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.

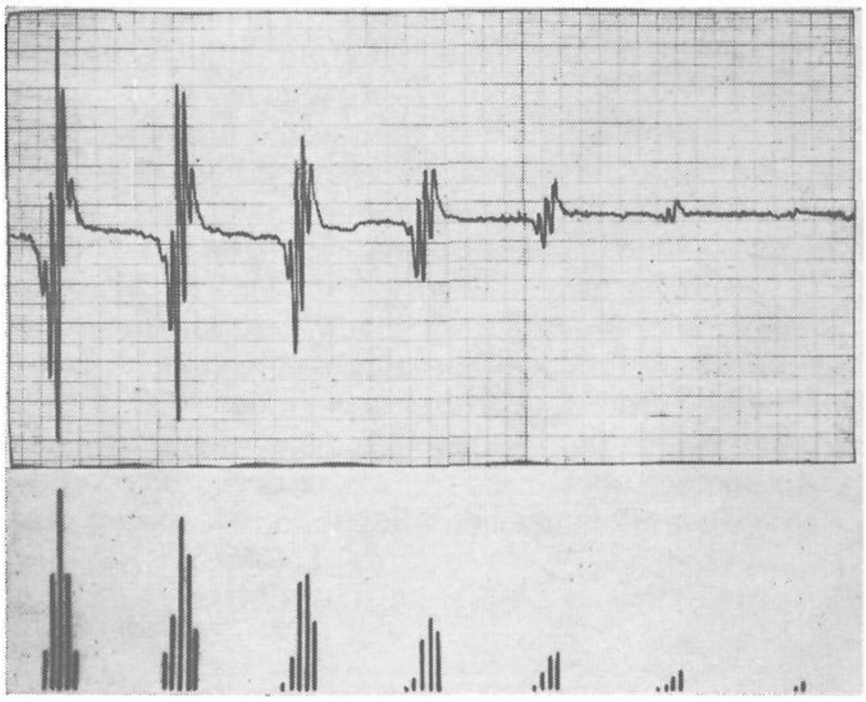

Figure 1. Radical A from tetramethylhydrazine and acetic anhydride (half of the spectrum is shown). The stick spectrum below gives predicted intensities assuming 2 equivalent nitrogens, 12 equivalent hydrogens.

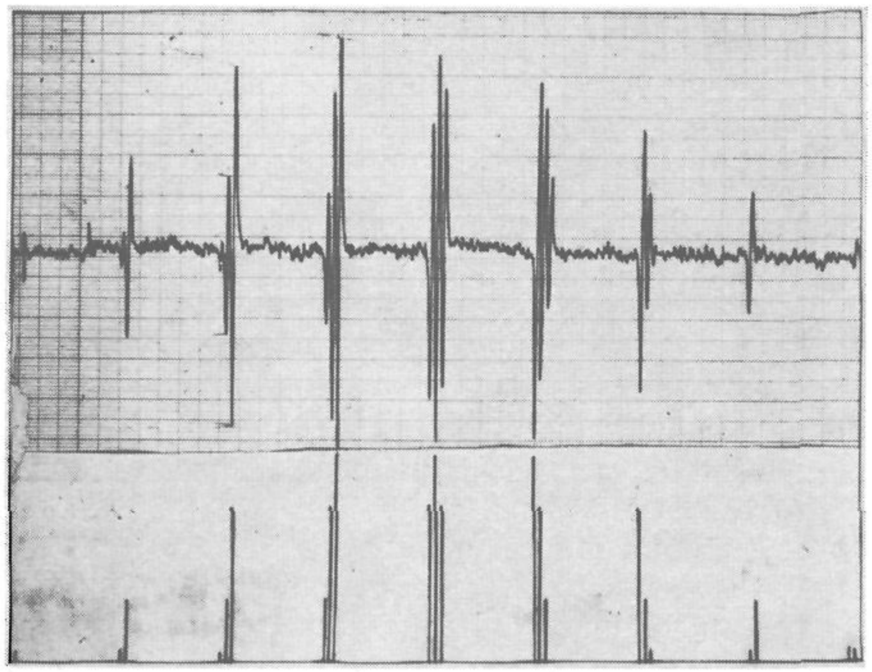

Figure 2. Radical B from glyoxal bis(dimethylhydrazone) and dichloromaleic anhydride in acetonitrile. The intensity decreases from left to right due to radical decomposition. The stick spectrum shows predicted line intensities for one nitrogen, six equivalent hydrogens.

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

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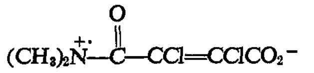
[1] A Varian V-4502 spectrometer, variable-temperature apparatus, and electrolytic cell were used. Peroxylaminedisulfonate was used as standard.

[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).

evolved vigorously at 0°, and a different esr spectrum (B) results (Figure 2). B gives splittings for one nitrogen (a_N = 9.95 gauss) and six equivalent hydrogens (a_H = 10.66 gauss). Spectrum B also is formed when glyoxal bisdimethylhydrazone or 1-phenyl-3,3-dimethyltriazene is treated with dichloromaleic anhydride, although acetic and maleic anhydrides do not result in observable radical formation. The spectrum is not caused by dimethyl nitroxide.[5] From the observed splitting constants it is clear that there is extensive delocalization of spin from the nitrogen, and the g factor of 2.0046 ± 0.0002 shows that some spin density is on atoms heavier than nitrogen, for the g factor is determined mainly by the spin–orbit coupling constants of the atoms bearing spin density.[6] We propose that the structure of B is III, which is consistent with extensive

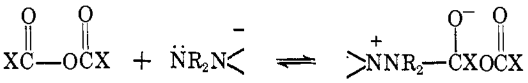


$$(CH_3)_2\overset{+\cdot}{N}-\overset{\overset{O}{\|}}{C}-CCl{=}CClCO_2^-$$

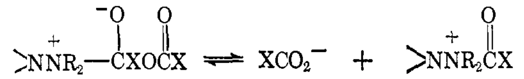
III

delocalization to a "transparent" group and the higher g factor of B than A, as well as being mechanistically reasonable. One might have predicted[7] electron transfer from DMF, leading to the DMF cation radical. If exchange were rapid on the esr time scale, the hyperfine structure would collapse. Hyperfine structure is observed in DMF (line widths of *ca.* 350 mg were observed), so electron transfer from DMF to B must be slow. Experiments are in progress to assign the structure of B more firmly; we do not feel that lack of rapid electron transfer from DMF excludes III, which we favor for the structure of B.

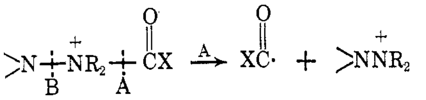
The following mechanism is proposed for the radical-forming reactions (R = CH_3).



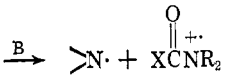
$$X\overset{\overset{O}{\|}}{C}-O\overset{\overset{O}{\|}}{C}X + \ddot{N}R_2\overset{-}{N}\!< \;\rightleftharpoons\; >\!\overset{+}{N}NR_2-\overset{\overset{O^-}{|}}{C}XO\overset{\overset{O}{\|}}{C}X \qquad (2)$$



$$>\!\overset{+}{N}NR_2-\overset{\overset{^-O}{|}}{C}XO\overset{\overset{O}{\|}}{C}X \;\rightleftharpoons\; XCO_2^- + >\!\overset{+}{N}NR_2\overset{\overset{O}{\|}}{C}X \qquad (3)$$

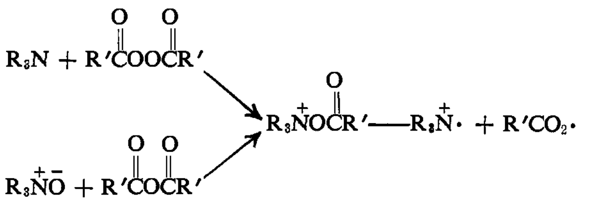


$$>\!N\underset{B}{\vdots}\overset{+}{N}R_2\underset{A}{\vdots}\overset{\overset{O}{\|}}{C}X \xrightarrow{A} X\overset{\overset{O}{\|}}{C}\cdot + >\!\overset{+}{N}NR_2 \qquad (4A)$$



$$\xrightarrow{B} >\!N\cdot + X\overset{\overset{O}{\|}}{C}\overset{+\cdot}{N}R_2 \qquad (4B)$$

Equations 2 and 3 are not novel. Equation 4, the homolysis step, has analogy in the amine-induced diacyl peroxide decomposition, and the reaction of amine oxides with anhydrides thought to proceed through a common intermediate.[8]



$$\left.\begin{array}{l} R_3N + R'\overset{\overset{O}{\|}}{C}OO\overset{\overset{O}{\|}}{C}R' \\ R_3\overset{+}{N}\overset{-}{O} + R'\overset{\overset{O}{\|}}{C}O\overset{\overset{O}{\|}}{C}R' \end{array}\right\} \rightarrow R_3\overset{+}{N}O\overset{\overset{O}{\|}}{C}R' \longrightarrow R_3\overset{+}{N}\cdot + R'CO_2\cdot \qquad (5)$$

In eq 4 a C–N+ (4A) or N–N+ (4B) homolysis replaces the O–N+ homolysis of eq 5. Whether bond A or B cleaves is determined by the stability of the radicals formed. The other radicals formed in steps 4A and 4B are not stable enough for convenient observation, but whereas no other absorptions besides those of II were observed with acetic anhydride and I, with phthalic anhydride other lines were obvious, though weak. Radical A (II) is observed at steady-state concentration in the anhydride reaction for, although the spectrum persists for several hours after mixing the components, the half-life of electrolytically generated II is about 2 min at room temperature. Maximum concentrations of A in the chemical generation are observed at about −20°. Below this temperature homolysis competes less effectively with radical decomposition. The behavior of spectrum B with temperature is similar. We have no evidence as yet on the relative timing of nitrogen loss and C–N homolysis in forming II from I.

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[5] For which splittings a_N = 16.1, a_H = 13.4 gauss (G. Chapelet-Letourneux, *et al.*, *Bull. Soc. Chim. France*, **11**, 3283 (1965)) and a_N = 15.2, a_H = 12.3 gauss (J. Q. Adams, S. W. Nicksic, and J. R. Thomas, *J. Chem. Phys.*, **45**, 654 (1966)) have been reported.

[6] B. M. Trost and S. F. Nelsen, *J. Am. Chem. Soc.*, **88**, 2876 (1966).

[7] We wish to thank a referee for this suggestion.

[8] C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p 590 ff.

A Search for Hydrogen–Deuterium Exchange on Clean Aluminum Surfaces

Sir:

Aluminum films deposited at pressures in the neighborhood of 10^{-5} torr have given ample evidence of surface variability.[1–3] This variation, characterized by time-dependent changes in reflectance, is probably due to adsorption of oxygen and formation of coherent oxide layers. Aluminum deposited under high-vacuum conditions[4] showed much more stability and has a higher initial reflectance in the infrared than do films deposited under low-vacuum conditions.

Trapnell's[5] work and the work of Eley and Wilkinson[6] indicate that aluminum *does not* chemisorb hydrogen, though some workers, Couper, Eley, Hulatt, and Rossington[7] and Holden and Rossington,[8] deduce some hydrogen chemisorption from data on ortho–para hydrogen conversion. Aluminum films deposited at 10^{-6} torr in an ambient air atmosphere should adsorb a monolayer of oxide in less than 10 sec, and the aluminum oxide thus formed may catalyze ortho–para conversion.[9]

A bakeable, ultrahigh vacuum system, routinely capable of pressures of the order 10^{-10} torr, was constructed

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[2] L. Holland, *Brit. J. Appl. Phys.*, **9**, 336 (1958).

[3] R. P. Madden, L. R. Canfield, and G. Hass, *J. Opt. Soc. Am.*, **53**, 620 (1963).

[4] H. E. Bennett, M. Silver, and E. J. Ashley, *ibid.*, **53**, 1089 (1963).

[5] B. M. W. Trapnell, *Proc. Roy. Soc.* (London), **A218**, 566 (1953).

[6] D. D. Eley and P. R. Wilkinson, *ibid.*, **A254**, 327 (1959).

[7] A. Couper, D. D. Eley, M. J. Hulatt, and D. R. Rossington, *Bull. Soc. Chim. Belges*, **67**, 343 (1958).

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[9] C. M. Cunningham and H. L. Johnston, *J. Am. Chem. Soc.*, **80**, 2382 (1958).