

tivity cell of conventional design. Resistance measurements were taken at 1–2-min. intervals with an Electro-Measurements, Inc., impedance bridge, Model 250-DA. A variable capacitor attached to the capacitance terminals of the bridge was used to maximize the sensitivity of the bridge. Infinity points were taken after at least 10 half-lives. Rate constants were calculated for each point using the usual integrated first-order rate equation with hydrochloric acid concentrations derived from the resistance measurements and previously determined calibrations. A typi-

cal run is shown in Table IV. Since this run contained 81 points, only every fifth point is reproduced.

The equilibrium constant was determined by adding a solution of hydrochloric acid in 80% aqueous acetone to weighed amounts of benzhydrol. The resistance of the acid solution was taken before and after the addition using equilibrium values in the 25.00° thermostat. The depression of the hydrochloric acid concentration was taken as the equilibrium concentration of benzhydryl chloride.

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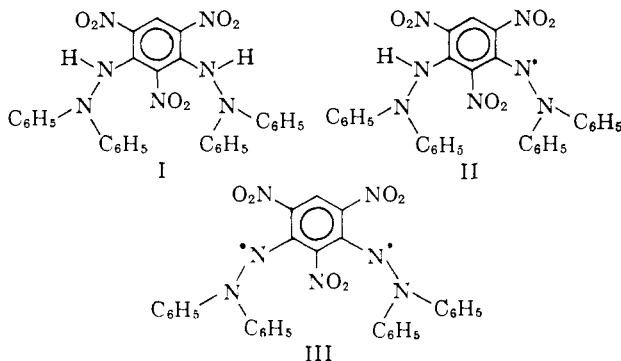
Dihydrazyl. Synthesis and Magnetic Properties¹

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Synthesis and characterization of the previously undescribed 1,3-bis(1,1-diphenylhydrazyl)-2,4,6-trinitrobenzene is described. Removal of the two hydrazinic hydrogen atoms by oxidation with PbO₂ proceeds in two steps, leading first to an unstable radical very similar to DPPH (e.p.r., color) and then yielding the (very unstable) "dihydrazyl" molecule. The latter was shown, by e.p.r. and n.m.r. measurements below -30°, to be a diamagnetic, spin-paired species.

Recently, a number of studies on the synthesis and magnetic properties of triplet molecules and biradicals have yielded detailed information about the electron correlation in these systems. Herein, an investigation of the potentially paramagnetic molecule 1,3-bis(1,1-diphenylhydrazyl)-2,4,6-trinitrobenzene (III, dihydrazyl) will be reported.



The previously undescribed substance 1,3-bis(1,1-diphenylhydrazyl)-2,4,6-trinitrobenzene (I), precursor to formation of the dihydrazyl, was prepared as follows.

Condensation of pyridinium styphnate with phosphine in acetone at 35° gave 1,3-dichloro-2,4,6-trinitrobenzene (IV) in 90% yield, m.p. 129°. 1,1-Diphenylhydrazine (4.4 moles), m.p. 35°, which had been purified immediately before the reaction, and IV (1 mole) in boiling ethanol in 2 hr. yielded the dark red, crystalline dihydrazine I (yield 90%). Recrystallization from ethyl acetate and subsequent drying *in vacuo* at 60° afforded the pure product; I undergoes color changes when heated and melts with decomposition at 164°. *Anal.* Calcd.: C, 62.4; H, 4.0; N, 17.0. Found: C, 62.5; H, 4.0; N, 16.6. Compound I contains two acidic hydrogens and its molecular weight could be determined by potentiometric titration in pyridine with a 0.1 M solution of triethyl-*n*-butylammonium hydroxide

(1) Based on work performed under the auspices of the U. S. Atomic Energy Commission.

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(3) H. B. Hass, H. Feuer, and A. A. Harban, *J. Am. Chem. Soc.*, **72**, 2282 (1950).

in benzene using a glass electrode as indicator and a calomel electrode as reference⁴; mol. wt. calcd. 578, found 567 and 592. Further evidence for the structure of I was obtained by means of high-resolution proton magnetic resonance studies in methylene chloride at 60 Mc./sec. employing a Varian A-60 instrument. The weak peaks⁵ at 314 and 240 c./sec. are attributed to the NH and picryl proton, respectively, and the strong doublet at 113 and 108 c./sec. to the phenyl protons. There is ample analogy for these assignments.⁶

Oxidation of I in methylene chloride or 2-methyltetrahydrofuran solution was effected by PbO₂ (well washed with acetone, then with the solvent to be used) freshly prepared by hydrolysis of Pb(CH₃COO)₄ in glacial acetic acid in the presence of CHCl₃.⁷ Since the oxidation products II and III were found to be unstable at room temperature, all preparations and experiments with these were carried out at temperatures below -30°. The oxidation was followed by recording the e.p.r. spectra of the radical produced. The clearly resolved five-line spectrum of a deeply violet (mono) radical II appeared immediately; its intensity increased as the oxidation proceeded and then decreased markedly but could not be made to vanish entirely without irreversible decomposition. The *g*-value, nitrogen hyperfine-coupling constants *A* and *A'*, and line-widths Δ measured in degassed 2-methyltetrahydrofuran solution at -50° were found to be very similar for the radical II (*g* = 2.0035 ± 0.0003, *A* = 8.5 ± 0.3 oe. (oersted), *A'* = 8.9 ± 0.3 oe., Δ = 5.5 ± 0.1 oe.) and 1,1-diphenyl-2-picrylhydrazyl (DPPH).⁸

When the PbO₂ was removed by centrifugation from the oxidized solution and an excess of dihydrazine (I) was added, the intensity of the e.p.r. signal from II increased to more than twice the maximum intensity observed during the course of the oxidation, whereas the spectral pattern remained unchanged.

(4) J. A. Weil and G. A. Janusonis, *J. Org. Chem.*, **27**, 1248 (1962).

(5) Spectrum taken at -60°. Peak positions are relative to the CH₂Cl₂ peak. Conversion to the τ scale can be made using τ (CH₂Cl₂) = 4.67.

(6) J. Heidberg, J. A. Weil, G. A. Janusonis, and J. K. Anderson, *J. Chem. Phys.*, **41**, 1033 (1964).

(7) W. K. Wilmarth and N. Schwartz, *J. Am. Chem. Soc.*, **77**, 4543 (1955).

(8) M. M. Chen, K. V. Sane, R. I. Walter, and J. A. Weil, *J. Phys. Chem.*, **65**, 713 (1961).

Although the hydrazyl hydrogen atom is known to be labile, presence of excess diphenylpicrylhydrazine in DPPH solutions does not affect the e.p.r. spectrum, indicating that the rate of the proton transfer from hydrazine to hydrazyl is small compared to the hyperfine splitting. The great similarity of the e.p.r. spectra (e.g., line-widths) of DPPH and radical II suggests that, in the latter case, the effects of intramolecular hydrogen transfer are also not appreciable.

Even after prolonged oxidation no e.p.r. signal attributable to biradical III was observed and there was no absorption in rigid 2-methyltetrahydrofuran solution ($2 \times 10^{-3} M$) at -170° other than one at $g = 2$, which was assigned to the monoradical II. However, it was possible to show that the oxidation had effected the removal of the hydrogen atom of the second hydrazyl group to yield a mesomeric or tautomeric form of III. When a standardized solution of I was fully oxidized and treated with an excess of 1,1-diphenyl-2-picrylhydrazine after removal of the PbO_2 by centrifugation, the small five-line e.p.r. signal at $g = 2$ immediately increased to an intensity corresponding to 1.5 to 2 moles of DPPH per mole of I, as revealed by comparison of its e.p.r. spectrum with that of a standardized DPPH solution in the same solvent (CH_2Cl_2 , $CHCl_3$, 2-methyltetrahydrofuran). Moreover, it could be confirmed that the nuclear framework of dihydrazyl was not fragmented during oxidation, since its reductive titration with hydroquinone caused first an increase by a factor 2-3 of the intensity of the e.p.r. signal of the always present monoradical, then a decrease, and finally the disappearance of the spectrum, demonstrating that the first reduction product of III is the monoradical II, which is further reduced to the diamagnetic dihydrazine I.

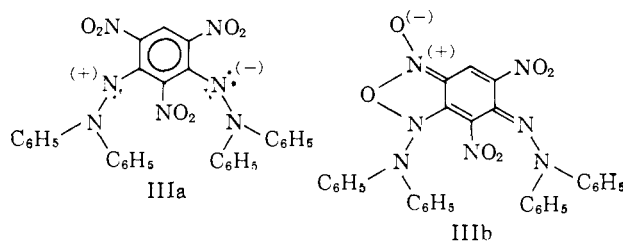
In accord with the nonobservability of an e.p.r. spectrum attributable to III, the ground state of III proved to be diamagnetic. Since the application of conventional methods to measure the static susceptibility χ of III in diluted solution [$c(\text{saturation}) \leq 10^{-2} M$] in the presence of the paramagnetic monoradical II appeared to be difficult, proton magnetic resonance was employed for the determination of χ .⁹ A capillary, o.d. ~ 2.5 mm., containing a solution of 1,1-diphenyl-2-picrylhydrazine in CH_2Cl_2 was placed into the standard n.m.r. sample tube which was filled with a methylene chloride solution of about the same concentration of dihydrazyl, accompanied as usual by II.

(9) D. F. Evans, *J. Chem. Soc.*, 1959, 2003.

Two resonance lines were observed from the protons of CH_2Cl_2 in the two solutions because of the difference in their volume susceptibilities, the broader line from the paramagnetic solution lying at higher field. The frequency separation $\Delta\nu$ of the two lines is given by $\Delta\nu = (2\pi/3)\nu\Delta\chi$. The observed $\Delta\nu$ corresponded quantitatively ($\pm 20\%$) to the concentration of II, as measured by e.p.r. Addition of 1,1-diphenyl-2-picrylhydrazine to the dihydrazyl solution caused an upfield shift of the broad line and an increase of $\Delta\nu$ by the same factor (2 to 4 corresponding to 1-4 c./sec. at $\nu = 60$ Mc./sec.) as for the increase of the intensity of the e.p.r. signal under the same conditions. Also the magnitude, 2.4×10^{-5} , of the mass susceptibility of DPPH derived from these measurements was in agreement with literature values.⁸ If dihydrazyl were a diradical with two independent unpaired spins, there should have been no change in $\Delta\nu$ on addition of the hydrazine; if it were a ground-state triplet molecule, $\Delta\nu$ should have become smaller.

Association of dihydrazyl molecules cannot be ruled out but appears improbable for structure III, since DPPH does not dimerize. The only known reaction of DPPH with radicals is their addition to the *para* carbon atom of the phenyl ring with formation of the corresponding hydrazine.¹⁰ A single linking in this manner of two dihydrazyl molecules followed by re-oxidation would lead to a paramagnetic species with two or four unpaired electrons, contrary to observation.

The two zwitterion structures of type IIIa, as well as



quinoid ionic structures invoking charge withdrawal by the nitro groups (similar to those used to describe the salts of 1,1-diphenyl-2-picrylhydrazine⁴), may be important in describing the singlet ground state of monomeric dihydrazyl. The latter may also be stabilized by the formation of a dihydrofurazan ring,¹¹ as in structure IIIb.

(10) S. Goldschmidt and K. Renn, *Ber.*, **55**, 628 (1922); J. A. Weil, K. V. Sane, and J. M. Kinkade, Jr., *J. Phys. Chem.*, **65**, 710 (1961).

(11) P. Karrer, "Organic Chemistry," 1st Ed., Elsevier Press, New York, N. Y., 1938, p. 731.