absorption spectrum of III. This has led to the assignment of at least two and possibly three absorption bands of III as well as its fluorescence spectrum. The spectra of other diphenylmethylenes have also been obtained and they are reported here.



III

Results and Discussion

1. Emission Spectrum of Diphenylmethylene (III). A solution of diphenyldiazomethane (10^{-4} *M*) in 2-methyltetrahydrofuran was photolyzed, and the emission spectrum was recorded as a function of photolysis time. The emission consists of a broad band (λ_{max} 480 mμ) with a shoulder at longer wavelength (Figure 1). The same spectrum was obtained for all excitation wavelengths in the range 230–470 mμ and all solute concen-

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(1) J. Hine, "Divalent Carbon," The Ronald Press Co., New York, N. Y., 1964; W. Kirmse, "Carbene Chemistry," Academic Press Inc., New York, N. Y., 1964.

(2) (a) R. W. Murray, A. M. Trozzolo, E. Wasserman, and W. A. Yager, *J. Am. Chem. Soc.*, **84**, 3213 (1962); (b) A. M. Trozzolo, R. W. Murray, and E. Wasserman, *ibid.*, **84**, 4990 (1962); (c) A. M. Trozzolo, R. W. Murray, G. Smolinsky, W. A. Yager, and E. Wasserman, *ibid.*, **85**, 2526 (1963); (d) E. Wasserman, L. Barash, A. M. Trozzolo, R. W. Murray, and W. A. Yager, *ibid.*, **86**, 2304 (1964); (e) E. Wasserman and R. W. Murray, *ibid.*, **86**, 4203 (1964); (f) A. M. Trozzolo, E. Wasserman, and W. A. Yager, *ibid.*, **87**, 129 (1965); (g) E. Wasserman, L. Barash, and W. A. Yager, *ibid.*, **87**, 2075, 4974 (1965).

(3) R. W. Brandon, G. L. Closs, and C. A. Hutchison, Jr., *J. Chem. Phys.*, 37, 1878 (1962).

(4) (a) R. A. Bernheim, R. J. Kempf, P. W. Humer, and P. S. Skell, *ibid.*, 41, 1156 (1964); (b) R. A. Bernheim R. J. Kempf, J. V. Gramas, and P. S. Skell, *ibid.*, 43, 196 (1965).

(5) (a) A. M. Trozzolo and W. A. Gibbons, Abstracts of Papers, 150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept. 1965, p 29V; (b) W. A. Gibbons and A. M. Trozzolo, *J. Am. Chem. Soc.*, **88**, 172 (1966).

(6) P. Venkateswarlu, *Phys. Rev.*, 77, 79, 676 (1950); E. B. Andrews and R. F. Barrow, *Nature*, **165**, 890 (1950); R. K. Laird, E. B. Andrews, and R. F. Barrow, *Trans. Faraday Soc.*, **46**, 803 (1950); B. A. Thrush and J. J. Zwolenik, *ibid.*, **59**, 582 (1963); D. E. Milligan, D. E. Mann, M. E. Jusk, and R. A. Mitsch, *J. Chem. Phys.*, **41**, 1199 (1964); J. P. Simons, *J. Chem. Soc.*, 5406 (1965), for a summary.

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(14) I. Moritani, S. Murihashi, N. Nishino, K. Kimura, and H. Tsubimora, *Tetrahedron Letters*, 373 (1966).

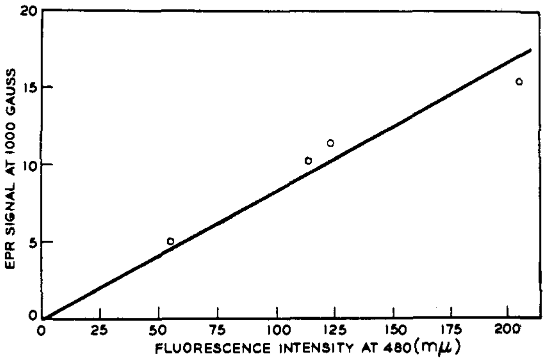

Figure 2. Correlation of esr signal and fluorescence of diphenylmethylene.

trations (10^{-4}–10^{-6} M). Using sufficiently pure solutes and solvents and well-degassed solutions, the only additional emission which was detected in some runs was a weak fluorescence at 430 mμ, attributable to tetraphenylethylene.[15]

The emission at 480 mμ was identified as *fluorescence* from diphenylmethylene (III), a triplet ground-state molecule, by the following.

(a) A plot of the intensity of the known low-field esr absorption of diphenylmethylene[16] against the intensity of the 480-mμ emission gave a good straight line which passed through the origin (Figure 2). Since at short irradiation times no monoradical esr signal nor any other luminescent product was detected, it was concluded that the luminescence is in fact due to III.

(b) The emission at 480 mμ is completely different from that of other possible products of the photolysis of diphenyldiazomethane (benzophenone, tetraphenylethane, tetraphenylethylene, diphenylmethyl radical, and benzophenone azine).

(c) Upon warming the photolyzed solutions from 77°K, the fluorescence at 480 mμ disappeared with the concomitant appearance of a new emission spectrum, which was identified as the phosphorescence of benzophenone. When the solution was thoroughly degassed, the latter emission was not observed. This chemiluminescent reaction had been reported previously, and it involves the reaction of III with oxygen.[2b]

(d) The lifetime of the species emitting at 480 mμ is $<10^{-3}$ sec, and the spectrum is the mirror image of the long-wavelength band in the absorption spectrum attributed to III (see below).

(e) The absorption spectrum and the fluorescence excitation spectrum are identical within experimental error, and they are qualitatively similar to the corresponding spectra of the diphenylmethyl radical (see Table I).

It should be pointed out that there is only one other published example of triplet–triplet emission from aromatic molecules.[17] Attempts to detect phosphorescence from III have been unsuccessful thus far.

2. Absorption and Excitation Spectra of Diphenylmethylene. Provided that one species is responsible for a given emission, that quenchers are absent, that the quantum yield is independent of wavelength, and that one is using a properly calibrated light source and detector, the excitation spectrum should correspond to the absorption spectrum of the emitting species. As noted above, both the esr and luminescence studies have shown that, at short exposure time (<2 min), the photolysis of diphenyldiazomethane in a rigid glass produces III almost exclusively.

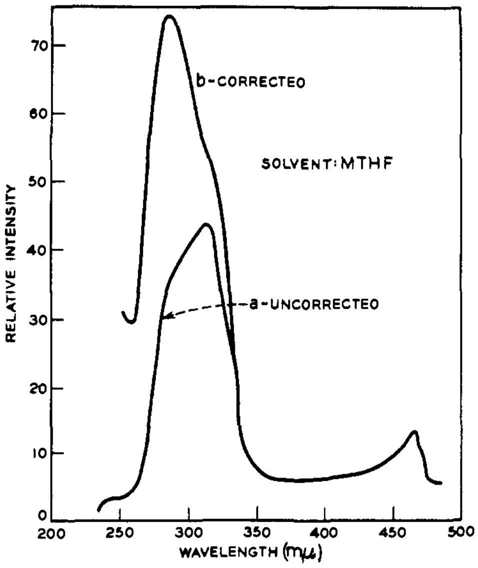

Figure 3. Excitation spectrum of diphenylmethylene fluorescence at 77°K.

Table I. Comparison of Diphenylmethylene with Odd-Alternant Radicals

Species	Absorption maxima, mμ	Emission maximum, mμ
$C_6H_5\dot{C}H_2$	319, 450[a–c]	462[c]
$(C_6H_5)_2\dot{C}H$	336, 515[b,c]	535[d]
$(C_6H_5)_2\dot{C}\cdot$	300, 465[d]	580[d]

[a] I. Norman and G. Porter, *Proc. Roy. Soc.* (London), **A230**, 399 (1955). [b] G. Porter and E. Strachan, *Trans. Faraday Soc.*, **54**, 431 (1958). [c] S. Leach and L. Grajcar, 5th International Symposium on Free Radicals, Uppsala, 1961. [d] Present work.

The excitation spectrum which corresponds to the 480-mμ fluorescence is shown in Figure 3. This spectrum was independent of emission wavelengths in the range 475–550 mμ, thus showing again that the emission is that of only one species, diphenylmethylene. The shape of the excitation spectrum also was independent of solute concentrations in the range 10^{-4}–10^{-6} M. As previously stated,[5] these results indicate that III absorbs in the range 240–470 mμ with principal maxima at 465 and 280–300 mμ. (There also appears to be another band at approximately 240 mμ.)

The absorption spectrum of a photolyzed sample of diphenyldiazomethane also was taken (Figure 4). It showed the same bands as the fluorescence excitation spectrum of III. Both the absorption and the fluorescence spectrum of III disappeared on warming the frozen solutions. In some absorption experiments, III was produced "quantitatively," *i.e.*, a known concentra-

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(15) At longer exposure times, additional products were detected; see ref 5b.

(16) A. M. Trozzolo, E. Wasserman, and W. A. Yager, *J. Chim. Phys.*, **61**, 1663 (1964).

(17) (a) F. Dupuy, G. Nouchi, and A. Rousset, *Compt. Rend.*, 3256, 2976 (1963). (b) A luminescence associated with diphenylmethylene has been observed by R. Harrell, unpublished results.

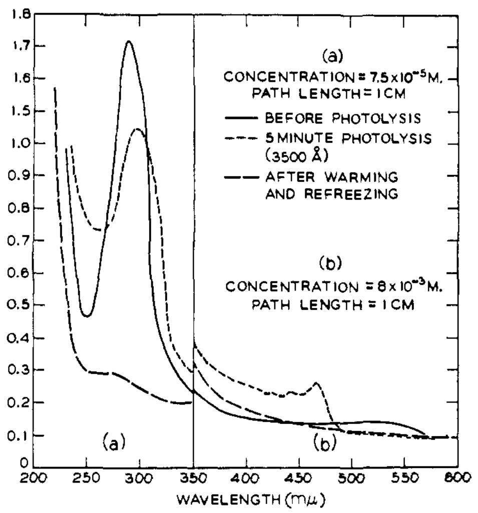


Figure 4. The photolysis of diphenyldiazomethane in a hydrocarbon glass at 77°K.

tion of diphenyldiazomethane was destroyed. Under these conditions, the following minimum extinction coefficients were calculated: 25,000 (λ_{max} 301 mμ) and 300 (λ_{max} 465 mμ).

3. Spectral Assignments. Diphenylmethylene, in contrast to the vast majority of organic molecules, has a triplet ground state. The absorptions at 465, 300, and 240 mμ must therefore correspond to electronic transitions from the ground state to higher levels in the triplet manifold. Previous esr studies[18,19] have shown that III is essentially a planar molecule, the Ar–C–Ar angle being approximately 140–150°. The unpaired electrons are largely localized in each of the two unshared orbitals of the methylene carbon atom. The nodal plane of one of these orbitals corresponds to the molecular plane and is designated p_y, and the other in-plane orbital is designated p_x. A diagram is shown in Figure 5.

The following observations are of importance in assigning the electronic transitions of diphenylmethylene.

(a) There is a qualitative resemblance between the spectra (absorption and emission) of III and those of the diphenylmethyl radical (see Table I). This is not unexpected if the transitions in both cases involve orbitals whose nodal planes coincide with the molecular plane If it is assumed that the p_z electron is not involved in the transitions, then the π system of III can be considered (like the diphenylmethyl radical) as that of an odd-alternant hydrocarbon radical having 13 π electrons. It has been shown previously[20] that, in systems of this type, a strong absorption band in the ultraviolet region and a weak band in the visible region should be expected. This is exactly what has been found for the benzyl, diphenylmethyl, and triphenylmethyl radicals,[21] and it suggests that the finding of two similar bands in III is consistent with a π–π^* assignment for the absorptions. There are indications that III has still a third absorption band at ~240 mμ which would agree with the recent finding of an analogous band in the benzyl radical spectrum.[22]

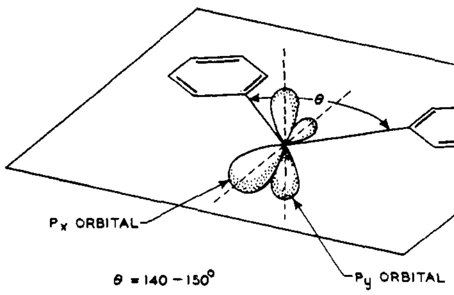


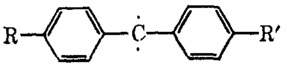
Figure 5. Structure of diphenylmethylene.[18]

(b) Polarization studies are of interest. If the above assignments are correct, then both the high-energy (300 mμ) and low-energy (465 mμ) absorption bands should be polarized in the molecular plane. The fluorescence spectrum should be polarized similarly. Only the polarization of the long-wavelength absorption band has been reported,[13] and it was found that only light which was polarized parallel to the line of the phenyl ring centers was absorbed.

Attempts to detect phosphorescence from III were unsuccessful. This is unfortunate since this phosphorescence could have arisen from radiative processes involving either an excited singlet state or an excited quintet state. It thus might have been possible to obtain directly triplet–singlet energy level differences which would be useful in the field of carbene chemistry.

4. Spectra of Substituted Diphenylmethylenes. The photolysis of 4-chlorophenyl-, 4-bromophenyl-, and 4-methylphenylphenyldiazomethane gave almost exclusively the corresponding substituted diphenylmethylenes, which, in each case, esr studies[23] have shown to be ground-state triplet molecules. The maxima of both the absorption and emission band were shifted to longer wavelengths from those of III (see Table II). As in III, the short-wavelength bands were more intense than the visible-range bands.

Table II. Spectra of Diphenylmethylenes in 2-Methyltetrahydrofuran

 R; R′	Absorption maxima, mμ	Emission maximum, mμ
H; H	300; 465	480
Cl; H	311, 475	487
Br; H	316; 475	488
CH_3; H	301; 472	487
OCH_3; H	335–345[a]	495
NO_2; H	265; 370, 555	No emission
C_6H_5; H	355[a]	555
OCH_3; OCH_3	335–345[a]	507

[a] Obtained from the fluorescence excitation spectrum rather than the absorption spectrum.

The photolysis of 4,4′-bismethoxydiphenyldiazomethane (IV) proved rather anomalous. At low con-

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[18] E. Wasserman, A. M. Trozzolo, W. A. Yager, and R. W. Murray, *J. Chem. Phys.*, 40, 2408 (1964).

[19] R. W. Brandon, G. L. Closs, C. E. Davoust, C. A. Hutchison, Jr., B. E. Kohler, and R. Silbey, *ibid.*, 43, 2006 (1965).

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[21] E. J. Land, *Progr. Reaction Kinetics*, **3**, 370 (1965).

[22] G. Porter and M. I. Savadatti, *Spectrochim. Acta*, **22**, 803 (1966).

[23] Unpublished results.

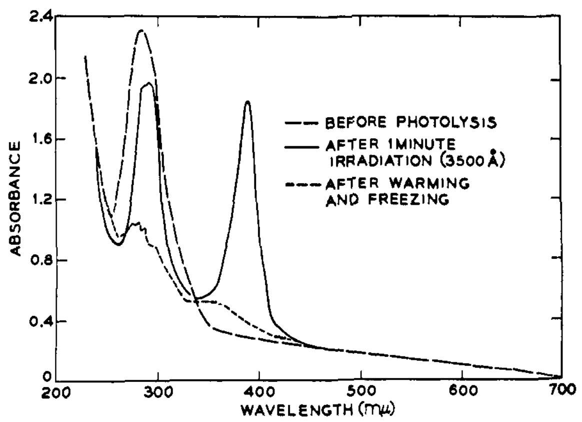

Figure 6. Photolysis of 4,4'-dimethoxydiphenyldiazomethane in MTHF at 77°K.

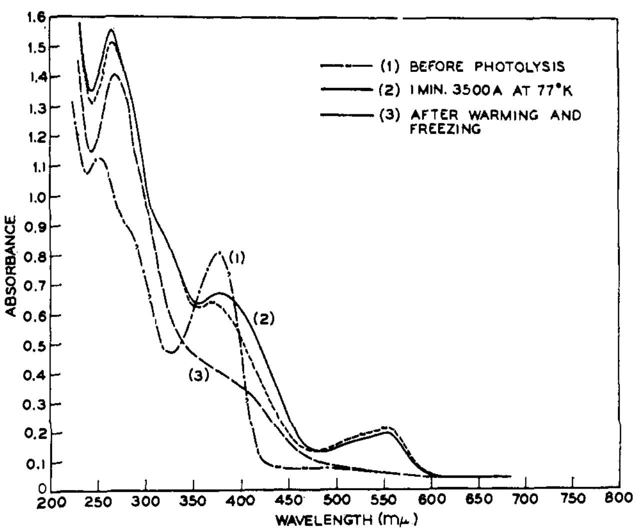

Figure 7. Photolysis of 4-nitrophenylphenyldiazomethane in MCIP glass at 77°K.

centrations the corresponding ground-state triplet methylene is not detected by fluorescence studies nor by esr spectroscopy. However, *in absorption studies* (Figure 6), the spectrum of IV disappears, upon photolysis, to be replaced by that of a species V which absorbs at 294 and 390 mμ. On warming and refreezing, the spectrum of V disappears. The lack of an esr signal in the region of 3350 gauss shows that V is not a free radical, so it must be assumed that V is a singlet molecule formed by photodecomposition or rearrangement of IV. At first one might suspect that it is 4,4'-bismethoxydiphenylmethylene (dianisylmethylene) (VI), which would therefore be a ground-state singlet molecule. Further experiments proved this suggestion to be erroneous, since photolysis of more highly concentrated solutions of IV gave the intermediate V as well as the esr and fluorescence spectrum of the ground-state triplet VI, the latter emitting at 507 mμ and its fluorescence excitation spectrum exhibiting a maximum at 330–350 mμ. (The excitation spectrum is of doubtful reliability since, even at the higher concentration of IV, the principal absorbing species is the intermediate V.) Attempts to photolyze V in order to demonstrate that it is a precursor of VI led to inconclusive results.

These experiments are significant because not only do they show the power of the combined use of esr, fluorescence, and absorption spectroscopy in identifying reactive intermediates in rigid media, but they also show that *great caution should be exercised in assigning a given absorption to a methylene even if the esr spectrum has been obtained in different experiments under rather similar conditions.*

The photolysis of 4-methoxyphenylphenyldiazomethane is very similar to that of IV. Absorption studies showed that an unstable intermediate, VII (λ_{max} 379 mμ), is the principal photolysis product. However, the fluorescence excitation spectrum of the emission at 495 mμ is vastly different from the absorption of VII. Esr studies showed that VII is not the ground-state triplet 4-methoxyphenylphenylmethylene (VIII),[23] nor is it a free radical.

The photolysis of 4-nitrophenylphenyldiazomethane in 2-methyltetrahydrofuran at 77°K gave a bright red solution which exhibited absorption maxima at 265, 370, and 555 mμ (Figure 7). Esr studies[23] established that this is the ground-state triplet, 4-nitrophenylphenylmethylene (IX). In common with most simple nitro aromatic molecules, IX did not fluoresce.

The photolysis of 4-biphenylylphenyldiazomethane was also studied. A weak emission was found at 555 mμ. The fluorescence excitation spectrum indicated an absorption maximum at 355 mμ.

Experimental Section[24]

The emission and excitation spectra were recorded on either an Aminco-Kiers spectrophotofluorometer, a Spex 1400 f6.8 scanning spectrometer, or a spectrofluorometer described by Bovey and Longworth.[25]

The absorption spectra were recorded on a Cary 15 spectrometer fitted with a low-temperature attachment. Quartz cells and dewars were obtained from the Thermal American Fused Quartz Co.

The photolysis experiments were performed in a Rayonet photochemical reactor with light of wavelength >300 mμ, the maximum output being at 350 mμ.

The diazo compounds were prepared by the oxidation of the corresponding hydrazones in ether solution with lead dioxide. The esr spectra were obtained as described previously.[2,26]

Photolyses were run in the following solvents: 2-methyltetrahydrofuran (MTHF), methylcyclohexane (MC), methylcyclohexane-isopentane (MCIP), 3-methylpentane (MP). The concentration range of the diazo compounds was 10^{-3}–10^{-6} M.

Acknowledgments. The authors wish to thank Drs. R. W. Murray and E. Wasserman for several interesting discussions.

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(24) The authors are grateful to Drs. J. Ferguson and J. W. Longworth for assistance with some of the spectral measurements.

(25) F. A. Bovey and J. W. Longworth, to be published.

(26) The authors wish to thank W. A. Yager and R. M. R. Cramer for assistance in the esr experiments.