propanes in ethanol for days (3 mole % HME) or in DMF solution for many hours (experiment discontinued after 5 hr, 5 mole % HPE).

Kerber, Urry, and Kornblum suggested the occurrence of step 2 to rationalize the observation that *o*- and *p*-nitrobenzyl chlorides but not *m*-nitrobenzyl chloride underwent the coupling reaction.[3] We observe that the photochemical coupling reaction between 1 equiv of 2-nitro-2-propyl anion and 0.5 equiv of *m*- and *p*-nitrobenzyl chlorides in ethanol proceeds until the *p*-nitrobenzyl chloride is consumed; none of the *m*-nitrobenzyl chloride is attacked. Photolysis of *m*-nitrobenzyl chloride in the presence of the 2-nitro-2-propyl anion produces a stable radical anion believed to be the *m*-nitrobenzyl chloride radical anion.

The interaction of a free radical with a carbanion is apparently an important reaction for the formation of carbon–carbon bonds. This reaction has been suggested to occur in the photochemical coupling of phenyllithium in THF solution.[11] Kornblum has suggested that the 2-nitro-2-propyl radical will attack the nitrite ion to yield a radical anion.[12]

[11] E. E. van Tamelen, J. I. Brauman, and L. E. Ellis, *J. Am. Chem Soc.*, 87, 4964 (1965).

[12] H. Feuer, *Tetrahedron Suppl.*, 1, 107 (1964) (see footnote 16).

[13] National Institutes of Health Predoctoral Fellow, 1965–1966.

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Structure of 2,2-Diphenyl-1-picrylhydrazyl Free Radical[1]

Sir:

Since its discovery over 40 years ago,[2] the stable free radical 2,2-diphenyl-1-picrylhydrazyl (DPPH) has been widely used as a homogeneous radical detector. The magnetic properties of this radical have been extensively studied both by static susceptibility methods and by electron paramagnetic resonance (epr). DPPH has frequently been used as a calibration standard for epr investigations.[3]

It has been established that DPPH crystallizes in several different forms,[4] with the crystal often containing molecules of solvation. One of the widely used forms is that obtained by crystallization from benzene solution, in which case a benzene molecule is incorporated into the crystal structure for each molecule of DPPH. We report here preliminary results of an X-ray diffraction study on single-crystal DPPH–C_6H_6.

Crystallographic data for DPPH–C_6H_6 have previously been reported by Sternberg.[5] We have remeasured the lattice constants and find a = 7.764, b = 10.648, c = 14.780 A, and β = 109.05° for the acentric space group setting Pc. The crystal structure was solved with the aid of multiple Patterson function superpositions followed by successive Fourier electron density syntheses. Refinement by full-matrix least squares (139 independent variables) has proceeded far enough that all atoms are well resolved, with $R = 8\%$ for three-dimensional data.

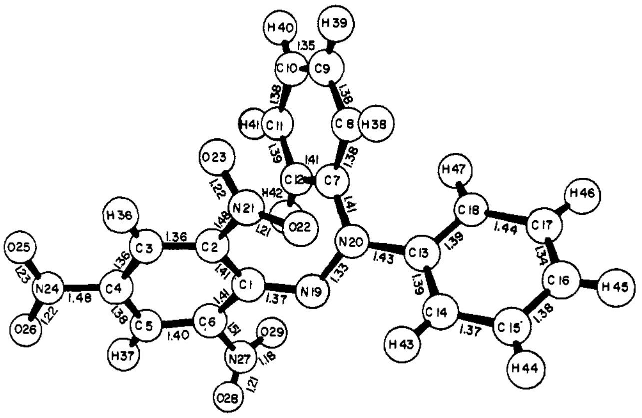

Figure 1. The shape of the DPPH molecule in the DPPH–C_6H_6 crystal. The hydrogens are placed at calculated positions.

The shape of the DPPH molecule is shown in Figure 1. Atoms $N_{19}N_{20}C_7C_{18}$ are coplanar, but C_1 is over 0.5 A from this plane. The angle between planes C_1N_{19}-N_{20} and $N_{19}N_{20}C_7C_{13}$ is 31°; and the angle between planes $C_1N_{19}N_{20}$ and C_1–C_6 is 32°. Thus, looking from N_{20} toward the picryl group, bonds $N_{20}N_{19}$ and $N_{19}C_1$ are successively twisted counterclockwise about 30° each. Such a twist in the hydrazyl backbone of the molecule was not predicted by an epr analysis on dilute solutions of DPPH.[6] Molecular orbital calculations on DPPH have often assumed planarity of at least the hydrazyl backbone.[7] Epr measurements on DPPH in dilute solid solution in the parent hydrazine indicated that 0.889 of the unpaired electron density is at the hydrazyl nitrogens.[8] There is evidence, however, that DPPH undergoes a change of conformation in a crystal of the parent hydrazine.[9]

The nonplanarity of the picryl group with respect to the hydrazyl backbone would be expected to reduce the stabilization of the radical by conjugation. The nitro substituents on the picryl group, in turn, probably do not stabilize[10] the radical very much since removal of the *p*-nitro group has little effect. Removal of one of the *o*-nitro groups, however, greatly increases the reactivity by removing steric hindrance from the hydrazyl backbone.[11,12] Phenyl ring C_7–C_{12} is inclined at 48° and is not important in conjugative stabilization of the molecule. Phenyl group C_{13}–C_{18}, however, is inclined at only 22°. This ring would thus have some unpaired electron density, as is indicated by proton magnetic resonance studies.[13,14]

If one includes an unshared electron pair on N_{19}, the configuration around both N_{19} and N_{20} is very nearly

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[1] Contribution No. 1957; this work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission.

[2] S. Goldsmidt and K. Renn, *Chem. Ber.*, 55, 628 (1922).

[3] D. J. E. Ingram, "Free Radicals," Academic Press Inc., New York, N. Y., 1958; A. L. Buchachenko, "Stable Radicals," Consultants Bureau, New York, N. Y., 1965.

[4] (a) J. A. Weil and J. K. Anderson, *J. Chem. Soc.*, 5567 (1965); (b) D. E. Williams, *ibid.*, 7535 (1965).

[5] M. Sternberg, *Compt. Rend.*, 240, 990 (1955).

[6] N. W. Lord and S. M. Blinder, *J. Chem. Phys.*, 34, 1693 (1961).

[7] R. Bersohn, *Arch. Sci.* (Geneva), 11, 177 (1958).

[8] R. W. Holmberg, R. Livingston, and W. T. Smith, Jr., *J. Chem. Phys.*, 33, 541 (1960).

[9] R. Lefebvre, J. Maruani, and R. Marx, *ibid.*, 41, 585 (1964).

[10] J. Hine, "Physical Organic Chemistry," 2nd ed, McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 410.

[11] A. T. Balaban, P. T. Frangopol, M. Marculescu, and J. Bally, *Tetrahedron*, 13, 258 (1961).

[12] A. T. Balaban, M. Marculescu, J. Pascaru, M. Rotaru, A. Valeriu, and M. Weiner, *Z. Physik. Chem.* (Leipzig), 219, 285 (1962).

[13] M. Anderson, G. Pake, and T. Tuttle, *J. Chem. Phys.*, 33, 1581 (1960).

[14] Yu. S. Karimov and I. F. Shchegolev, *Soviet Phys. JETP*, 13, 1 (1961).

trigonal. Angle $C_1N_{19}N_{20}$ is 117°, while angles $N_{19}N_{20}C_7$, $N_{19}N_{20}C_{13}$, and $C_7N_{20}C_{13}$ are 123, 116, and 120°, respectively. The geometry is thus reasonably consistent with sp^2 hybridization around both nitrogens, with the remaining unshared pair and the unpaired electron primarily in p- or π-type orbitals. The N_{19}–N_{20} bond (1.33 A) is intermediate in length between the value expected for a single bond (1.45 A) and a double bond (1.23 A).

The exceptional unreactivity of DPPH must be due in large part not to conjugative stabilization but to effective shielding of the hydrazyl backbone by surrounding parts of the molecule. N_{19} is closely surrounded by C_{13} (2.34), C_6 (2.34), C_7 (2.41), H_{43} (2.43), C_2 (2.55), N_{27} (2.69), H_{42} (2.70), C_{14} (2.72), O_{29} (2.76), O_{22} (2.90), C_{12} (2.91), and N_{21} (3.08 A). N_{20} is closely surrounded by C_1 (2.30), C_{12} (2.42), C_{14} (2.42), C_{18} (2.44), C_8 (2.44), H_{43} (2.61), H_{42} (2.62), H_{47} (2.64), H_{38} (2.66), O_{22} (2.68), C_2 (3.01), and N_{21} (3.02 A).

The benzene molecules in the crystal pack into spaces between the irregularly shaped DPPH molecules. The closest approaches between the benzene and DPPH molecules (and also between DPPH molecules) appear to be at normal van der Waals distances.

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Nitrogen Radicals from Anhydrides and Hydrazine Derivatives

Sir:

The reaction of anhydrides with a number of compounds containing N–N bonds leads to formation of radicals, detected by esr spectroscopy.[1] When tetramethyltetrazene (I) is treated with acetic anhydride, nitrogen is evolved at 0° and the esr spectrum of a radical (hereafter called A) appears (Figure 1). Relative peak intensities show that the splittings observed are caused by two equivalent nitrogens ($a_N = 13.41 \pm 0.05$ gauss) and twelve equivalent hydrogens ($a_H = 12.69$ gauss). The g factor was 2.0035 ± 0.0002 and the line width 400 mgauss. Of the 65 lines, 12 with expected intensity of less than 0.5% of the most intense could not be observed due to the low modulation amplitudes necessary to resolve the tight clusters of lines. Spectrum A was also obtained with succinic, maleic, dichloromaleic, and phthalic anhydrides in DMF, THF, and acetonitrile; there is no significant variation of splitting constants in these solvents. Proof that A is the tetramethylhydrazine cation (II) is given by the fact that the spectrum is also generated from dichloromaleic anhydride and tetramethylhydrazine and by the electrolytic oxidation of tetramethylhydrazine in 0.1 M tetraethylammonium perchlorate in acetonitrile.

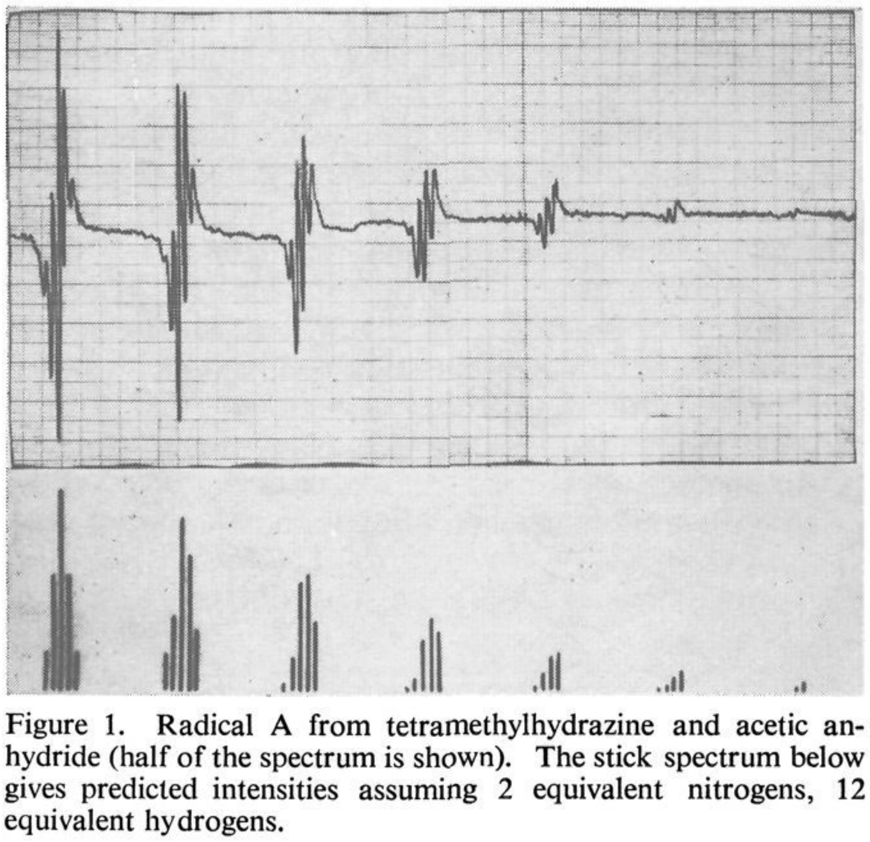

Figure 1. Radical A from tetramethylhydrazine and acetic anhydride (half of the spectrum is shown). The stick spectrum below gives predicted intensities assuming 2 equivalent nitrogens, 12 equivalent hydrogens.

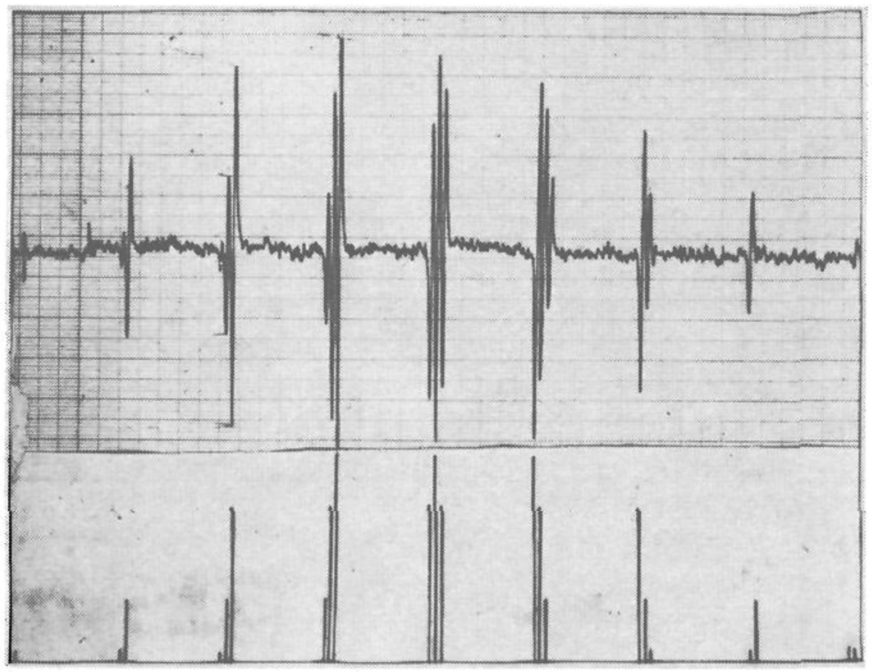

Figure 2. Radical B from glyoxal bis(dimethylhydrazone) and dichloromaleic anhydride in acetonitrile. The intensity decreases from left to right due to radical decomposition. The stick spectrum shows predicted line intensities for one nitrogen, six equivalent hydrogens.

$$\underset{\text{I}}{(CH_3)_2NN{=}NN(CH_3)_2} \longrightarrow N_2 + \underset{\text{II}}{(CH_3)_2\ddot{N}-\overset{+\cdot}{N}(CH_3)_2} \qquad (1)$$

It is generally agreed that, while spin induction is responsible for splitting constants of hydrogens attached to spin-bearing atoms, splitting constants for hydrogens of methyl groups attached to such atoms arise almost entirely from hyperconjugation.[2] The relative size of hydrogen splitting constants of isopropyl radical and II will then be a measure of the relative amount of hyperconjugation to a radical-bearing carbon and half-positive nitrogen; both have two methyl groups per formal spin-bearing center. The methyl hydrogen splitting constant of isopropyl radical,[3] 24.68 gauss, would be twice that of II if both had the same amount of hyperconjugation. Since the hydrogen splitting of II is 12.69 gauss, this is almost exactly correct. The ratio $a_H:a_N$ for II, 0.95, is close to that for other dimethylamino-containing radicals.[4]

When I is treated with a large excess of dichloromaleic anhydride in THF, acetonitrile, or DMF, nitrogen is

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[1] A Varian V-4502 spectrometer, variable-temperature apparatus, and electrolytic cell were used. Peroxylaminedisulfonate was used as standard.

[2] J. P. Colpa and E. de Boer, *Mol. Phys.*, **7**, 333 (1963); J. R. Bolton, A. Carrington, and A. D. McLachlan, *ibid.*, **5**, 31 (1962).

[3] R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **39**, 2147 (1963).

[4] W. M. Tolles, D. W. Moore, and W. E. Thorn, *J. Am. Chem. Soc.*, **88**, 3476 (1966).