and e.s.r. results on irradiated CD_3OH. Step 3 shows a series of reactions, some of which also contribute to the over-all process.

$$H^+ + (CH_3OH)^- \longrightarrow H\cdot + CH_3OH \qquad (3a)$$

$$H^+ + CH_3O^- \longrightarrow CH_3OH \qquad (3b)$$

$$H\cdot + CH_3OH \longrightarrow \cdot CH_2OH + H_2 \qquad (3c)$$

$$H\cdot + H\cdot \longrightarrow H_2 \qquad (3d)$$

$$H\cdot + C_6H_6 \longrightarrow C_6H_7\cdot \qquad (3e)$$

$$CH_3O\cdot + CH_3OH \longrightarrow CH_3OH + \cdot CH_2OH \qquad (3f)$$

After appropriate combination of these steps, one is left with three paramagnetic species: the methanol radical, the cyclohexadienyl radical, and the solvated electron; and an ionic species, probably $(CH_3OH_2)^+$. According to Smith and Pieroni[11] there is an average of 40–50 Å. distance separating the trapped electron and the positive ion, and there probably is a significant coulombic attraction between these species. Consequently, on bleaching as represented in step 4 there is a release of the electron and neutralization of the positive ion leaving the observed radicals $\cdot CH_2OH$ and $C_6H_7\cdot$. Other conjugated aromatic ring systems such as toluene and naphthalene are under study, and preliminary results indicate that here also the hydroxyl hydrogen liberated from alcohols by radiation adds to the ring.

$$(CH_3OH_2)^+ + e^-_{solv} \rightsquigarrow CH_3OH + H\cdot \qquad (4a)$$

$$CH_3O^+ + e^-_{solv} \rightsquigarrow CH_3O\cdot \qquad (4b)$$

An Electron Spin Resonance Study of the Anion Radical of Azodicarbonitrile

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Received August 12, 1965

Abstract: The e.s.r. spectrum of the anion radical of azodicarbonitrile was obtained. The ^{14}N hyperfine splittings are 7.37 and 2.11 oersteds. The observed ^{14}N splittings are considered with respect to the σ–π parameters reported for other azine and nitrile anion-radical systems. The σ–π parameters of Stone and Maki, when used to calculate the azine splitting, give good agreement with the experimental value. The values of Rieger and Fraenkel for nitrile nitrogen do not yield satisfactory results, and more satisfactory values are suggested.

The isotropic nitrogen hyperfine splittings in azine radicals are of significant interest.[1] The rationalization of such splittings in terms of the relationship between π-electron spin densities and ^{14}N coupling constants based on the Karplus–Fraenkel[2] treatment of ^{13}C is of considerable concern in studies of the electronic structure of nitrogen-containing radicals.

Nitrogen hyperfine splittings arising from azodicarbonitrile (I) anion radical[3] and their rationalization in terms of the Karplus–Fraenkel treatment are reported.

$$\underset{1}{N}\equiv\underset{2}{C}-\underset{3}{N}=N-C\equiv N$$

I

Experimental Section

The anion radical of azodicarbonitrile was prepared in 1,2-dimethoxyethane as described elsewhere.[3] The spectrometer was a Varian e.s.r. spectrometer equipped with a dual cavity, 12-in. electromagnet, and a flux stabilizer to scan the magnetic field. The spectra were obtained at room temperature.

Results

The e.s.r. spectrum of an 8×10^{-4} *M* solution of azodicarbonitrile anion radical consists of five lines, each further split into five lines. The relative intensities of each set are those expected for two equivalent nitrogens, *i.e.*, 1:2:3:2:1. The hyperfine splittings are 7.37 and 2.11 oersteds. Assignment of the splitting constants is based upon LCAO–MO calculations and the knowledge that nitrile nitrogens yield small splittings, *i.e.*, in the range 0.5 to 3 oersteds.

Discussion

A. Possible Structures of the Anion Radical. Azodicarbonitrile exists in *cis* and *trans* isomeric forms.[3] The observed e.s.r. spectrum of the anion radical could arise from any of the following structural forms: *cis*, *trans*, linear, or a mixture of *cis* and *trans* isomers. If the e.s.r. spectrum arises from a mixture of *cis* and *trans* isomers, the two isomers either have identical resonance spectra or they undergo interconversion at frequencies larger than the difference between the spectral positions (expressed in units of frequency) associated with each isomer. Finally, a comment about the linear structure: one could conjecture that increased conjugation of the type $^-N=C=N-N=C=N\cdot$ might lead to stabilization of the linear over the *cis* and *trans* forms. Unfortunately the results of this study cannot allow more to be said with regard to the anion-radical structure.

B. MO Calculations. Both simple Hückel and McLachlan[4] MO-SCF calculations of π-spin densities were made. The results are shown in Table I. In

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[1] D. H. Geske and G. R. Padmanabhan, *J. Am. Chem. Soc.*, **87**, 1651 (1965), and references cited therein.

[2] M. Karplus and G. K. Fraenkel, *J. Chem. Phys.*, **35**, 1312 (1961).

[3] F. D. Marsh and M. E. Hermes, *J. Am. Chem. Soc.*, **87**, 1819 (1965).

[4] A. D. McLachlan, *Mol. Phys.*, **3**, 233 (1960).

Table I. Calculated Spin Density in the Anion Radical of Azodicarbonitrile[a]

Molecular position[b]	Hückel	McLachlan
1	0.125	0.130
2	0.043	0.021
3	0.333	0.350

[a] Parameter values: $\gamma = 1.2$, $\alpha_{N1} = \alpha_C + 1.1\beta_{CC}$, $\alpha_{N3} = \alpha_C + 0.75\beta_{CC}$, $\beta_{12} = 2\beta_{CC}$, $\beta_{23} = 1.2\beta_{CC}$, and $\beta_{34} = 1.25\beta_{CC}$. [b] See formula I for numbering.

general, spin densities obtained from the McLachlan procedure, which takes into consideration spin polarization, have given so much better agreement with theory than the simple Hückel calculations that they are to be preferred.

The MO parameters used in the calculations are given under Table I. The azine nitrogen parameters are those given by Stone and Maki[5]. Those selected for the nitrile nitrogen are in the range found acceptable by Rieger and Fraenkel.[6] It was decided to select parameters given in the literature to test their general applicability and to facilitate the later comparison of calculated hyperfine splittings.

C. Calculation of Nitrogen Hyperfine Splittings. The relationship between π-spin densities and ^{14}N hyperfine splitting has been adequately discussed.[2,5,6] The expression for the nitrogen hyperfine splitting is of the form

$$A_N = (S^N + \Sigma_i Q_{NX_i}{}^N)\rho^N + \Sigma_i Q_{X_iN}{}^N \rho^{X_i} \quad (1)$$

where S^N, $Q_{NX_i}{}^N$, and $Q_{X_iN}{}^N$ are spin polarization parameters for the 1s electrons and 2s electrons of the nitrogen polarized by the π electron at the nitrogen and for the 2s electrons at the nitrogen polarized by π electrons at nuclei adjacent to the nitrogen.

The values for the σ–π parameters reported by Stone and Maki[5] of $(S^N + Q_{NC}{}^N) = 21.1\ (\pm 0.4)$ and $Q_{CN}{}^N = -2\ (\pm 2)$ for *s*-tetrazine, pyridazine, and phthalazine are in good agreement with the observed azine splitting of 7.37 oersteds (see Table II).

The values obtained by Rieger and Fraenkel[6,7] for nitrile nitrogen give poor agreement with the experimental results. The calculated splitting is too large as shown in column II of Table II. These parameters also yield calculated hyperfine splittings which are too large for the anion radicals of tetracyanoquinodimethane (TCNQ) and tetracyanoethylene (TCNE) as shown in Table III. A much better fit to the experimentally observed nitrile hyperfine splittings for these radicals is given by $(S^N + Q_{NC}{}^N) = 16.1\ (\pm 0.7)$ and $Q_{CN}{}^N = 9.0\ (\pm 4.7)$. These values for the σ–π parameters were obtained by averaging the solutions obtained from the three pairs of simultaneous equations derived from eq. 1. The experimental values for A_N and the calculated values for the McLachlan[4] spin densities were used. The uncertainties given are root-mean-square deviations.

Table II. Calculated ^{14}N Hyperfine Splittings in the Anion Radical of Azodicarbonitrile[a]

Molecular position	I[b]	II[c]	III[d]	IV[e]
1	...	2.86 (±0.23)	2.28 (±0.19)	2.11
3	7.35 (±0.18)	...	...	7.37

[a] Calculated using McLachlan spin densities. [b] Reference 5; $(S^N + Q_{NC}{}^N) = 21.1\ (\pm 0.4)$, $Q_{CN}{}^N = -2\ (\pm 2)$. [c] Reference 6; $(S^N + Q_{NC}{}^N) = 23.1\ (\pm 1.4)$, $Q_{CN}{}^N = -6.8\ (\pm 2.2)$. [d] See text; $(S^N + Q_{NC}{}^N) = 16.1\ (\pm 0.7)$, $Q_{CN}{}^N = 9.0\ (\pm 4.7)$. [e] Experimental results.

The nitrile nitrogen hyperfine splittings calculated from these new parameters are given in Tables II and III. The uncertainties are those calculated from the uncertainties associated with the σ–π parameters.

Table III. Calculated Spin Density and ^{14}N Hyperfine Splitting for TCNE and TCNQ Anion Radicals[a]

Molecular positions and compd.	ρ^b	I[c]	II[d]	III[e]
TCNE				
N	0.0841	1.76 (±0.18)	1.61 (±0.19)	1.574
C(C≡N)	0.0276	...	...	...
TCNQ				
N	0.0590	1.35 (±0.09)	0.97 (±0.05)	1.009
C(C≡N)	0.0016	...	...	...

[a] Parameters used in spin density calculation are given in Table I. [b] McLachlan spin densities. [c] Reference 6; $(S^N + Q_{NC}{}^N) = 23.1\ (\pm 1.4)$, $Q_{CN}{}^N = -6.8\ (\pm 2.2)$. [d] See text; $(S^N + Q_{NC}{}^N) = 16.1\ (\pm 0.7)$, $Q_{CN}{}^N = 9.0\ (\pm 4.7)$. [e] Experimental results, see ref. 8.

Conclusion

The σ–π parameters reported by Stone and Maki for azine nitrogen give results in good agreement with experiment, whereas those reported for the nitrile nitrogen by Rieger and Fraenkel yield results which are too large. Smaller values for the σ–π parameters for nitrile nitrogen have been suggested. A major problem associated with the semiempirical evaluation of σ–π parameters lies in the fact that they are very sensitive to the choice of spin density. Hence, until absolute values for spin density can be obtained, one can expect discrepancies such as these.

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(5) E. W. Stone and A. H. Maki, *J. Chem. Phys.*, 39, 1635 (1963).

(6) P. H. Rieger and G. K. Fraenkel, *ibid.*, 37, 2795 (1962).

(7) $(S^N + Q_{NC}{}^N) = 23.1\ (\pm 1.4)$; $Q_{CN}{}^N = -6.8\ (\pm 2.2)$.

(8) M. T. Jones and W. R. Hertler, *J. Am. Chem. Soc.*, **86**, 1881 (1964).