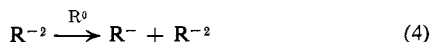
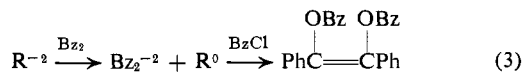
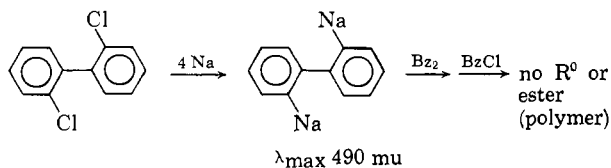


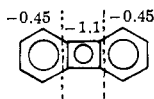
tained, from the hexane-insoluble fraction (3). Finally, addition of 1 molar equiv. of  $R^0$  to solutions of  $R^{-2}$  regenerated the familiar  $R^{-1}$ - $R^{-2}$  equilibrium mixture (4). The possibility of ring opening of  $R^{-2}$  to *o,o'*-



dimetallobiphenyl was specifically excluded as shown below.



The dianion  $R^{-2}$  is of especial interest as an analog of the cyclobutadiene dianion, a  $4n + 2$  system. That the analogy is reasonably close, electronically, is indicated by the following lines of evidence. The HMO (Hückel molecular orbital) charge distribution, shown below, indicates a very high ( $-1.1$ ) charge accrual on the central, cyclobutadienoid, part of the system.<sup>2</sup> This calculation is in fair agreement with the e.p.r.



spectrum of the anion radical.<sup>5,6</sup> The transannular resonance required for cyclobutadienoid character is demonstrated by the quantitative transfer of electrons from the phenanthrene and naphthalene anion radicals to biphenylene and by the polarographic reduction potential of the latter.<sup>3</sup> These facts indicate that  $R^{-2}$  (a) is fully cyclically delocalized, unlike its parent hydrocarbon<sup>4</sup> and (b) is similar to the cyclobutadiene dianion in charge distribution.

The most important observation is of the extensive disproportionation of  $R^{-1}$ . This behavior is relatively rare among anion radicals, the most familiar example being that of cyclooctatetraene anion radical, which disproportionates to a  $4n + 2$  dianion.<sup>7,8</sup>

It therefore seems that  $R^{-2}$  is fittingly called the "dibenzocyclobutadiene dianion," that it has a degree of special stability, and that, because the analogy seems fairly close, simple cyclobutadiene dianions should

(2) Assuming all  $\beta$ 's equal. Streitwieser<sup>3</sup> assumes  $\beta$  (transannular) =  $0.8\beta$  because the central bonds appear to be single in biphenylene.<sup>4</sup> We doubt, however, that this is the case in the electronated species and therefore assume all  $\beta$ 's equal.

(3) A. Streitwieser, Jr., and I. Schwager, *J. Phys. Chem.*, **66**, 2316 (1962).

(4) T. C. W. Mack and J. Trotter, *J. Chem. Soc.*, 1 (1962).

(5) C. A. McDowell and J. R. Rowlands, *Can. J. Chem.*, **38**, 503 (1960).

(6) A. Carrington and J. Dos Santos-Veiga, *Mol. Phys.*, **5**, 285 (1962).

(7) The entry of the second electron is usually more difficult than that of the first, owing to added repulsions; however, tetraphenylethylene anion radical also disproportionates,<sup>9</sup> and this we ascribe to an increase in phenyl-phenyl repulsions accompanying the shortening of the previously single phenyl-to-olefin bonds when the system becomes fully delocalized in  $R^{-1}$  and  $R^{-2}$ . These repulsions are avoided in  $R^0$  causing a disproportionation of  $2R^{-1}$  to  $R^0$  and  $R^{-2}$ .

(8) T. J. Katz, *J. Am. Chem. Soc.*, **82**, 3784 (1960).

(9) E. R. Zabolotny and J. F. Garst, *ibid.*, **86**, 1645 (1964).



Figure 1. Visible spectrum of  $R^{-1}$  and  $R^{-2}$ : solid line at 30% conversion, broken line at ca. 90% conversion. As sodium salt in 0.10 *M* THF.

also be expected to exhibit similar stability, as predicted by the  $4n + 2$  rule.

Nathan L. Bauld, Don Banks

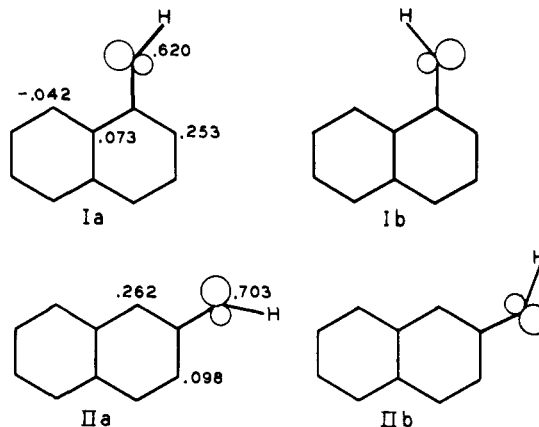
Department of Chemistry  
The University of Texas, Austin 12, Texas

Received November 4, 1964

## Geometric Isomers of Methylenes

Sir:

We wish to report the observation and assignment of the geometric isomers of 1- and 2-naphthylmethylenes (Ia, Ib and IIa, IIb, respectively) by electron spin



resonance.<sup>1</sup> This is the first detection of such isomers in ground-state triplets. The isomerism is dependent upon the nonlinearity of the bonds to the divalent carbon atom and may be considered as direct evidence for a bent structure. Previously, deductions from the e.s.r. spectrum of phenylmethylene and diphenylmethylene gave indirect evidence for bending.<sup>2</sup>

(1) Ia and Ib may be characterized as *trans*- and *cis*-H-1-naphthylmethylene, respectively.

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

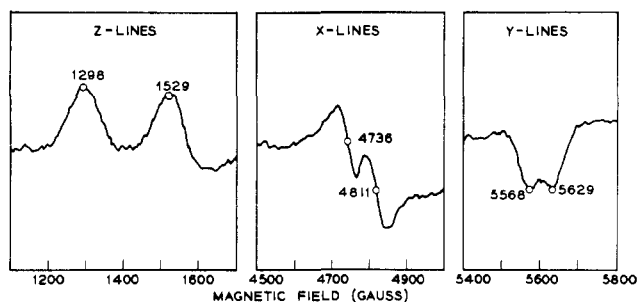


Figure 1. E.s.r. of 1-naphthylmethylene in benzophenone at 77° K. ( $h\nu = 9.349$  kMc.p.s.).

The corresponding diazo compounds<sup>3</sup> were irradiated in dilute "solid solutions" at 77 and 4°K. and the spectra obtained<sup>2,4</sup> and analyzed<sup>5</sup> 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  $\text{cm}^{-1}$ ):  $D_{Ia} = 0.4555$ ,  $E_{Ia} = 0.0202$ ;  $D_{Ib} = 0.4347$ ,  $E_{Ib} = 0.0208$ ;  $D_{IIa} = 0.4711$ ,  $E_{IIa} = 0.0243$ ;  $D_{IIb} = 0.4926$ ,  $E_{IIb} = 0.0209$ . 9-Anthrylmethylene (III) had one triplet with  $D_{III} = 0.3008$ ,  $E_{III} = 0.0132$   $\text{cm}^{-1}$ . In the glassy matrices, Nujol, 2-methyltetrahydrofuran, Fluorolube, and decalin-cyclohexane, similar results were observed<sup>6</sup>; one triplet with III and two with I and II. The parameters were largely unchanged with (in  $\text{cm}^{-1}$ ):  $|\Delta D_I| \approx 0.021$ ,  $|\Delta E_I| \approx 0.001$ ;  $|\Delta D_{II}| \approx 0.021$ ,  $|\Delta E_{II}| \approx 0.003$  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  $\Delta D$  and  $\Delta E$  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.<sup>7</sup> However,  $\Delta D$  and  $\Delta E$  depend there on the specific host, and no splitting is observable in a glassy matrix.<sup>8</sup> The lack of splitting with III or phenylmethylene<sup>2,4</sup> (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,<sup>2,9</sup> 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  $\Delta D$  and  $\Delta E$  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  $\pi$ -system at the  $o$ -carbon atoms,  $\rho_o$  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  $\pi$ -electron are given with the formulas.<sup>10</sup> 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  $\text{cm}^{-1}$ ):  $\Delta D_I = +0.017$  and  $\Delta E_I = -0.005$ ;  $\Delta D_{II} = -0.012$  and  $\Delta E_{II} = +0.003$ .<sup>11</sup> 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  $\Delta D$  and  $\Delta E$  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  $\pi$ -electron spin density at the divalent carbon, since the dominant interaction is the one-center term.<sup>9,12</sup> Consequently, the ratio of that spin density<sup>10</sup> to  $D$  (in  $\text{cm}^{-1}$ ) should be approximately constant. The computed ratios, taking the average of the isomers for I and II, are I,  $0.620/0.445 = 1.39$ ; II, 1.46; III, 1.39; IV, 1.43.

**Acknowledgments.** We wish to thank Dr. L. C. Snyder for making his computations of spin densities available and for some helpful discussions. We are also indebted to Mr. R. M. R. Cramer for his aid in obtaining the e.s.r. spectra.

(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).

A. M. Trozzolo, E. Wasserman, W. A. Yager  
Bell Telephone Laboratories, Incorporated,  
Murray Hill, New Jersey  
Received November 23, 1964

## Photoisomerization of *trans*-15,16-Dimethyldihydropyrene

Sir:

Recently, we reported the synthesis of *trans*-15,16-dimethyldihydropyrene<sup>1,2</sup> (I) and some of its properties.<sup>3</sup> 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).