

Figure 1. E.s.r. of 1-naphthylmethylene in benzophenone at 77° K. ($h\nu = 9.349$ kMc.p.s.).

The corresponding diazo compounds³ were irradiated in dilute "solid solutions" at 77 and 4°K. and the spectra obtained^{2,4} and analyzed⁵ as described previously. The spectrum of I in benzophenone is given in Figure 1 and indicates the presence of two triplets. The assignments of the zero-field parameters, D and E , in benzophenone (see below) are (in cm^{-1}): $D_{Ia} = 0.4555$, $E_{Ia} = 0.0202$; $D_{Ib} = 0.4347$, $E_{Ib} = 0.0208$; $D_{IIa} = 0.4711$, $E_{IIa} = 0.0243$; $D_{IIb} = 0.4926$, $E_{IIb} = 0.0209$. 9-Anthrylmethylene (III) had one triplet with $D_{III} = 0.3008$, $E_{III} = 0.0132$ cm^{-1} . In the glassy matrices, Nujol, 2-methyltetrahydrofuran, Fluorolube, and decalin-cyclohexane, similar results were observed⁶; one triplet with III and two with I and II. The parameters were largely unchanged with (in cm^{-1}): $|\Delta D_I| \approx 0.021$, $|\Delta E_I| \approx 0.001$; $|\Delta D_{II}| \approx 0.021$, $|\Delta E_{II}| \approx 0.003$ where, e.g., $\Delta D_I = D_{Ia} - D_{Ib}$.

The appearance of two triplets for I or II in glassy media and the comparative constancy of ΔD and ΔE with environmental variations indicate two different species. Two slightly different values of D and E can arise from a given triplet in a close-fitting crystalline host due to different local environments.⁷ However, ΔD and ΔE depend there on the specific host, and no splitting is observable in a glassy matrix.⁸ The lack of splitting with III or phenylmethylene^{2,4} (IV) eliminates hyperfine interactions as a cause. The small values of $\Delta D/D$ and $\Delta E/E$ imply that the triplets are closely related, and stereoisomers are likely. Since E/D is essentially determined by the bond angle at the divalent carbon,^{2,9} the similar ratios for I-IV imply similar angles. The presence of but a single species with III or IV makes unlikely a pair in which the hydrogen is out of the molecular plane in one and in the plane in the other. A reasonable choice for the isomeric pairs is then Ia, Ib and IIa, IIb.

More quantitative considerations allow the assignment of the individual isomers. The appearance of ΔD and ΔE is associated with the asymmetry in the distribution of the unpaired electron in the in-plane

sp-hybrid orbital due to bending at the divalent carbon atom. For an HCC angle of 140° approximately two-thirds of the unpaired electron is in the larger lobe, and one-third is in the smaller. If the unpaired spin densities in the π -system at the o -carbon atoms, ρ_o and $\rho_{o'}$, are not the same, the two isomers will have different spin-spin interactions between the unpaired electrons resulting in different zero-field parameters. The spin densities for the π -electron are given with the formulas.¹⁰ Because of the $1/r^3$ dependence of D and E only the nearest atoms need be considered. From the spin distribution we compute (in cm^{-1}): $\Delta D_I = +0.017$ and $\Delta E_I = -0.005$; $\Delta D_{II} = -0.012$ and $\Delta E_{II} = +0.003$.¹¹ Since the computed values depend on $\Delta\rho_o = \rho_o - \rho_{o'}$, similar results obtain from other sets of spin densities, e.g., those of Hückel theory. The computed signs of D are the basis of the assignments given above. From the similarity of the $|\Delta\rho_o|$ for I and II it is expected that $|\Delta D_I| \approx |\Delta D_{II}|$ as is observed experimentally.

The fact that only a single triplet is observed with compounds which formally have $\Delta\rho_o \neq 0$, as m -nitrophenylmethylene, is undoubtedly due to the values of ΔD and ΔE being too small to permit resolution within the line widths available.

The variation of D with I-IV is due to the variation in the π -electron spin density at the divalent carbon, since the dominant interaction is the one-center term.^{9,12} Consequently, the ratio of that spin density¹⁰ to D (in cm^{-1}) should be approximately constant. The computed ratios, taking the average of the isomers for I and II, are 1, 0.620/0.445 = 1.39; II, 1.46; III, 1.39; IV, 1.43.

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(10) By the method of A. T. Amos and L. C. Snyder, *ibid.*, **41**, 1773 (1964), particularly eq. 59. These values were kindly supplied by Dr. Snyder.

(11) Each lobe of the p-orbital or the sp-hybrid was represented by a point dipole approximately at the center. One of the causes for the deviations from the observed values may be the neglect of the steric interactions with the *peri*-hydrogen in Ia and Ib.

(12) For the analogous case with nitrenes, see G. Smolinsky, L. C. Snyder, and E. Wasserman, *Rev. Mod. Phys.*, **35**, 576 (1963).

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Photoisomerization of *trans*-15,16-Dimethyldihydropyrene

Sir:

Recently, we reported the synthesis of *trans*-15,16-dimethyldihydropyrene^{1,2} (I) and some of its properties.³ The possibility of valence tautomerism has been one of the points of interest in this series and was discussed earlier in relation to a possible synthetic route

(1) V. Boekelheide and J. B. Phillips, *J. Am. Chem. Soc.*, **85**, 1545 (1963).

(2) V. Boekelheide and J. B. Phillips, *Proc. Natl. Acad. Sci. U.S.A.*, **51**, 550 (1964).

(3) F. Gerson, E. Heilbronner, and V. Boekelheide, *Helv. Chim. Acta*, **47**, 1123 (1964).

(3) Prepared by the mercuric oxide oxidation of the appropriate hydrazone; see W. Treibs, M. Quarg, and E. J. Poppe, *Ann.*, **598**, 32 (1956).

(4) A. M. Trozzolo, R. W. Murray, and E. Wasserman, *J. Am. Chem. Soc.*, **84**, 4990 (1962).

(5) E. Wasserman, L. C. Snyder, and W. A. Yager, *J. Chem. Phys.*, **41**, 1763 (1964); P. Kottis and R. Lefebvre, *ibid.*, **41**, 379 (1964).

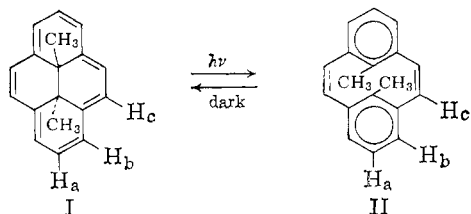
(6) Some combinations of solute and solvent were not observed due to lack of solubility or unstable signals.

(7) See, for example, E. Wasserman and R. W. Murray, *J. Am. Chem. Soc.*, **86**, 4203 (1964), footnote 4.

(8) A. M. Trozzolo, E. Wasserman, and W. A. Yager, *J. chim. phys.*, to be published.

(9) J. Higuchi, *J. Chem. Phys.*, **39**, 1339 (1963).

to *trans*-15,16-dimethyldihydropyrene.⁴ We wish now to report that *trans*-15,16-dimethyldihydropyrene is converted by visible light to its valence tautomer having the metacyclophane structure II. In the dark the metacyclophane isomer reverts back to the more stable dihydropyrene system. Furthermore, the interconversions of I and II by the photochemical and dark reactions can be carried out repeatedly without deterioration of the sample.



The photochemical transformation is best described by giving details for a particular experiment. A solution of 30 mg. of I in 1 l. of pentane was subjected to irradiation using four ordinary Mazda lamps (a total of 500 w.) for 6 hr. After concentration of the solution, a spectral comparison of the irradiation product with pure I showed the presence in the irradiation product of a photoisomer (II) which does not absorb above 300 μ . In this instance the ratio of I:II was roughly 1:1, although in other experiments employing other solvents the proportion of II in the irradiation product may be as high as 95%.

The n.m.r. spectrum of the product mixture after irradiation can be interpreted readily since the signals for the protons in II are quite distinct and do not overlap the signals for the protons present in I. Also, there is no evidence that by-products are formed to any extent. The n.m.r. signals observed are summarized in Table I in terms of the individual protons as denoted in structures I and II.

Table I. N.m.r. Signals of the Irradiation Product^a

I			II		
δ , p.p.m.			δ , p.p.m.		
H(CH ₂ -)	-4.20	Singlet	H(CH ₂ -)	1.52	Singlet
H _a	8.00	A ₂ B	H _a	6.95	AB ₂
H _b	8.50		H _b	6.56	
H _c	8.55	Singlet	H _c	6.24	Singlet

^a The spectrum was determined using a Varian A-60 and a Varian A-100 with carbon tetrachloride as solvent and tetramethylsilane as an internal standard.

The change in the n.m.r. spectrum in going from I to II is in good accord with what would be predicted. Thus, the signal at -4.20 p.p.m., corresponding to the internal methyl groups in I, is replaced by a signal at 1.52 p.p.m. as is appropriate for the internal methyls of a metacyclophane.⁵ In I the H_a and H_b protons form a A₂B system with a spin-coupling constant $J_{AB} = 7.5$ c.p.s. In II these protons form an AB₂ system with a spin-coupling constant of 7.2 c.p.s., the signals occurring in the usual benzene region but at much higher field than I. Thus, the n.m.r. spectrum is par-

(4) W. S. Lindsay, P. Stokes, L. G. Humber, and V. Boekelheide, *J. Am. Chem. Soc.*, **83**, 943 (1961).

(5) D. J. Wilson, V. Boekelheide, and R. W. Griffin, Jr., *ibid.*, **82**, 6302 (1960).

ticularly striking in supporting the conclusion that the photoisomer does indeed have the metacyclophane structure II.

The dark reaction by which II is converted back to I has been followed both by absorption spectroscopy and by n.m.r., the agreement between the two methods being excellent. The dark reaction follows first-order kinetics and its rate is temperature dependent. A convenient method for carrying out these studies is to dissolve I in a polyvinyl chloride foil, irradiate, and then observe the dark reaction. Under these conditions the half-life of II at 50° is about 2 hr.

Other derivatives of *trans*-15,16-dimethyldihydropyrene also show a similar photoisomerization. For example, the 2-nitro derivative is readily converted by visible light to the corresponding metacyclophane structure. In this case the dark reaction, when measured using a polyvinyl chloride foil at 50°, is about 40 times faster than that of the unsubstituted hydrocarbon.

The photochemical transformation of dihydropyrene derivatives to metacyclophanes and their spontaneous reversion back to the dihydropyrene structure is an unusual interconversion allowing temporary storage of photochemical energy. Further studies are underway investigating the fundamental details of both processes.

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Cyclobutadiene- and Benzocyclobutadiene-Iron Tricarbonyl Complexes¹

Sir:

Although the isolation of metal complexes of tetraphenylcyclobutadiene² and tetramethylcyclobutadiene^{3,4} may provide adequate verification of the prediction made by Longuet-Higgins and Orgel⁵ that cyclobutadiene might form stable metal complexes, nonetheless no complexes of cyclobutadiene itself have been prepared. A substance which initially appeared to be a silver ion complex of cyclobutadiene has recently been shown to be a complex of a dimer of cyclobutadiene.⁶

(1) This work was reported at the Regional Meeting of the Southeastern Section of the American Chemical Society, Charleston, W. Va., October 15-17, 1964.

(2) (a) W. Hubel and E. H. Braye, *J. Inorg. Nucl. Chem.*, **10**, 250 (1959); (b) R. P. Dodge and V. Schomaker, *Nature*, **196**, 798 (1960); (c) A. Nakamura and N. Hagihara, *Bull. Chem. Soc. Japan*, **34**, 452 (1961); (d) H. H. Freedman, *J. Am. Chem. Soc.*, **83**, 2194 (1961); (e) L. Malatesta, G. Santarella, L. Vallarino, and F. Zingales, *Angew. Chem.*, **72**, 34 (1960); (f) A. T. Blomquist and P. M. Maitlis, *J. Am. Chem. Soc.*, **84**, 2329 (1962); (g) P. M. Maitlis and M. L. Games, *ibid.*, **85**, 1887 (1963).

(3) (a) R. Criegee and G. Schroder, *Ann.*, **623**, 1 (1959); (b) J. D. Dunitz, H. C. Mey, O. S. Mills, and H. M. M. Shearer, *Helv. Chim. Acta*, **45**, 627 (1962).

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(5) H. C. Longuet-Higgins and L. E. Orgel, *ibid.*, 1969 (1956).

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