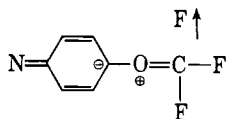
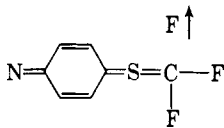


It seems plausible to suggest therefore that the positive Q 's of the OCF_3 and SCF_3 groups at the *para* position arise from the contribution of structures such as



Utilization of the empty d-orbitals of the sulfur atom in the $-\text{SCF}_3$ compound enables additional structures of the type



to be written which may account for the higher Q -value (+4.1 gauss) in the SCF_3 compound than for the OCF_3 compound (+1.5 gauss).¹⁵ A recent study of the F^{19} chemical shifts in trifluoromethoxy and trifluoromethylthio aromatic compounds has also indicated that $-\text{S}-$ is a better conjugating group than $-\text{O}-$ in these compounds by a factor of between two and three.¹⁶ This is in good qualitative agreement with the ratio of the Q -values reported here.

Conjugation of this type does not account for the negative sign of the *meta* Q -values. It is possible in principle that spin polarization through three bonds could produce this negative coupling, *i.e.*



However the magnitude seems rather large for such a long-range effect. It may also be noted that the ratio of the *p*- CF_3 to *p*- OCF_3 Q -values (25.6) is markedly larger than the ratio for the corresponding CH_3 compounds² (7.4). This is indicative that in the *p*- OCF_3 compound there is also a competing mechanism tending to place negative spin at the fluorine. In the

(15) W. A. Sheppard, *J. Am. Chem. Soc.*, **85**, 1314 (1963); pK_a measurements have provided some evidence for d-orbital participation in the bonding of the SCF_3 group.

(16) D. R. Eaton and W. A. Sheppard, *ibid.*, **85**, 1310 (1963).

case of the SO_2CF_3 group, a Q -value is available only for the *meta* compound. The negative sign obtained for this parameter suggests that similar considerations will probably apply to this group. The value obtained (-2.8 gauss) is about half that for the corresponding SCF_3 compound.

The SF_5 compound was of particular interest in view of results recently obtained in a study of the chemical shifts of this group in aromatic compounds.¹⁶ A marked difference was observed in the behavior of the chemical shifts of the basal and apical fluorines, and the present results show that the contact shifts are also very different. The Q -values obtained range from +30 to -2 gauss, and it seems unlikely that they can be accounted for by a single mechanism. The contact shifts are very much larger for the basal fluorines than for the apex fluorine, and it is probable that a direct interaction between these basal fluorines and the aromatic π -system is involved. This again is consistent with the deductions made from the chemical shift measurements. These results may also be compared with the contact shifts of analogous fluorobenzene derivatives which have been interpreted in terms of fluorine double bonding.^{7,8} There is a similarity, especially for the basal fluorines, in that the largest positive Q -values are found at the *para* positions where conjugation effects are expected to be strongest.

Significant F^{19} contact shifts have been observed in all the compounds examined in this study. It appears that both spin delocalization (conjugation) and spin polarization can provide effective mechanisms for transmitting spin density from an aromatic π -system to the F^{19} nucleus. The n.m.r. approach, which enables the signs of the I-S coupling constants to be obtained, in conjunction with measurements on the same group substituted at different positions, seems to provide the best hope of disentangling the various effects; n.m.r. contact shifts differ from the more familiar chemical shifts in that they depend upon spin densities rather than charge densities. However, there is clearly a relationship between the two types of measurement, and a combination of the results from both may well provide a powerful approach to the study of problems of chemical bonding.

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The Electron Spin Resonance Spectrum of Electrolytically Generated 7,7,8,8-Tetracyanoquinodimethane Radical Anions

By P. H. H. FISCHER¹ AND C. A. McDOWELL

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The electron spin resonance spectrum of the radical ion of 7,7,8,8-tetracyanoquinodimethane has been observed with all the expected hyperfine components completely resolved. The radical was generated by electrolysis at a platinum wire cathode operating at a potential of -0.1 v. with respect to a saturated calomel electrode. The solvent was a mixture of 80% dimethoxyethane and 20% acetonitrile with tetra-*n*-propylammonium perchlorate as supporting electrolyte. In addition to observing all the 45 lines due to hyperfine interactions caused by four equivalent nitrogen nuclei and four equivalent hydrogen nuclei, several additional lines of weak intensity due to C^{13} hyperfine splitting were found. The analysis of the spectrum leads to the following values for the hyperfine coupling constants for the nitrogen and hydrogen nuclei, namely, $a^N = 1.02$ gauss and $a^H = 1.44$ gauss.

I. Introduction

In the course of our studies of the electron spin resonance spectra of a number of organic radical anions produced by electrolysis, we obtained in the case of many nitrile radical anions results closely similar to those recently reported by Rieger, Bernal, Reinmuth, and Fraenkel.² These authors were unable to obtain

satisfactory results in the case of the anion formed from 7,7,8,8-tetracyanoquinodimethane (TCQN). They found only a single broad line when the TCQN was electrolyzed in acetonitrile solution. We have been able to prepare the radical anion of TCQN without difficulty by electrolysis at a platinum electrode in a

(1) Holder of a National Research Council Studentship, 1960-1963.

(2) P. H. Rieger, I. Bernal, W. H. Reinmuth, and G. K. Fraenkel, *J. Am. Chem. Soc.*, **85**, 683 (1963).

mixed solvent consisting of 80% dimethoxyethane and 20% acetonitrile. Furthermore, we have observed a well-resolved electron spin resonance spectrum for this radical anion and here report our results. The spectrum is readily interpreted as arising from the expected hyperfine interactions of the unpaired electron with four equivalent nitrogen nuclei and four equivalent hydrogen nuclei. In addition, we also observed several extra weak lines which are readily assigned to the hyperfine splittings caused by the C^{13} nuclei present at various positions in the radical anion. The experimental values observed for the isotropic hyperfine coupling constants for the nitrogen and hydrogen nuclei in this radical anion are of interest in view of recent theories³⁻⁵ of N^{14} and C^{13} hyperfine interactions in the electron spin resonance spectra of organic anions.

II. Experimental

The electrolysis method of generating radical anions introduced by Geske and Maki⁶⁻⁸ was followed in principle though we used a cell which is an improved version of that described by Hausser, Häbich, and Franzen.⁹ The radical was generated at a potential of -0.1 v. with respect to a saturated calomel electrode in a mixture of 80% dimethoxyethane and 20% acetonitrile. Both solvents were carefully purified, dried, and thoroughly degassed before use. Tetra-*n*-propylammonium perchlorate at a concentration of 10^{-1} M was used as the supporting electrolyte and the 7,7,8,8-tetracyanoquinodimethane was present at a concentration of 10^{-4} M.

The electron spin resonance spectra were obtained using essentially a Varian 100-kc. modulation X-band spectrometer with a model V4012B 12-in. magnet. The field calibration was obtained using a stabilized proton resonance spectrometer with the appropriate frequency counters.

III. Results and Discussion

The electron spin resonance spectrum observed for the electrolytically generated 7,7,8,8-tetracyanoquinodimethane radical anion in the dimethoxyethane-acetonitrile mixture is shown in Fig. 1. The theoretically calculated spectrum is given at the bottom portion of the figure. The numbers given as ordinates on the diagram represent the relative intensities of the lines of the theoretical spectrum. It is at once apparent that there is excellent agreement between the observed spectrum and the theoretically predicted one. This analysis of the spectrum leads to the following values for the isotropic hyperfine coupling constants for the nitrogen and hydrogen nuclei, respectively: $a^N = 1.02 \pm 0.01$ gauss and $a^H = 1.44 \pm 0.01$ gauss. These values are to be compared with those of $a^N = 1.10$ and $a^H = 1.57$ gauss by Phillips,¹⁰ who prepared the anion by reduction of the parent compound with lithium metal in tetrahydrofuran.

It is well known that the isotropic hyperfine coupling constants are related to the π -electron spin densities at the particular nuclei with nonzero nuclear spins. For protons attached directly to carbon atoms the hyperfine splitting constant a_i^H is given by McConnell's¹¹ equation

$$a_i^H = Q_{CH^H} \rho_i^\pi \quad (1)$$

In this equation ρ_i^π is the π -electron spin density and Q_{CH^H} is the σ - π interaction parameter which is assumed to be constant for all carbon atoms with sp^2 hybridization. Various values¹¹⁻¹⁴ ranging from -22.5 to -30

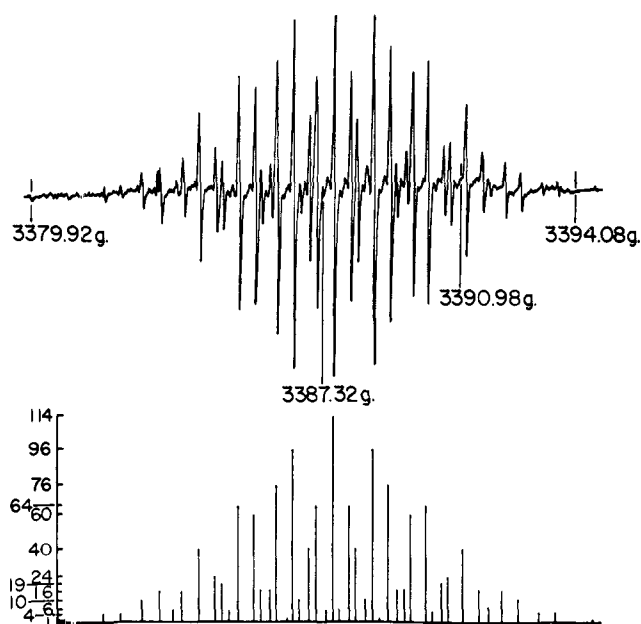
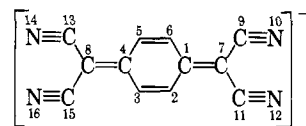


Fig. 1.—Comparison of observed and theoretical e.s.r. spectra of 7,7,8,8-tetracyanoquinodimethane radical anion.

gauss have been proposed for Q_{CH^H} , but we shall use the value $Q_{CH^H} = -23.7$ gauss as given by Karplus and Fraenkel⁴ and which is based on theoretical work. The values for the π -electron spin densities, ρ_i^π , are usually calculated on the basis of the Hückel LCAO molecular orbital method, or occasionally SCF molecular orbital spin densities are available. Of the latter approximations the procedure introduced by McLachlan¹⁴ is perhaps the easiest to apply in cases like the present one.

Calculations of the π -electron spin densities for the radical anion of 7,7,8,8-tetracyanoquinodimethane were



carried out using the Hückel LCAO method with the coulombic integral $\alpha_N = \alpha_C + h\beta_{CC}$ and the exchange integral written as $\beta_{CN} = k\beta_{CC}$. Values of $h = 0.8$ to 1.2 and $k = 1.0$ to 2.4 were chosen. The values obtained for ρ_2^π varied from 0.0454 to 0.0560. Our experimental value of $a^H = 1.44$ on using $Q_{CH^H} = -23.7$ gauss yields from eq. 1 a required value of ρ_2^π (expt.) = 0.008. Even Rieger and Fraenkel's¹⁵ chosen values of $h = 1.1$ and $k_{CN} = 2.0$ and $k_{CC} = 0.9$ yield a value of ρ_2^π (Hückel) = 0.0539. The approximate configuration-interaction method of McLachlan⁴ yields a less satisfactory value for the spin density at carbon atom 2, namely, ρ_2^π (McLachlan) = 0.0430 (see ref. 15). Thus the agreement between the experimental and the theoretical values for the hydrogen hyperfine splitting constant, a^H , for this radical is not as good as has been found in several other cases. It should be noted, however, that had a value of $Q_{CH^H} = -25$ gauss been used there would have resulted a value of ρ_2^π (expt.) = 0.0576. This value for the spin density at carbon atom 2 is close to the largest value given by the Hückel LCAO method with the choice of parameters mentioned above.

Theories^{3,4} of the hyperfine splitting from N^{14} and C^{13} have shown that eq. 1 is not strictly applicable to these

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(4) M. Karplus and G. K. Fraenkel, *ibid.*, **35**, 1312 (1961).

(5) J. C. M. Henning and C. de Waard, *Phys. Letters*, **3**, 139 (1962).

(6) D. H. Geske and A. H. Maki, *J. Am. Chem. Soc.*, **82**, 2671 (1960).

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(12) S. I. Weissman, T. R. Tuttle, and E. de Boer, *J. Phys. Chem.*, **61**, 28 (1957).

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cases. Karplus and Fraenkel⁴ have derived the equation

$$a_i^X = (S^X + \sum_i Q_{XY_i^X})\rho_X^\pi + \sum Q_{Y_i^X} \rho_{Y_i}^\pi \quad (2)$$

for C¹³ and N¹⁴, when these atoms form three sp² bonds. In this equation ρ_X^π and $\rho_{Y_i}^\pi$ are the π -electron spin densities on atoms X and Y_i, respectively; S^X is the contribution of the 1S electrons of atom X, and Q_{XY_i^X has its usual meaning. Rieger and Fraenkel¹⁵ have modified this equation to the following for the case of the nitrogen atom in nitriles where there is an unshared pair of electrons in an sp orbital}

$$a^N = (P^N + Q_{NC^N})\rho_N^\pi + Q_{C^N} \rho_C^\pi \quad (3)$$

where P^N is the contribution of the 1S polarization and also the contribution to the 2S polarization arising from the unshared pair of electrons on the N atom. This equation is of the same form as that suggested earlier by Ward¹⁶ to interpret the N¹⁴ hyperfine interactions observed in the electron spin resonance spectra of heterocyclic anions.¹⁶⁻²¹ This author wrote the following type of expression for a^N

$$a^N = Q_1^N \rho_N + Q_2^N \sum \rho_i \quad (4)$$

In eq. 4 ρ_N is spin density at the nitrogen atom, calculated according to the Hückel LCAO method, ρ_i represents the spin densities at those atoms adjacent to the nitrogen atom; Q₁ and Q₂ are appropriately chosen constants. Recently Henning and de Waard⁵ have shown that there is good experimental evidence in favor of eq. 4 and found that the "best" values of Q₁^N and Q₂^N are +18.5 and +9.6, respectively. It was further shown that the values of Q₁^N and Q₂^N are only slightly dependent on the value chosen for Q_{CH^H}. Using these values for Q₁^N and Q₂^N we calculate a^N = 0.98 gauss for Hückel spin densities, and a^N = 0.99 gauss for spin densities calculated according to the McLachlan's method. Equation 3 with Rieger and Fraenkel's values¹⁵ for (P^N + Q_{NC^N}) and Q_{C^N} leads to the following values for the nitrogen hyperfine coupling constant, a (McLachlan) = 1.24 gauss and a^N (Hückel) = 1.15 gauss. As Q_{NC^N} is so much smaller than P^N, a McConnell type equation could, of course, be used to calculate a^N as has been done by other authors.¹⁷⁻²¹ Rieger and Fraenkel write this type of equation in the form a^N = KQ_N and give K = 18.9 gauss for McLachlan spin densities and K = 19.8 gauss for Hückel spin densities. With this equation we get a^N (McLachlan) = 1.015 gauss and a^N (Hückel) = 0.92 gauss. It is thus apparent that eq. 4 with the parameter values suggested by Henning and de Waard⁵ gives good agreement between the experimental values for a^N and those calculated from both the McLachlan and the Hückel spin densities.

Various theories of line-width variations in the e.s.r. spectra have shown that these are related to anisotropy in the g-tensor and the nuclear hyperfine interaction tensor.²²⁻²⁵ These theories show that the line widths of

the individual hyperfine components vary with the value of M_I, the nuclear spin quantum number; the width depending on two terms which are proportioned to M_I and M_I², respectively. There is evidence^{20,22} that aromatic nitrogen atoms require the linear dependency on the nuclear spin quantum number to be of the form -BM_I, since it is reasonable to assume that g_x ≈ g_y > g_z (z being perpendicular to the molecular planes). If a^N is positive the lines on the low-field side of the spectrum should be narrower and sharper than those on the high-field side. Henning and de Waard⁵ have found this requirement is obeyed for several heterocyclic nitrogen aromatic anions. Careful examination of our spectrum for the TCQN anion also shows that the lines on the low field side are narrow and sharper than those on the high field side of the spectrum, which is in agreement with the view that a^N is positive in these cases.

Equation 2 can be used to estimate the magnitude of the C¹³ hyperfine splitting constants for the TCQN radical anion. In this radical there are four different types of carbon atoms; namely, C(1), C(2), C(7), and C(9). Appropriate values for the various parameters needed to calculate theoretical values for C¹³ splittings are available in the literature.^{4,15}

In Table I we give the calculated C¹³ hyperfine splitting constants and also the experimentally estimated values. There is good agreement as regards the magnitude of the various C¹³ splitting constants. Those at positions C(1) and C(9) are calculated to be negative in sign. Our experimental results do not enable us to determine the absolute sign of the splitting constants. The assignment of the C¹³ hyperfine splitting constants was made on the basis of clearly resolved lines. The intensities of the observed C¹³ lines enabled us to distinguish between the two sets of four equivalent carbon atoms on the one hand and the two sets of two equivalent carbon atoms on the other. Within each set, however, the assignment was made on the basis of agreement between the calculated splittings and the experimentally observed values. Many lines due to C¹³ overlapped either with other C¹³ lines or hyperfine lines due to other nuclei and these were not, of course, included in the analysis.

TABLE I

CALCULATED AND EXPERIMENTAL C¹³ HYPERFINE INTERACTION CONSTANTS FOR THE TETRACYANOQUINODIMETHANE RADICAL ANION

Position	Calculated (gauss)		Experimental (gauss)
	Hückel	McLachlan	
C(7)	+5.23	+8.49	7.18
C(1)	-3.11	-5.02	4.40
C(2)	+0.48	+0.79	0.62
C(9)	-7.17	-8.44	6.38

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