and filtered with suction through two thicknesses of filter paper. The filtrate was then extracted six times with 200-mL portions of chloroform. The chloroform layers were combined and washed with 5 M aqueous sodium hydroxide solution (2 × 25 mL), and concentrated to ca. 500 mL by distillation; this also effected azeotropic drying of the solution. The chloroform solution was filtered through a Dierite cone (to catch the fine particles). Removal of the solvent on the rotary evaporator gave a golden yellow oil, which slowly solidified to a pale yellow mass. The yield of crude dione **1** was 56.1 g (96.1% based on the crude keto ester; 82.9% from tetraester **4**), yellowish granules, mp 43–46 °C. Again, further purification was not necessary. If desired, purer material could be obtained by sublimation [35–40 °C (0.01 mm)] onto a cold finger kept at 0 °C. Recovery was about 97%. The sublimed product was in the form of blocky crystals, mp 45.1–46.3 ° (lit.[4b] 46–46.5 °C) with the expected spectral properties: IR (Nujol) 5.73 μm; NMR (δ, CCl_4) 2.90 (2 H, br s), 2.20 (8 H, br s).

2,2,6,6-Bis(ethylenedioxy)bicyclo[3.3.0]octane (7). Ketalization of Bicyclooctanedione 1. The crude dione (209 g, 1.5 mol) was added to a mixture of ethylene glycol (200 mL, ca. 3.95 mol, 32% excess), *p*-toluenesulfonic acid hydrate (3.8 g, 0.02 mol), and benzene (1.5 L). This mixture was refluxed with separation of water (Dean–Stark trap, 64 mL, 118%) and magnetic stirring for 44 h. Nearly all of the water distilled over during the first 12 h. The brownish solution was cooled and washed as follows: 1 × 100 × 200 mL of saturated aqueous sodium bicarbonate, 2 × 200 mL of water, and 2 × 100 mL of saturated aqueous sodium chloride solution. The combined aqueous washings were extracted four times with 200-mL portions of ether, which were combined and washed once with saturated sodium chloride solution. This ether extract, combined with the original benzene layer, was filtered through a Drierite cone. Removal of the solvent on the rotary evaporator gave a brownish, oily liquid, which was distilled in vacuum. The fraction, bp 93–95 °C (0.15 mm), homogeneous by GC (column A, 170 °C; column B, 190 °C), was collected to give 327 g (96.5%) of a colorless, oily liquid. Repeated fractional freezing of this liquid in an ice–acetone bath gave an analytical sample. The spectra of this purified material, which were superimposable on those obtained from the distillate, were as follows: IR (neat) 3.41, 3.49, 6.82, 7.47, 8.24, 8.6–9.15, 9.64, 10.53 μm; NMR (δ, CCl_4) 3.87 (8 H, s), 2.37 (2 H, br m), 1.62 (8 H, br m).

Anal. Calcd for $C_{12}H_{18}O_4$: C, 63.70; H, 8.02. Found: C, 63.67; H, 8.02.

Other preparations, on 0.2–0.6-mol scales, gave yields of 96.1–96.4%. In view of the ca. 97% purity of the crude dione **1**, the yield must be close to quantitative. Other boiling points observed were 100 °C (0.2 mm), 88 °C (0.05 mm), and 84 °C (0.015 mm).

2,2,6,6-Bis(ethylenedioxy)-3,7-dibromobicyclo[3.3.0]octane (8). Bromination of Ketal 7. Pyridinium tribromide was prepared according to Fieser and Fieser,[7] starting with approximately 1 lb of bromine and scaling the other reactants accordingly. During the recrystallization of the product from acetic acid, the mixture was stirred frequently to keep the crystals small. We and others[8] have found that finely divided tribromide gives better results than coarse material. Yields of the purified tribromide were in the range 72–78%.

The diketal **7** (45.2 g, 0.2 mol) was dissolved in dry tetrahydrofuran (400 mL, distilled from CaH_2) in a 1-L three-necked flask equipped with a mechanical stirrer, a drying tube, and a stopper. This solution was cooled, with stirring, to ca. −70 °C in a dry ice–acetone bath, and pyridinium tribromide (140 g, 0.438 mol) was added in one portion. The mixture, which rapidly decolorized, was stirred at ca. −70 °C for 1 h, then allowed to warm to room temperature. The pale yellow suspension was then poured slowly into 2.5–3 L of vigorously stirred cold water, whereupon the product precipitated. After 5 min more stirring, the solid was collected by filtration, washed repeatedly with water, and sucked fairly dry. This yellowish product was then covered with methanol (ca. 200 mL), the lumps were broken up, and the stirred mixture was gently boiled for a few minutes. It was then cooled to −10 °C for several hours, and the white product was collected, washed once with cold methanol, and air dried to give 69 g (90%) of white crystals (needles and granules), mp 152–156 °C (sinters 128 °C, further softens 142–145 °C, with gradual darkening from 128 °C on). Other runs on a similar scale (0.2–0.25 mol) gave yields in the range 88–91%.

2,2,6,6-Bis(ethylenedioxy)bicyclo[3.3.0]octa-3,7-diene (9). Dehydrobromination of Bromoketal 8. The methanol-washed mixture of isomeric bromo ketals (87 g, 0.227 mol) prepared from **7** was added in one portion to a stirred slurry of sodium methoxide (73.5 g, 200% excess) in dimethyl sulfoxide (400 mL) in a 1 L, three-necked flask equipped with a mechanical stirrer, a thermometer, and a gas bubbler. Occasional cooling (ice bath) was used to keep the reaction temperature below 60 °C. After the exothermic reaction had ceased (ca. 30 min) the mixture was heated to 70 °C for 2 h. It was then cooled to room temperature and poured into 2.5 L of stirred water and ice and the flask was rinsed with an additional 100 mL of water. Solid sodium chloride was added to nearly saturate the solution, and the crude solid product was collected by filtration. The filtrate was then extracted eight times with 500-mL portions of ether, each of which was roughly dried by washing with 50 mL of saturated sodium chloride, and evaporated as it was obtained. The residue from these extracts was combined with the original solid product, dissolved in cyclohexane (ca. 1200 mL), and refluxed with water separation (Dean–Stark trap). When water ceased to distill over, the hot cyclohexane solution was filtered, concentrated by distillation to a volume of about 500 mL, and allowed to cool. The product, 44.8 g (89%) of fine colorless needles, mp 101–102 °C, was then collected. Concentration of the mother liquor afforded an additional crop (1.5 g, 3%) of slightly yellowish needles, mp 97–100 °C. Other runs on the same scale gave total yields of 89–93%.

Bicyclo[3.3.0]octa-3,7-diene-2,6-dione (2). Deketalization of Ketal 9. The diene diketal **9** (44.5 g, 0.2 mol) and sulfosalicylic acid (0.3 g) were dissolved in acetone (500 mL) with gentle warming, and the solution was allowed to stand at room temperature for several hours. The acetone and its ethylene ketal were removed on the rotary evaporator. The residue was taken up in acetone, allowed to stand for 30 min, and the volatile material again removed. After a third acetone treatment, the solid residue was sublimed at 70 °C (0.01 mm) onto a carbon tetrachloride–slush cooled condenser, yielding 25.2 g (94%) of white, blocky crystals, mp 76.5–78.5 °C. Recrystallization of this material, although not necessary, could be achieved using cyclohexane as solvent. This gave colorless or white needles, mp 78–79 °C (lit.[3] 78–79.5 °C), in nearly quantitative recovery (three crops): IR (Nujol) 5.88 (strong and broad), 6.35 μm; NMR (δ, CCl_4) 7.66 (2 H, d of m, J = 5.6 Hz), 6.08 (2 H, d of d with additional fine structure, J = 5.6 Hz, J' = 1.4 Hz), 3.67 (2 H, m).

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Registry No.—**1**, 17572-87-1; **2**, 4945-71-5; **3**, 1119-40-0; *meso*-**4**, 63569-68-6; *dl*-**4**, 63569-69-7; **5**, 63569-70-0; **7**, 63569-71-1; **8**, 63569-72-2; **9**, 63569-73-3; glutaric anhydride, 108-55-4.

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Persistent Free Radicals from the Reaction of Sulfenamides with Tetracyanoethylene

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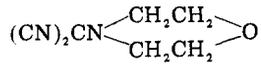
It was reported earlier that tetracyanoethylene reacts with sulfenamides but no identification of the products of the reaction was given.[1] This note reports the observation of persistent radicals in these reaction mixtures. The radicals were observed when degassed benzene, dichloromethane, or tetrahydrofuran solutions of the sulfenamides[2] were mixed with

Table I. Hyperfine Coupling Constants for Aminodicyanomethyl Radicals in Benzene

Registry no.	Radical	a^N	$a^N_{C=N}$	a^H_β	Comments
62681-10-1	$(CN)_2CN(CH_3)_2$	9.55	2.05	8.60	
63533-57-3	$(CN)_2CN(C_2H_5)_2$	9.84	2.12	5.36	a^H_γ = 0.21 g
63533-58-4	$(CN)_2CN(CH_3)Ph$	7.70	2.15	7.88	$a_{o,p}$ = 1.28; a_m = 0.69[4]
63533-59-5		10.42	2.17	17.66	Coupling to only 2β hydrogen atoms
63533-60-8	$(CN)_2CN(CH_2)_4$	9.88	2.10	13.87	Coupling to four equivalent β hydrogen atoms; g value 2.003
63533-61-9	$(CN)_2CN(CH_2)_5$	10.72	2.15	13.24, 0.05	Coupling to two sets of two equivalent β hydrogen atoms

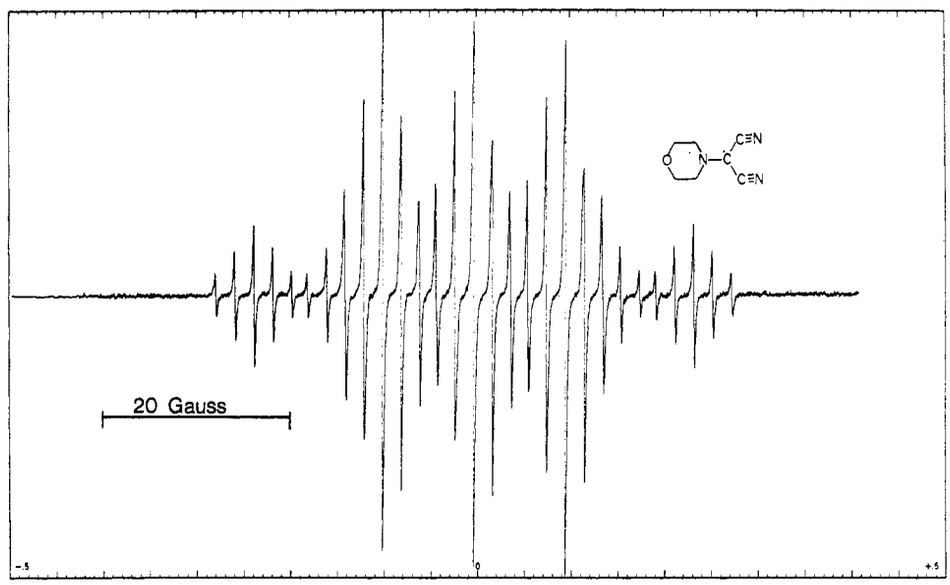
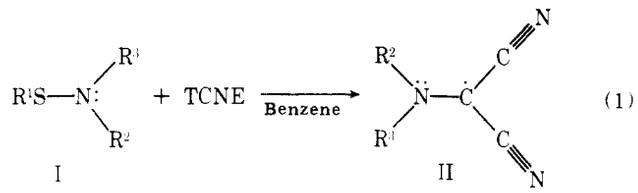


Figure 1. EPR spectrum of morpholinodicyanomethyl radical in benzene solution at room temperature. The width of the central line is 0.4 G.

saturated solutions of tetracyanoethylene in the same solvent. Immediately after mixing the dichloromethane solution a blue color was observed which rapidly disappeared, and an EPR spectrum of the resulting pale-yellow solution was obtained.[3] The reaction occurring is presumed to be that shown in reaction 1.



I II (1)

a, R^1 = Ph; R^2 = R^3 = CH_3
b, R^1 = Ph; R^2 = R^3 = C_2H_5
c, R^1 = C_2H_5; R^2 = CH_3; R^3 = Ph
d, R^1 = i-C_3H_7; R^2 = CH_3; R^3 = Ph
e, R^1 = t-C_4H_9; R^2 = CH_3; R^3 = Ph
f, R^1 = Ph; R^2, R^3 = $(CH_2CH_2)_2O$
g, R^1 = n-Bu; R^2, R^3 = $(CH_2CH_2)_2O$
h, R^1 = n-Pr; R^2, R^3 = $(CH_2)_4$
i, R^1 = Ph; R^2, R^3 = $(CH_2)_5$
j, R^1 = p-nitrophenyl; R^2 = R^3 = CH_3
k, R^1 = 4-chloro-2-nitrophenyl; R^2 = R^3 = CH_3

The spectrum observed is independent of the group initially attached to the sulfur atom in the sulfenamide; however, that group apparently can control whether an observable radical is formed. This can be seen in the series of compounds where R^2 = CH_3–, R^3 = C_6H_5–, and R^1 is either ethyl, isopropyl, or *tert*-butyl. The same radical was observed from the first two compounds; however, when R^1 was t-C_4H_9 no radical was detected. Similarly, the same spectrum was obtained from both morpholine derivatives, R^1 = phenyl and n-butyl. In the *N,N*-dimethylamino series, radicals were not observed when the *S*-aryl group contained a nitro group. Apparently, the reaction does not yield observable radicals when either the sulfur substituent is sterically bulky (t-butyl) or contains electron-withdrawing groups (p-nitrophenyl or 2-nitro-4-chlorophenyl).

All of the spectra observed were characterized by one large hyperfine coupling constant from a single nitrogen atom of between 7.70 and 10.72 G, a smaller hyperfine coupling constant from two equivalent nitrogen atoms of 2.10 to 2.54 G, and proton coupling constants from the protons on carbon atoms attached to the aminonitrogen atom. The observed coupling constants and proposed structures are shown in Table I. The *N,N*-dimethylaminodicyanomethyl radical has recently been reported to have been observed in solutions of dimethylaminomalononitrile.[5] The reported spectrum agrees well with the spectrum obtained from IIa and TCNE in benzene.

The radicals derived from the morpholine and piperidine derivatives are apparently conformationally frozen on the EPR time scale, since there is a large coupling constant to only two of the possible four β protons. This would be expected if the six-membered heterocyclic ring existed in a chair conformation with the dicyanomethyl group occupying an

equatorial position at nitrogen. This would allow one proton on each β carbon atom to be in the axial position for which a large coupling constant would be expected, and the remaining β protons would be equatorial and would be expected to show a small coupling constant.[6] The spectrum of the morpholine derivative is shown in Figure 1 and shows a coupling to only two of the four possible β protons. In the pyrrolidine derivative, conformational interconversion at room temperature is apparently rapid enough to average the β-proton coupling constants, and as a result four equivalent β protons are seen. Evidence for a preferred tetrahedral geometry at nitrogen is found in the results of INDO calculations.[7] These calculations predict an amino nitrogen coupling constant of 12.01 G for the tetrahedral conformation of *N,N*-dimethylaminodicyanomethyl radical as compared with a 4.10-G coupling constant for the planar conformation. The cyano nitrogen coupling constants are predicted to be nearly the same for the tetrahedral model, 2.42 G, as for the planar model, 2.59 G. The calculation did not predict the proton coupling constants well (2.40 G predicted vs. 8.60 G observed). The tetrahedral model is calculated to be lower in energy than the planar conformation. MINDO/3 calculation allowing full optimization of the geometry predicts that the planar conformation should be more stable; however, the MINDO/3 method is known to predict incorrectly the geometry of tertiary amines.[7c]

The amino nitrogen hyperfine coupling constants are lower than those observed for other nitrogen centered radicals, CH_3N–O–t-Bu (a^N = 14.47 g),[8] $(CH_3)_2N\cdot$ (a^N = 14.78 g),[9] and $(CH_3)_2NO$ (a^N = 16.1 g).[10] This may result from the unpaired electron being delocalized over the dicyanomethyl system. The cyano nitrogen coupling constant observed here is slightly larger than that in tetracyanoethylene anion, 1.61 G,[11] suggesting that slightly more than half the electron density is in the dicyanomethyl portion of the molecule, and as a result the spin density on the amino nitrogen is smaller than in the nitrogen-centered radicals.

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Supplementary Material Available: The EPR spectra of the radicals for which coupling constants are given in Table I, except for the morpholine derivative (5 pages). Ordering information is given on any current masthead page.

Registry No.—Ia, 24380-79-8; Ib, 6667-19-2; Ic, 63533-62-0; Id, 63533-63-1; If, 4837-31-4; Ig, 19117-36-3; Ih, 63533-64-2; Ii, 29959-86-2; TCNE, 670-54-2.

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(3) EPR spectra were obtained on a Varian E-4 spectrometer and were still observable 1 day after formation. The hyperfine coupling constants are reported relative to the constants for anthracene cation which was taken as having hyperfine complex constants of 6.53, 3.06, and 1.38 G; J. R. Bolton and G. K. Fraenkel, *J. Chem. Phys.*, **40**, 3307 (1964).
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Acid-Catalyzed Deuterium Exchange of the Indole Ring Protons in Tryptamine Derivatives

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Indole ring hydrogens, like those of other aromatic rings, undergo acid- and base-catalyzed proton exchanges. The rate of the acid-catalyzed proton exchange depends on basicity or nucleophilicity, which is reflected in the ground-state electronic structure of the molecule,[2] as well as on the stability of the protonated transition state,[3] a conjugated acid in terms of Brønsted.

Both acid- and base-catalyzed deuterium exchanges of hydroxyindole derivates have been observed,[4] but the results are qualitative and limited to the hydroxy derivatives. Furthermore, slow deuterium exchanges were not observed. In order to quantitatively assess the electronic structures of tryptamine derivatives and their ring-protonated conjugate acids, we have investigated acid-catalyzed deuterium ex-

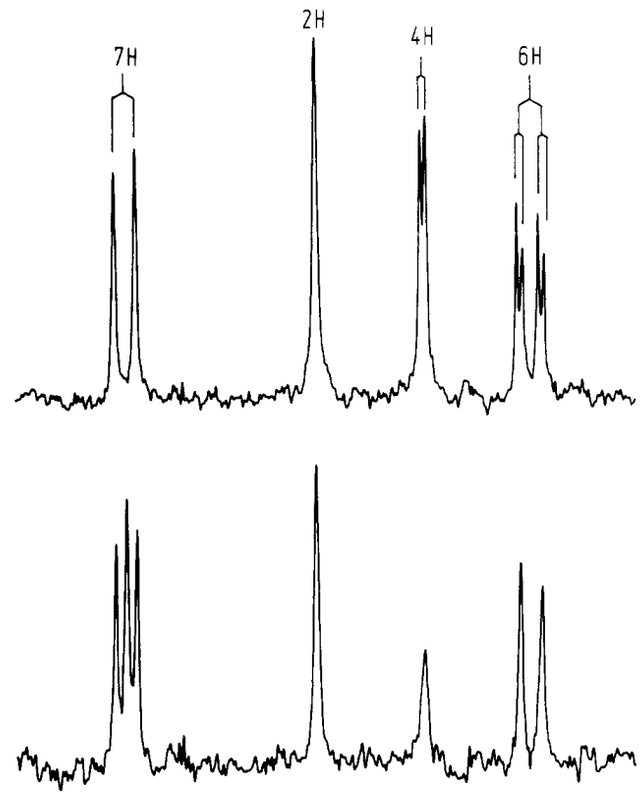

Figure 1. NMR spectra of the aromatic protons of 5-hydroxytryptamine in DCl solution. The upper spectrum is for t_0, and the lower one for t_x (see Table II). Total scanning is 1640–1563 Hz.