physical characterization on isolated, often single crystal forms. Only in this way will the necessary compositional, X-ray, spectroscopic, and magnetic susceptibility data be forthcoming. This isolation may not be easy inasmuch as NO complexes are notoriously unstable, and the paramagnetic species reported here may only exist in solution where the equilibrium of eq. 1 can be forced to the right.

The e.s.r. characteristics of the complexes reported in the present study point strongly to the presence of d^7 iron. E.s.r. characteristics with respect to g value and relaxation times as judged by line widths are very similar to those reported for $[Fe(CN)_5(NO)]^{-3}$ [16-18] and $Fe(NO)(S_2CNMe_2)_2$.[12] In fact, the similarities in N^{14} hyperfine splitting in the $Fe(NO)(S_2CNMe_2)_2$ complex and the Fe–NO complexes with maleonitriledithiol (VIII), benzene-1,2-dithiol (IX), and 1,1-dicyanoethylene-2,2-dithiol (X) indicate strongly that the geometrical

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(17) J. B. Raynor, *Nature*, 201, 1216 (1964).
(18) D. A. C. McNeil, J. B. Raynor, and M. C. R. Symons, *Proc. Chem. Soc.*, 364 (1964).

and electronic structures of these four complexes must be very similar.

Structures of the complexes $Fe(NO)_2(A)_2$ are open to somewhat more question, and their only structural analogs would appear to be the dissociated form of the red Roussin's salt. It seems clear from the e.s.r. characteristics that iron in these complexes possesses the d^7 configuration. In the frozen state, e.s.r. signal intensities of the Fe–NO–phosphate complex exhibit Curie law behavior between -20 and $-155°$. It cannot, however, be unequivocally demonstrated from the e.s.r. results reported here whether the iron is tetrahedrally coordinated or, perhaps, pentahedrally or even octahedrally coordinated. Our results only demonstrate that the single unpaired electron of each of the complexes is in the isotropic hyperfine splitting environment of one iron atom, two nitric oxide molecules, and two anionic ligands such as phosphate, arsenate, cysteine, or β-mercaptoethanol. One or two water molecules could be involved as additional ligands about iron. However, the analogy with the red Roussin's salts is considered to be compelling, if not conclusive.

The Electron Spin Resonance Spectra of 2,1,3-Benzoxadiazole, -Benzothiadiazole, and -Benzoselenadiazole Radical Anions. Electron Withdrawal by Group VI Elements[1]

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Radical anions of the title compounds have been prepared by electron transfer from carbanions to the parent aromatics. On the basis of hydrogen hyperfine splitting constants it is concluded that sulfur and selenium atoms in these heterocyclics accept the unpaired electron more readily than oxygen. LCAO-MO calculations have been performed for the benzoxadiazole and benzothiadiazole systems. Good agreement between experimental and calculated spin densities was obtained with a simple Hückel treatment. A p-orbital model for the sulfur atom gave results as good as those obtained using a d-orbital model.

The electron-withdrawing ability of group VI elements is a subject of considerable interest. From electronegativity considerations, oxygen should be electron withdrawing relative to carbon, whereas sulfur and selenium should have a slight electron-supplying ability.[3] In conjugated systems the inductive effect is

supplemented by resonance interactions involving the unshared p-electrons of the heteroatom

Thus, the *m*-methoxy group is electron withdrawing but the *p*-methoxy group is electron supplying on the basis of the ionization constants of substituted benzoic acids.[4]

The electronic situation is more complicated in the case of sulfur and selenium atoms because of the presence of vacant 3d- or 4d-orbitals. These orbitals may interact with a conjugated system to enhance the electron-attracting power of the atom. This can account for the fact that the *m*-thiomethyl group is strongly electron attracting.[4]

Electron spin resonance offers a direct method of determining the effect of an atom on the odd-electron distribution, *i.e.*, that of the highest occupied molecular orbital. The hyperfine splitting of hydrogen atoms in a benzenoid system is given by $a_{CH}^H = Q_{CH}^H \rho_C$ where a^H is the hyperfine splitting constant (h.f.s.c.), ρ_C is the spin density on the carbon bound to the hydrogen
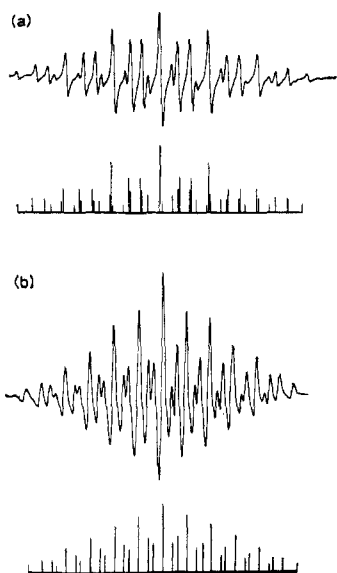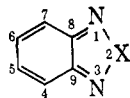
Figure 1. First derivative e.s.r. spectra of radical anions of (a) 2,1,3-benzoxadiazole and (b) 2,1,3-benzothiadiazole in dimethyl sulfoxide (80%)-t-butyl alcohol (20%) at 30°. Synthetic absorption spectra composed from h.f.s.c. given in text.

Figure 2. First derivative e.s.r. spectrum of 2,1,3-benzoselenadiazole radical anion in dimethyl sulfoxide (80%)-t-butyl alcohol (20%) solution at 30°.

atom, and Q is a constant that can be estimated empirically.[5]

We chose 2,1,3-benzoxadiazole (benzofurazan), 2,1,3-benzothiadiazole, and 2,1,3-benzoselenadiazole for this study because the radical anions are readily formed and

X = O, S, Se

are stable at room temperature, because there are no obvious steric complications in planar molecules wherein the heteroatom is part of a ring system, and because the benzene ring angles in these compounds are known to vary only slightly from pure sp² hybridization (120°).[6] The latter is an important consideration since Q_{CH}^H depends on the hybridization angle.[7,8]

Experimental

Electron Spin Resonance Spectra. E.s.r. spectra were obtained using either a Varian V-4500 spectrometer equipped with a 6-in. magnet and 100-kc./sec. field modulation or a Varian V-4502 spectrometer with a 9-in. magnet and 100-kc./sec. field modulation. Sweep rates were calibrated from the spectrum of p-benzosemiquinone.[9] The radical anions were formed at 25–30° by electron transfer from the anions of propiophenone or 9,10-dihydroanthracene in dimethyl sulfoxide (80%)-t-butyl alcohol (20%) solution containing an excess of potassium t-butoxide.[10] The concentration of the electron acceptor varied from 0.005 to 0.01 M with the concentration of the donor five times that of the acceptor and of base ten times that of the ac-

ceptor. The deoxygenation apparatus and mixing chamber has been described elsewhere.[10]

The spectra for the radical anions of 2,1,3-benzoxadiazole, 2,1,3-benzothiadiazole, and 2,1,3-benzoselenadiazole are given in Figures 1a, 1b, and 2, respectively. The 29 peaks of the e.s.r. spectrum of 2,1,3-benzoxadiazole (Figure 1a) yield the following h.f.s.c.: $a_{1,3}^N = 5.24$, $a_{4,7}^H = 3.33$, and $a_{5,6}^H = 2.02$ gauss. The hydrogen splitting constants were assigned on the basis of LCAO–MO calculations to be mentioned later. 2,1,3-Benzothiadiazole reacted with the anions derived from dihydroanthracene in the absence of oxygen to give a purple solution which slowly changed to wine-red. The 33-line spectrum (Figure 1b) could be analyzed on the basis of the following h.f.s.c.: $a_{1,3}^N = 5.26$, $a_{4,7}^H = 2.63$, and $a_{5,6}^H = 1.53$ gauss. Reduction of 2,1,3-benzoselenadiazole with the propiophenone anion gave a yellow-brown solution which slowly became red-brown. The 17-line spectrum obtained (Figure 2) is consistent with $a_{1,3}^N = 5.97$, and $a_{4,5,6,7}^H = 5.97/3$ gauss. The line widths are so broad that any difference between H-4(7) and H-5(6) could not be observed. Theoretical peak height intensities with $a^H = \frac{1}{3}a^N$ are 1:4:6:6:9:12:11:14:18:14..... The experimental spectrum yielded the average ratios of 1.2:3.0:4.5:5.-1:8.0:10.8:10.3:14.1:18..... The agreement is reasonable, but better resolution, possibly at lower temperatures, might bring about further splitting.

Reagents. 2,1,3-Benzoxadiazole was synthesized, m.p. 52–54°, lit.[11] m.p. 55°. 2,1,3-Benzothiadazole and 2,1,3-benzoselenadiazole (Aldrich Chemical Co.) were used without purification. Dimethyl sulfoxide (Crown Zellerbach Corp.) was distilled under a reduced pressure from calcium hydride and stored over molecular sieves. Commercial pure grade t-butyl alcohol was dried over anhydrous sodium sulfate. The potassium t-butoxide was commercial material (Alfa Inorganics, Inc., and Mine Safety Appliance Corp.).

Discussion

A quantitative comparison of the effect of the heteroatom on the odd electron density is immediately available from the values of the hydrogen h.f.s.c. or from the empirical spin densities calculated from them. In Table I, spin densities calculated using a value of $Q_{CH}^H = 24.2$ gauss are given.[12] The Hückel molecular orbital calculations on 2,1,3-benzoxadiazole were made in the ordinary manner using the parameters for the

(5) H. M. McConnell, *J. Chem. Phys.*, **24**, 632 (1956).
(6) V. Lazzati, *Acta Cryst.*, **4**, 193 (1951).
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(8) I. Bernal, P. H. Rieger, and G. K. Fraenkel, *ibid.*, **37**, 1489 (1962).
(9) E. W. Stone and A. H. Maki, *ibid.*, **36**, 1944 (1962).
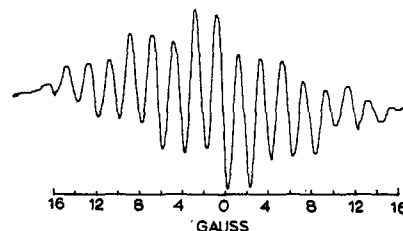(10) G. A. Russell, E. G. Janzen, and E. T. Strom, *J. Am. Chem. Soc.*, **86**, 1807 (1964).

(11) D. L. Hammick, W. A. M. Edwardes, and E. R. Steiner, *J. Chem. Soc.*, 3308 (1931).
(12) A. D. McLachlan, *Mol. Phys.*, **3**, 233 (1960).

oxygen and nitrogen atoms suggested by Streitwieser,[13] except for β_{CN} which was varied to give the best fit with the experimental data.

$$\alpha_O = \alpha_C + 2.0\beta_{CC} \qquad \beta_{NO} = 0.7\beta_{CC}$$

$$\alpha_N = \alpha_C + 0.5\beta_{CC}$$

Table II summarizes the results with $\beta_{CN} = 1.25\,\beta_{CC}$.[14]

Table I. Splitting Constants and Summed Carbon Spin Densities for 2,1,3-Benzoxa-, -Benzothia-, and -Benzoselenadiazole Radical Anions

X	$a^{N\,a}$	$a^{H\,a}$	$a^{H\,a}$	$\Sigma\rho_{C-4-7}$
O	5.24	3.33	2.02	0.442
S	5.26	2.63	1.53	0.344
Se	5.97	1.99	1.99	0.328

^{a} Two equivalent nuclei.

Table II. Spin Densities in 2,1,3-Benzoxadiazole Radical Anion

	ρ_N	ρ_O	$\rho_{C-4,7}$	$\rho_{C-5,6}$	$\rho_{C-8,9}$
Exptl.			0.138	0.083	
Calcd.	0.227	0.083	0.141	0.079	0.025

Calculations for 2,1,3-benzothiadiazole were carried out with the assumption that carbon–sulfur resonance integrals in the literature could be used to describe nitrogen–sulfur resonance integrals. The carbon–sulfur integrals of Lucken (p-orbital model)[15]

$$\alpha_S = \alpha_C + \beta_{CC} \qquad \beta_{NS} = 0.566\beta_{CC}$$

$$\alpha_N = \alpha_C + 0.5\beta_{CC}$$

and of Longuet-Higgins (d-orbital model)[16] were used.

$$\alpha_S = \alpha_{S'} = \alpha_C \qquad \beta_{NS} = \beta_{NS}' = 0.80\beta_{CC}$$

$$\alpha_N = \alpha_C + 0.5\beta_{CC} \qquad \beta_{SS'} = \beta_{CC}$$

The value of β_{CN} was selected to give the best agreement between the experimental and calculated values. For both models the best value of β_{CN} was 1.10 β_{CC} (see Table III).

Table III. Spin Densities in 2,1,3-Benzothiadiazole Radical Anion

	ρ_N	ρ_S	$\rho_{C-4,7}$	$\rho_{C-5,6}$	$\rho_{C-8,9}$
Exptl.			0.109	0.063	
Calcd, p-orbital model	0.225	0.165	0.109	0.063	0.021
Calcd., d-orbital model	0.225	2(0.082)	0.109	0.063	0.021

The change in spin density at positions 4–7 (Table I) shows unequivocally that sulfur and selenium attract unpaired spin density better than oxygen. It is not obvious that there is much difference between sulfur and selenium. The difference in the summed spin densities is so small that variation in benzene ring angles may

play a part. For the benzothiadiazole $\angle C_3-C_4-C_5 = 120°$ and $\angle C_4-C_5-C_6 = 121°$ while for the corresponding selenium compound the corresponding angles are 118 and 123°.[6] Symmetrical cyclic radicals with ring angles both greater and less than 120° have been found to have values of $Q_{CH}{}^H > Q_{CH}{}^H(120°)$.[17] This would mean that the spin densities at C-4–C-7 in the selenium radical anion are less than that given in Table I and that selenium is more electron withdrawing than sulfur. The values of the ^{14}N hyperfine coupling in the two radical anions tends to reinforce this conclusion, but it must be remembered that the ^{14}N splitting is dependent upon the spin densities of the adjoining atoms,[18–20] as well as upon the ^{14}N spin density.

The MO calculations clearly indicate that C-4 and C-7 have a higher spin density than C-5 and C-6. Assignment of the larger value of a^H to the hydrogens attached to C-4,7 gives excellent agreement between the experimental and calculated spin densities, both at C-4,7 and at C-5,6 with the values of β_{CN} selected. The values of $\beta_{CN} = 1.25\beta_{CC}$ for the oxadiazole and $\beta_{CC} = 1.10\beta_{CN}$ for the thiadiazole are quite satisfactory values for this parameter.[14]

Since this work was completed a somewhat similar study by Gerdil and Lucken has been reported.[21] These authors considered the dibenzofuran, dibenzothiophene, and dibenzoselenophene radical anions. They found that much better agreement resulted in McLachan-type spin density calculations[22] using a p-orbital model for the sulfur atom rather than a d-orbital model although previously Lucken had found better agreement for the d-orbital model for dithiin radical cation.[15] The spin densities for dibenzofuran, -thiophene, and -selenophene radical anions also indicated that the electron-attracting abilities for odd-electron delocalization are Se > S > O.[21]

The parameters used to calculate the distribution of the unpaired spin in the highest molecular orbital of the diazole radical anions can also be used to calculate the distribution of the ten π-electrons in the parent diazoles. Using the optimum parameters selected to reproduce the experimental spin densities in the radical

Table IV. Calculated Electron Densities of Benzodiazoles

X	q_X	q_N	$q_{C-4,7}$	$q_{C-5,6}$	$q_{C-8,9}$
O	1.806	1.156	1.006	0.986	0.952
S^a	1.628	1.214	1.010	0.998	0.966
S^b	2(0.922)	1.156	1.004	0.982	0.938

^{a} p-Orbital model. ^{b} d-Orbital model.

anions, the electron densities of Table IV are calculated for the parent heteroaromatics.[23]

(13) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961, Chapter 5.
(14) The value recommended in ref. 13 for an aromatic carbon–nitrogen bond is $\beta_{CN} = \beta_{CC}$.
(15) E. A. C. Lucken, *Theoret. Chim. Acta*, **1**, 397 (1963).
(16) H. C. Longuet-Higgins, *Trans. Faraday Soc.*, **45**, 173 (1949).
(17) For a summary of pertinent data, see R. W. Fessenden and S. Ogawa, *J. Am. Chem. Soc.*, **86**, 3591 (1964).
(18) E. W. Stone and A. H. Maki, *J. Chem. Phys.*, **39**, 1635 (1963).
(19) B. L. Barton and G. K. Fraenkel, *ibid.*, **41**, 1455 (1964).
(20) E. T. Strom, G. A. Russell, and R. Konaka, *ibid.*, **42**, 2033 (1965).
(21) R. Gerdil and E. A. C. Lucken, *J. Am. Chem. Soc.*, **87**, 213 (1965).
(22) We chose Hückel rather than McLachlan[12] calculations because the Hückel spin densities were significant at all positions indicating the absence of negative spin densities.
(23) Electron densities (*q*) of the radical anions are the sums of the spin densities of the radical anions and the electron densities of the parent heteroaromatic.

If the p-orbital model for the thiadiazole is accepted, it is apparent that the electron density of the sulfur atom is less than the electron density of the oxygen atom in the oxadiazole. This could explain why the additional electrons in the radical anions have a greater preference for sulfur than for oxygen. On the other hand, the d-orbital model of the sulfur atom leads to the conclusion that sulfur has a higher electron density than oxygen in the parent heterocyclics and a still higher spin density than oxygen in the radical anions. Such behavior seems more consistent with the inductive effect associated with mercapto and alkoxy substituents in the benzoic acids than the effect predicted on the p-orbital picture.[24,25]

(24) The charge densities of sulfur (p-orbital model) and oxygen are +0.372 and +0.194, respectively, in the parent heterocyclics. If the inductive effect is restricted to polarization of σ-bonds alone, the ob-

served inductive effects of mercapto and alkoxy substituents in the benzoic acids can be explained with the involvement of only the p-orbitals of the sulfur atom.

(25) The σ_1-constants (inductive parameter for a *meta-* or *para-* substituted benzene derivative [R. W. Taft, Jr., *J. Am. Chem. Soc.*, 79, 1045 (1957)]) are +0.19 (CH$_3$S) and +0.26 (CH$_3$O). Thus, inductively the methoxy group is the strongest electron attractor. The σ-constants [D. H. McDaniel and H. C. Brown, *J. Org. Chem.*, 23, 420 (1958)] are +0.15 for *m*-CH$_3$S, +0.115 for *m*-CH$_3$O, 0.00 for *p*-CH$_3$S, and −0.268 for *p*-CH$_3$O. The σ°-values (substituent constants wherein direct conjugation is prohibited [R. W. Taft, Jr., *J. Phys. Chem.*, 64, 1805 (1960)]) are +0.13 for *m*-CH$_3$S, +0.06 for *m*-CH$_3$O, and −0.12 for *p*-CH$_3$O. The σ^n-values (substituent constants for reactions wherein direct conjugation is not important [H. v. Bekkum, P. E. Verkade, and B. M. Webster, *Rec. trav. chim.*, 78, 815 (1959)]) are +0.225 for *m*-CH$_3$S, +0.076 for *m*-CH$_3$O, +0.220 for *p*-CH$_3$S, and −0.111 for *p*-CH$_3$O. Values quoted are those listed by Wells.[4]

Nuclear Magnetic Resonance Studies of the Uranyl–Citrate System in Deuterium Oxide at Low pD

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Nuclear magnetic resonance spectra of uranyl nitrate–citric acid mixtures in D_2O, having citric acid concentrations 0.1 M and higher, showed that a uranyl–citrate complex exists at unexpectedly high acidity. This "high acidity" species is different from the dimer existing in H_2O solution at lower concentration (0.01 M and less) and higher pH (>2). From the line-width broadening of citric acid transitions in the presence of uranyl nitrate, an average lifetime of the order of 0.006 sec. was calculated for the "high acidity" complex species. From the mean chemical shift of the methylene protons, a value of 3.16 ± 0.08 was obtained for the logarithm of the stability constant of this complex under the assumption that it is the monomer $UO_2D_2Cit^+$. A calculation is presented relating the low-field shift of the methylene deuterons to the electrostatic field and the magnetic anisotropy of the uranyl entity in the complex.

Introduction

This work is a continuation of an extensive investigation of uranyl–hydroxypolycarboxylate systems.[4] Previous work treated aqueous systems at pH above 2 and reactant concentrations 0.01 *M* and lower. The present

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(3) Supported in part by Special Research Fellowship GSP-17500, Division of General Medical Sciences, U. S. Public Health Service, and in part by the U. S. Atomic Energy Commission through contract at the University of Rochester Atomic Energy Project, Rochester, N. Y.

(4) The most recent paper in this series is: I. Feldman, C. A. North, and H. Hunter, *J. Phys. Chem.*, 64, 1224 (1960).

paper concerns n.m.r. studies on solutions of higher concentrations and higher acidities in D_2O.

Experimental

Proton spectra were obtained with a Varian 4300B spectrometer converted to operate at 100 Mc./sec., and with a Perkin-Elmer R-60 spectrometer at 60 Mc./sec. The Varian spectrometer was calibrated with audiofrequency side bands from a Muirhead–Wigan decade oscillator. Spinning samples of 4.5-mm. internal diameter were used. Spectra at 100 Mc./sec. were recorded at 25 ± 1°, those at 60 Mc./sec. at 33.4 ± 0.1°. All chemicals used were A.R. grade. As a general rule, spectra were obtained from solutions prepared by weighing the appropriate components into volumetric flasks and adding DCl, D_2O, or NaOD solution, as appropriate, to the proper volume. This procedure was not adopted during the addition of excess UO_2^{2+} to 0.1 *M* acid solutions. Here, a concentrated solution of uranyl nitrate was added from a microburet to the 0.1 *M* acid solution, and each sample was returned to the bulk acid solution before further samples were taken. In this manner, the concentration dropped slightly but the ratio of uranyl ions to acid was always accurately known.

Results

The results of n.m.r. studies of uranyl–citrate, –malate, and –tartrate systems are presented in graphical form (Figures 1–3). As far as possible, we have kept the coordinates of similar graphs on the same scale