carbon atom directly bonded to a metal atom. For purposes of comparison, $(CH_3)_2Zn$ gives a peak (line width 0.6 c.p.s.) 28.6 c.p.s. upfield from $(CH_3)_4Si$. A sample containing both $(CH_3)_3NbCl_2$ and $(CH_3)_2Zn$ and $(CH_3)_4Si$ in $CCl_4$ was also examined. Only one peak (line width 0.9 c.p.s.) 29.6 c.p.s. upfield from the internal standard was observed. The merging of the two peaks and the slight broadening are suggestive of methyl group exchange between $(CH_3)_2Zn$ and $(CH_3)_3$-$NbCl_2$. No n.m.r. spectra were obtained for $(CH_3)_3$-$TaCl_2$ because of the rapid decomposition of this material in $CCl_4$ at $-10°$.

Samples of $(CH_3)_3NbCl_2$ and $(CH_3)_3TaCl_2$ were pyrolyzed by passage at pressures $<1$ mm. through a quartz tube at $700°$. In both cases metallic films were formed. At present, only the niobium film has been found to be a superconductor. The volatile products from the pyrolysis were methane and a halogenated hydrocarbon unidentified at present.

Studies of the chemistry of these new compounds are continuing.

**Acknowledgment.**—The author wishes to thank Dr. Stanley L. Manatt for helpful discussions and for the n.m.r. spectra, and Mr. Daniel Kuwada for the mass spectra.

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## Electron Spin Resonance of Triplets from Benzene 1,4-Diazooxides

*Sir:*

We wish to report the electron spin resonance (e.s.r.) spectra, including hydrogen hyperfine structure, of the ground state triplets (Ia–d) produced by photolysis of some benzene 1,4-diazooxides (IIa–d). Such triplets have been suggested as intermediates in the reactions of IIa and its derivatives.[1] The interaction between the unpaired electrons in Ia indicates that the $\pi$-system approximates that of a phenoxyl radical. The $\sigma$-system should be similar to that of a phenyl radical, and the hyperfine interaction observed is of the order of magnitude expected for such a $\sigma$-radical. Ia may be also regarded as a triplet phenyl cation substituted by an oxygen anion. Such a triplet state of the phenyl cation with one $\pi$- and one $\sigma$-unpaired electron has been suggested by Taft.[2]

IIa–d were produced by diazotization of the corresponding $p$-aminophenols. Finely powdered samples at 77 or 4°K. were irradiated with a mercury lamp for 1 min. or less. IIa was in "solid solution" in $p$-dichlorobenzene and IIc in 1,2,3-trichlorobenzene; IIb and IId were neat. The spectra were determined with a Varian V-4500 spectrometer equipped with 100-kc. modulation. The spectrum for Ia is given in Fig. 1. The zero-field parameters obtained from these observations were[3]: for Ia, $D = 0.3179$, $E = 0.0055$ cm.$^{-1}$;

(1) For a recent review of the structure and reactivity of Ia and some derivatives see M. J. S. Dewar and K. Narayanaswami, *J. Am. Chem. Soc.*, **86**, 2422 (1964), and references cited therein.

(2) R. W. Taft, *ibid.*, **83**, 3350 (1961).

(3) E. Wasserman, L. C. Snyder, and W. A. Yager, *J. Chem. Phys.*, to be published; P. Kottis and R. Lefebvre, *ibid.*, to be published.
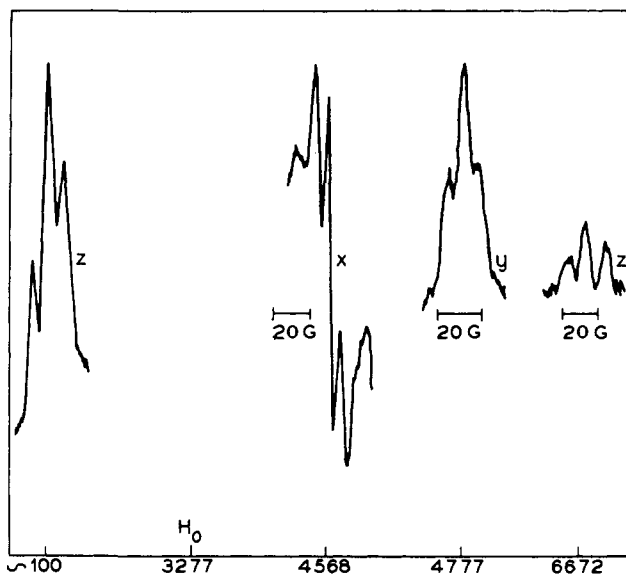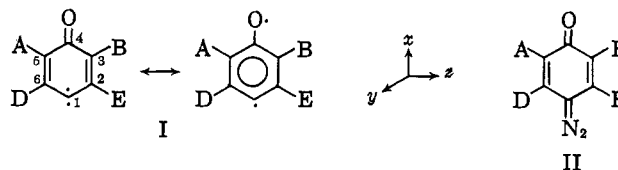
Fig. 1.—E.s.r. spectrum of Ia in $p$-dichlorobenzene. $H_0$ is the field for resonance of a free electron. Field measurements were not possible for the line near 100 gauss.

Ib, $D = 0.3284$, $E = 0.0086$ cm.$^{-1}$; Ic, $D = 0.3470$, $E = 0.0010$ cm.$^{-1}$; and Id,[4] $D = 0.3333$, $E = 0.0112$ cm.$^{-1}$.



a, A, B, D, E = H
b, A, B = Cl; D, E = H
c, A, B = H; D, E = Cl
d, A + D = -C_4H_4-; B, E = H

By arguments analogous to those employed with cyclopentadienylidene (III) and indenylidene (IV)[5] we can show that Ia–d each have one unpaired electron largely localized in a $\sigma$-orbital at C-1, the "divalent" carbon atom, and another delocalized in a $\pi$-orbital. For such a distribution of the unpaired electrons, $D$ is largely determined by $\rho_1$, the $\pi$-spin density at C-1. By comparison with III and IV[5] we expect $\rho_1 \sim 0.4$. This value is compatible with the $\pi$-system being similar to that of a phenoxyl radical. The hydrogen hyperfine splitting at the *para* position of the phenoxyl radical is 10.4 gauss[6] and indicates a $\rho_{para} \sim 0.42-0.45$.[7]

The small values of $E$ with Ia–d may be rationalized by assuming "bent bonds" at C-1[5,8] and by including the interaction of the unpaired $\sigma$-electron at C-1 and the $\pi$-spin density at other atoms.[5] The one-center and two-center terms occur with opposite sign and largely cancel.

The hyperfine splittings between the components of the triplets in Ia are 8.7, 6.6, and 10.6 gauss, along the

(4) A second set of lines corresponding to $D = 0.323$ and $E = 0.010$ cm.$^{-1}$ were also observed with 1d. Presumably, these were due to a second site in the crystal with a slightly different environment.

(5) E. Wasserman, L. Barash, A. M. Trozzolo, R. W. Murray, and W. A. Yager, *J. Am. Chem. Soc.*, **86**, 2304 (1964).

(6) T. J. Stone and W. A. Waters, *Proc. Chem. Soc.*, 253 (1962).

(7) H. M. McConnell, *J. Chem. Phys.*, **24**, 762 (1956); S. I. Weissman, T. R. Tuttle, and E. J. de Boer, *J. Phys. Chem.*, **61**, 28 (1957).

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

$x$-, $y$-, and $z$-axes, respectively. In Ib–d, the only structure observable was in the $z$-absorption below 1000 gauss. Here a triplet of lines was observed with Ib, a single line with Ic, and a doublet with Id. The splittings in Ib and Id were 10–12 gauss. The hyperfine structure in Ia may then be assigned to the protons attached to C-2 and C-6. The magnitude and signs of the anisotropic components (the deviations along the three axes from the isotropic value of 8.63 gauss) are compatible with this assignment and with the choice of axes given above with the formulas.[9] The anisotropic components indicate that the sign of the isotropic coupling is positive. We expect that the interaction of the unpaired $\sigma$-electron will dominate this isotropic coupling as $\rho_{meta} \approx 0.08$ for a phenoxyl radical.[6,7] The sign should be that for the *cis* proton of the vinyl radical, which Adrian and Karplus predict to be positive.[10]

The observed magnitude of the *cis*-hydrogen in the vinyl splitting (34 gauss[11]) may be compared with $2 \times 8.63 = 17.3$ gauss for Ia.[12] Since there are differences in the two systems in the $\sigma$- and $\pi$-systems as well as in the carbon–carbon bond lengths, the variation in the hyperfine coupling by a factor of two may not be unreasonable. The 17.3 gauss is, however, quite close to an $18 \pm 2$ gauss splitting obtained by Tolkachev, Chkheidze, and Buben[13] on photolysis of phenyl iodide adsorbed on silica gel and ascribed to the phenyl radical. Unfortunately, the relatively poor resolution of their spectrum and the possibility of anistropic effects leaves uncertain the assignment to an isotropic hyperfine interaction with the adjacent protons. The computations of Ingalls and Kivelson gave 21 gauss for the splitting in a phenyl radical with an sp$^2$ unpaired electron.[14]

**Acknowledgments.**—We wish to thank Mr. W. A. Yager and Mr. R. M. R. Cramer for their aid in obtaining the e.s.r. spectra.

(9) A simple dipolar approximation was used in which the spin density in each orbital lobe was approximated by a point dipole approximately at the center of the lobe.

(10) F. J. Adrian and M. Karplus, *J. Chem. Phys.*, **41**, 56 (1964).

(11) E. L. Cochran, F. J. Adrian, and V. A. Bowers, *ibid.*, **40**, 213 (1964); R. W. Fessenden and R. H. Schuler, *ibid.*, **39**, 2147 (1963).

(12) The $\Delta m = 1$ transitions of the triplets which we are observing involve one state ($m_s = 0$) in which there is no hyperfine interaction. The corresponding transitions for doublet species have hyperfine interactions in both levels. For comparison we must double the observed values in the triplet.

(13) V. A. Tolkachev, I. I. Chkheidze, and N. Ya. Buben, *Zh. Strukt. Khim.*, **3**, 709 (1962). We thank Dr. R. W. Fessenden for bringing this reference to our attention.

(14) R. B. Ingalls and D. Kivelson, *J. Chem. Phys.*, **38**, 1907 (1963).

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### Structural Identification of a Geometric Isomer of Tetrameric Phenylphosphonitrilic Chloride

*Sir:*

In the chemistry of trimeric phenylphosphonitrilic halides, two geometrical isomers have been isolated and identified for the bromides[1] and also for the chlorides.[2] However, with tetrameric phenylphosphonitrilic chloride four geometrical isomers may exist. Shaw and his co-workers[3] have discussed this isomer-

(1) (a) T. Moeller and P. Nannelli, *Inorg. Chem.*, **2**, 896 (1963); (b) *ibid.*, **2**, 659 (1963); (c) *ibid.*, **1**, 721 (1962).

(2) B. Grushkin, M. G. Sanchez, and R. G. Rice, *ibid.*, **3**, 623 (1964).

(3) (a) R. A. Shaw, B. W. Fitzsimmons, and B. C. Smith, *Chem. Rev.*, **62**, 251 (1962); (b) R. A. Shaw and C. Stratton, *Chem. Ind.* (London), 52 (1959).

ism and reported three isomers of $(C_6H_5PNCl)_4$, melting at 148, 202, and 248°, respectively, but could not assign any geometric configuration.
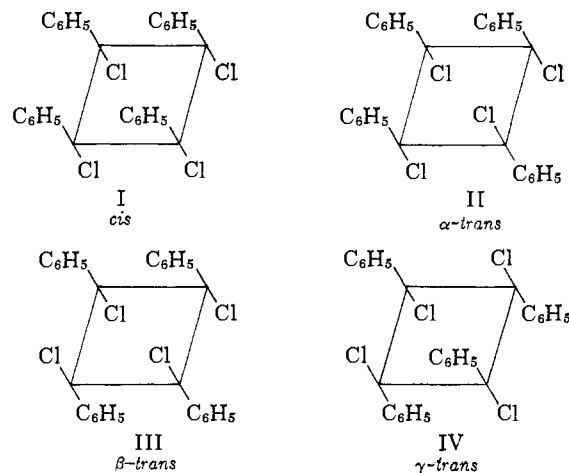
We have recrystallized a mixture of tetrameric phenylphosphonitrilic chlorides, m.p. 240–254°[2] to a melting range of 248–254°. This mixture then was dissolved in benzene, anhydrous ferric chloride was added, and the mixture was refluxed for 1 hr. We have shown earlier[4] that under these conditions no phenylation of *trans*-$(C_6H_5PNCl)_3$ takes place, but that some *cis*-$(C_6H_5PNCl)_3$ is formed by isomerization.

Decomposition of the mixture with water–HCl and extraction with benzene gave a solution from which was crystallized an isomer of $(C_6H_5PNCl)_4$, m.p. 202–205°. Careful recrystallization raised the melting point to 225–226°. Solidification and remelting gave the same value.

From the mother liquors we have isolated a second isomer of $(C_6H_5PNCl)_4$, m.p. 148–150.5° (same value on solidification and remelting) which we believe corresponds to the 148° isomer of Shaw. *Anal.* Calcd. for $C_{24}H_{20}Cl_4N_4P_4$: C, 45.75; H, 3.19; Cl, 22.50; N 8.90. Found: C, 46.05; H, 3.54; Cl, 22.84; N, 8.84. The infrared spectra of all reported compounds exhibited very strong absorption at about 1300 cm.$^{-1}$, indicative of the tetrameric phosphonitrilic ring.

Both of these chloro isomers were treated with excess dimethylamine in refluxing benzene producing, from the chloro tetramer melting at 225–226°, a 91% yield of a tetrakisdimethylamide (A), m.p. 153–155°, and from the chloro tetramer melting at 148–150.5°, an 85% yield of a tetrakisdimethylamide (B), m.p. 136–138°. *Anal.* Calcd. for $C_{32}H_{44}N_8P_4$: C, 57.80; H, 6.68; N, 16.86; P, 18.63. Found: C, 57.17; H, 6.57; N, 16.57; P, 18.08. Compounds A and B were examined by proton magnetic resonance spectroscopy. Based on the arguments given below, the n.m.r. spectra strongly indicate that both compound B and the tetrachloro isomer melting at 148–150.5° are $\alpha$-*trans* isomers having three phenyl groups on one side of the tetrameric PN ring, and one on the other side.

If the puckered tetrameric phosphonitrilic ring is represented for simplicity by a rectangle, then the four possible geometric isomers of $(C_6H_5PNCl)_4$ can be represented as



I
*cis*

II
$\alpha$-*trans*

III
$\beta$-*trans*

IV
$\gamma$-*trans*

(4) B. Grushkin, M. G. Sanchez, and R. G. Rice, presented before the Symposium on Inorganic Polymers, University of London, Ontario, Canada, Sept., 1963; to be submitted to *Inorg. Chem.*