

Figure 1. The molecular structure of  $(C_{14}H_8O_2)P(OC_2H_5)_3$ . The complete phenanthrene ring is not shown. The errors in the P-O distances are about 0.02 Å. The three P-O distances in the basal plane do not differ significantly; the mean value is indicated. The distances and angles in the isopropoxy groups and in the phenanthrene ring do not differ significantly from those expected.

spectrum (between +44 and +62 p.p.m. relative to 85%  $H_3PO_4$ ), which was taken as strong evidence that the phosphorus atom is covalently bound to five oxygen atoms. We have recently determined the crystal structure of this adduct and find that the conclusion of the previous study is well founded.

The adduct crystallized in the orthorhombic space group  $Pbca$  with eight molecules in a cell with dimensions  $a = 18.18 \pm 0.01$ ,  $b = 25.03 \pm 0.01$ , and  $c = 10.14 \pm 0.01$  Å. The X-ray density is 1.193 g./cc. The structure was determined by the usual Patterson, Fourier, and least-squares methods from data obtained from integrated Weissenberg photographs taken with  $Cu K\alpha$  radiation. The present agreement factor  $\sum |F_o| - |F_c| / \sum |F_o|$  is 0.13 for the 754 observed reflections. The details of the structure determination as well as the results of a refinement of a set of data obtained with a scintillation counter will be reported later.

In agreement with the earlier work,<sup>2</sup> we find that the phosphorus atom is indeed five-coordinated and is at the center of a nearly perfect trigonal bipyramid (Figure 1) with one isopropyl group in an apical position ( $O_I$ ) and two isopropyl groups in equatorial positions ( $O_{III}$  and  $O_{IV}$ ). One of the oxygens attached to the aromatic system ( $O_{II}$ ) is in an apical position, while the other ( $O_V$ ) occupies the third equatorial position.

Several significant points are:

(1) The apical P-O bond leading to the aromatic carbon is somewhat longer than the apical P-O bond joined to the aliphatic carbon, the latter being approximately equal in length to the three P-O bonds in the equator of the bipyramid.

(2) The five-membered ring is planar (and is in fact coplanar with the phenanthrene system) but is not a regular pentagon. The two P-O-C angles in this ring are equal and are less obtuse than the other P-O-C angles not involved in ring formation. The two O-C-C angles in the ring are not equal, and one of them ( $108^\circ$ ) is significantly different from the ideal aromatic angle of  $120^\circ$ .

(3) The isopropyl groups are oriented in such a way as to minimize intramolecular carbon-carbon and

carbon-oxygen repulsions; even so, the molecule is rather crowded, the closest nonbonded distances between oxygen atoms and carbon atoms in neighboring groups being 2.64, 2.73, 2.79, and 2.65 Å. We feel that the presence of a five-membered ring joining one of the equatorial ( $O_V$ ) and one of the apical ( $O_{II}$ ) oxygens contributes significantly to the stability of this compound by minimizing the number of short nonbonded interactions. This feature may be responsible for the stability of other cyclic unsaturated<sup>2</sup> and saturated<sup>3</sup> pentaoxyphosphoranes.

(3) F. Ramirez, N. Ramanathan, and N. B. Desai, *J. Am. Chem. Soc.*, **85**, 3465 (1963).

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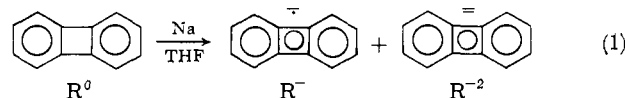
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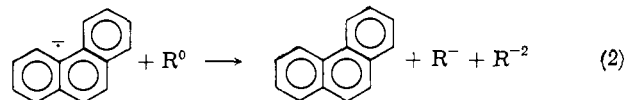
### The Dibenzocyclobutadiene Dianion

Sir:

Biphenylene reacts with sodium or potassium in tetrahydrofuran forming two species which can be shown to be the anion radical ( $\lambda_{max}$  588  $m\mu$ ) and dianion ( $\lambda_{max}$  565  $m\mu$ ) of biphenylene (1). At low conversions  $R^-$



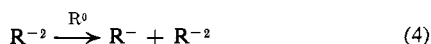
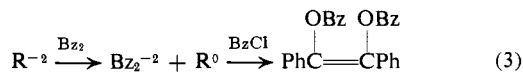
is predominant (see Figure 1), but already at 30% conversion to the anion radical (titration<sup>1</sup>) a dianion shoulder is clearly visible. At slightly less than stoichiometric conversion to  $R^-$  the dianion peak is quite prominent, indicating extensive disproportionation ( $2R^- \rightleftharpoons R^0 + R^{-2}$ ). As metal uptake continues to two atoms, the  $R^-$  peak disappears completely. Though the positioning of the peaks (anion radicals and their dianions generally absorb near one another in the visible region) and their response to metal uptake are alone suggestive of the structures assigned, further verification is available. To eliminate the possibility that the 565  $m\mu$  absorption arises from a spurious decomposition product of  $R^-$ , the latter was generated instantaneously from the naphthalene and also phenanthrene anion radicals (2). The same mixtures of  $R^-$  and  $R^{-2}$  as before were obtained. Also, the relative peak intensities did not change with time in the absence of excess alkali metal. Further, after com-



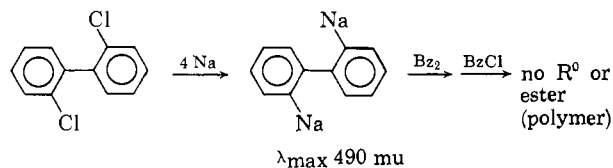
plete two-atom metal uptake a 40% yield of biphenylene could be isolated by electron transfer to benzil, quenching the benzil dianion with excess benzoyl chloride, and chromatographing the hexane-soluble fraction. A 50% yield of 1,2-dibenzoyloxystilbene was also ob-

(1) Aliquots of the solutions were added, with care, directly to water and titrated with acid to a phenolphthalein end point.

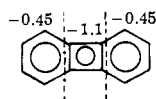
tained, from the hexane-insoluble fraction (3). Finally, addition of 1 molar equiv. of  $R^0$  to solutions of  $R^{-2}$  regenerated the familiar  $R^{-1}$ - $R^{-2}$  equilibrium mixture (4). The possibility of ring opening of  $R^{-2}$  to *o,o'*-



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.

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(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).

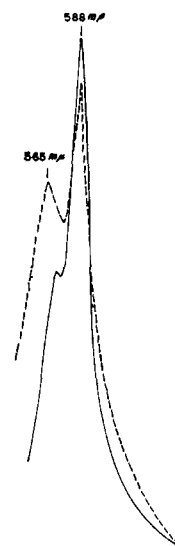


Figure 1. Visible spectrum of  $R^{-1}$  and  $R^{-2}$ : solid line at 30% conversion, broken line at ca. 90% conversion. As sodium salt in 0.10 *M* THF.

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

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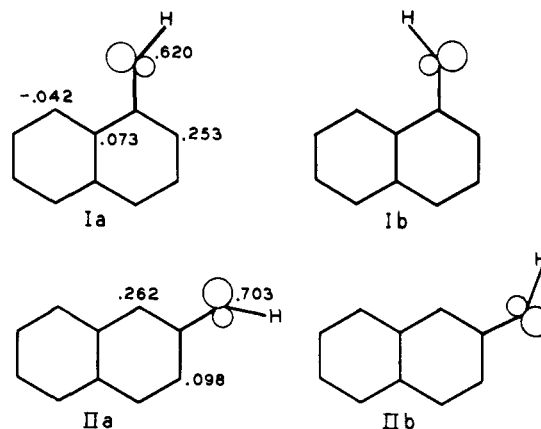
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## Geometric Isomers of Methylenes

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).