not seen in esr. On admission of oxygen

$$Ti^{3+} + O_2 \longrightarrow Ti^{4+} + O_2^-$$

while

$$O_2 + \text{hole} \longrightarrow O_2^+$$

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An Electron Spin Resonance Study of Tetra- and Pentacyanopyridine Anion Radicals[1a]

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Abstract: The anion radicals of tetra- and pentacyanopyridine have been studied by esr. The nitrogen hyperfine splittings have been interpreted in terms of the relationship between π-electron spin densities and ^{14}N coupling constants based upon the Karplus–Fraenkel treatment of ^{13}C. Moreover, the relevance of these results to the question of whether a permanent Jahn–Teller distortion has occurred in the radical prepared by reduction of tricyano-*s*-triazine is considered. These results plus calculations of the expected nitrogen hyperfine splittings from the anion radical of tricyano-*s*-triazine suggest that a permanent Jahn–Teller distortion does not adequately explain the experimental observations.

The isotropic nitrogen hyperfine splittings in radical systems continue to be of interest[2,3] as is 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[4] treatment of ^{13}C. The anion radicals of tetracyanopyridine and pentacyanopyridine have been studied by esr techniques for these reasons and as an aid in determining whether the radical observed upon reduction of tricyano-*s*-triazine is a manifestation of a permanent Jahn–Teller distortion.[5]

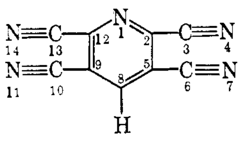
Experimental Details

The anion radicals were prepared by reduction of tetra- and pentacyanopyridine with potassium metal mirrors in 1,2-dimethoxyethane under vacuum by standard techniques. The esr spectrometer was a Varian V-4502 equipped with a dual cavity, a 12-in. electromagnet, and a flux stabilizer to scan the magnetic field.

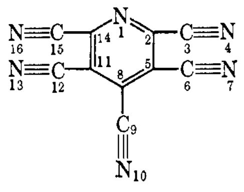
The spectra were recorded at room temperature. However, a few low-temperature experiments indicated possible ion-pairing phenomena. The anion radicals of both tetra- and pentacyanopyridine were stable for long periods of time under the experimental conditions.

The following numbering system was used in reporting hyperfine splittings and in the calculations.

The two compounds 2,3,5,6-tetracyanopyridine (mp 203–204°) and pentacyanopyridine (280–300° dec) were synthesized by Wallenfels and Neuman.[6]



i



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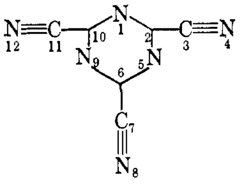

iii

Experimental Results

The esr spectra of ~3 × 10^{-4} *M* solutions of tetra- and pentacyanopyridine anion radicals consist of 13 and 11 lines, respectively. The line widths are rather large, ~0.3 oersted. The assignments of the hyperfine splittings, which are given in Table I, are unambiguous. However, it is gratifying and significant for later discussion regarding triacyano-*s*-triazine that these assignments are in reasonable agreement with the McLachlan[7]-modified MO calculations. The results of the calculations, which will be discussed later, are shown in Tables II and III.

Results of the Cyanopyridine Calculations

A. MO Calculations. Both simple Hückel and McLachlan[7] MO–SCF type calculations of π-spin den-

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(2) M. T. Jones, *J. Am. Chem. Soc.*, **88**, 227 (1966).

(3) P. H. Geske and G. R. Padmanabhan, *ibid.*, **87**, 1651 (1965), and references cited therein.

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(7) A. D. McLachlan, *Mol. Phys.*, **3**, 233 (1960).

Table I

Anion radical of	Hyperfine splittings, oersteds
Tetracyanopyridine	$A_4 = A_7 = A_{11} = A_{14} = 1.1\,(\pm 0.1)$ $A_1 = A_8\,(\mathrm{H}) = 2.2\,(\pm 0.2)$
Pentacyanopyridine	$A_4 = A_7 = A_{13} = A_{16} = 1.15\,(\pm 0.1)$ $A_1 = 2.65\,(\pm 0.2)$ $A_{10} \approx 0$

Table II

Radical	Position	Hückel calculation	McLachlan
i	1	0	−0.04457
	2	0.15238	0.17750
	3	0.03810	0.03123
	4	0.05953	0.06392
	5	0.15238	0.18138
	6	0.03810	0.03121
	7	0.05953	0.06429
	8	0	−0.05462
ii	1	0	−0.04352
	2	0.15238	0.17747
	3	0.03810	0.03117
	4	0.05953	0.06395
	5	0.15238	0.18366
	6	0.03810	0.03125
	7	0.05953	0.06476
	8	0	−0.05183
	9	0	−0.00025
	10	0	−0.00898

Parameter values

$\lambda = 1.2$

$\alpha_1 = \alpha_c + 0.75\beta$

$\alpha_4 = \alpha_7\ \text{(and so on)} = \alpha_c + 1.1\beta$

$\beta_{1,2} = 1.2\beta$

$\beta_{3,4} = 2\beta$

Table III. Comparison of Observed and Calculated Hyperfine Splittings[a,b]

Anion radical of	Position	Observed	Calculated
Tetracyanopyridine	1	2.2	−2.05
	4	1.1	+1.30
	8	2.2	−1.48
Pentacyanopyridine	1	2.65	−2.05
	4	1.15	+1.31
	7	1.15	+1.32
	10	0	−0.15

[a] Calculated using McLachlan spin densities. [b] Parameters used: $A_{\mathrm{N(C{\equiv}N)}} = (16.1 \pm 0.7)\rho_{\mathrm{N}} + (9.0 \pm 4.7)\rho_{\mathrm{c}}$ (see ref 1); $A_{\mathrm{N(hetero)}} = (30.9 \pm 2)\rho_{\mathrm{N}} - (2 \pm 2)\Sigma\rho_{\mathrm{c}}$ (see ref 7); $A_{\mathrm{H}} = 27\rho_{\mathrm{c}}$.

sities were made. The results are shown in Table II. In the McLachlan calculations, λ = 1.2 was used. The exact values of the other parameters used are given at the bottom of Table II. The values selected for the heterocyclic nitrogen are those of Stone and Maki.[8] Those used for the nitrile nitrogen are in the range found satisfactory by Rieger and Fraenkel.[9] These parameters were selected in part because they have been used with reasonable success to describe similar systems.[2,3,8,9] No attempt was made to improve upon the parameters. In fact, it is noteworthy that these parameters do give a reasonable fit to the experimental data, and on this basis should be useful in predicting the general features of unknown spectra of nitrogen-containing radicals and in checking assignments.

The comparison of the Hückel and McLachlan spin densities demonstrates the superiority of the latter for calculation of spin-density distributions in π-radical systems. The Hückel calculations predict zero spin density and hence a zero or small splitting by the heterocyclic nitrogen, whereas it is in fact the largest splitting observed.

B. Hyperfine Splitting Calculations. The expression for nitrogen hyperfine splitting is of the form

$$A_{\mathrm{N}} = (S^{\mathrm{N}} + \Sigma_i Q_{\mathrm{NX}_i}{}^{\mathrm{N}})\rho^{\mathrm{N}} + \Sigma_i Q_{\mathrm{X}_i\mathrm{N}}{}^{\mathrm{N}}\rho^{\mathrm{X}_i} \qquad (1)$$

where S^{N}, $Q_{\mathrm{NX}_i}{}^{\mathrm{N}}$, and $Q_{\mathrm{X}_i\mathrm{N}}{}^{\mathrm{N}}$ are spin polarization parameters for the 1s electrons and 2s electrons of the nitrogen, polarized by the π electrons at the nitrogen, and for the 2s electrons at the nitrogen polarized by π electrons at nuclei adjacent to the nitrogen.[4,8,9]

The values reported by Stone and Maki[8] for the σ–π parameters for heterocyclic nitrogen of $(S^{\mathrm{N}} + Q_{\mathrm{NC}}{}^{\mathrm{N}}) = 30.9\ (\pm 2)$ and $Q_{\mathrm{CN}}{}^{\mathrm{N}} = -2\ (\pm 2)$ give pretty fair agreement with the observed heterocyclic nitrogen splittings in tetra- and pentacyanopyridine anion radicals.

The values reported by Jones[2] for the σ–π parameters for nitrile nitrogen of $(S^{\mathrm{N}} + Q_{\mathrm{NC}}{}^{\mathrm{N}}) = 16.1\ (\pm 0.7)$ and $Q_{\mathrm{CN}}{}^{\mathrm{N}} = 9.0\,(\pm 4.7)$ were found to give reasonable agreement with the observed splittings. Table III compares the calculated and experimentally observed splittings for the cyanopyridine anion radicals studied.

No attempt was made to improve upon either the MO calculations or the σ–π parameters because the results shown in Table III agree as well as one can expect from such calculations at this point. In fact, we believe that it is an important observation that one can, with fair accuracy, now predict the expected hyperfine splitting from nitrogen-containing anion radicals.

Tricyano-*s*-triazine

Carrington and co-workers[5] obtained an esr spectrum from the reduction product of tricyano-*s*-triazine which arose from two sets of nitrogen atoms with splittings of 3.78 and 0.84 oersted. The sets contained two and four atoms, respectively, whereas one would have expected to observe two sets of three equivalent nitrogen atoms if the radical were the anion radical of tricyano-*s*-triazine. However, the authors pointed out that if one (1) assumes a static Jahn-Teller distortion, (2) assumes that the cyano and heterocyclic nitrogen atoms are described by identical MO parameters, and (3) uses simple Hückel theory, the results can be explained. We are particularly concerned with the latter two assumptions in that we believe that they do not constitute an adequate test of the first assumption. First, the cyano and heterocyclic nitrogen atoms are not well described by identical MO parameters. They are not the same chemically, and certainly they are not chemically bonded to their neighboring atoms in the same manner. That different MO parameters are necessary is becoming increasingly evident.[2,3,8,9] Second, simple Hückel MO theory does not, in general, give a satisfactory spin density distribution in organic free-radical systems, especially those containing heteroatoms.

Therefore, calculations have been made of the expected nitrogen hyperfine splittings for the two degenerate antibonding orbitals, in which the odd electron associated with the anion radical of tricyano-*s*-triazine must

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

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

Table IV. Spin Densities Calculated for Tricyano-*s*-triazine[a]

	Position	Hückel	McLachlan
Antisymmetric orbital	1	0	−0.05702
	2	0.19564	0.22863
	3	0.05710	0.04970
	4	0.08294	0.08973
	5	0.16431	0.18400
	6	0	−0.04121
	7	0	+0.00048
	8	0	−0.00637
Symmetric orbital	1	0.21908	0.26263
	2	0.06522	0.04779
	3	0.01903	0.01693
	4	0.02765	0.02553
	5	0.05477	0.02422
	6	0.26088	0.31953
	7	0.07612	0.06597
	8	0.11060	0.12204

[a] See Table II for parameters used in calculation.

be placed. These calculations make use of MO parameters found to be satisfactory in describing the spin density distributions and nitrogen hyperfine splittings in similar radical systems containing cyano and heterocyclic nitrogen, including the title compounds of this paper.

The results of simple Hückel and McLachlan MO–SCF calculations of π-spin density are shown in Table IV. The parameters used are the same as those selected for the cyanopyridine anion radicals and are given at the bottom of Table II. The Hückel calculations were performed using group theoretical techniques to aid in obtaining the proper electron density distribution in the two degenerate orbitals. McLachlan calculations were then made on each of the two different electron density distributions. One notes that the antisymmetric orbital is similar to that which describes the unpaired electron in the cyanopyridines. One slightly confusing point with respect to the results of the MO calculations is the appearance of a small but positive spin density at the number seven position in the antisymmetric orbital. It contrasts with the small but negative spin density at the equivalent position in the pentacyanopyridine anion radical. The source of this contrast is not known. However, because the absolute value of the spin density at this position is small, its sign has little effect upon the calculated hyperfine splittings of the adjacent nitrogens.

Table V. Calculated Hyperfine Splittings for Tricyano-*s*-triazine[a]

	Calculated hyperfine splittings	
Position	Antisymmetric	Symmetric
1	−2.68	+7.92
4	+1.89	+0.56
5	+5.31	+0.04
8	−0.10	+3.06

[a] See Table III for σ–π parameters used in the calculation.

Finally, the same σ–π parameters used to calculate the hyperfine splittings in the cyanopyridines were also used for tricyano-*s*-triazine. The results are given in Table V. The reasonably good agreement between calculated and experimental hyperfine splittings in tetra- and pentacyanopyridines gives us some confidence in the use of these calculations to predict expected nitrogen hyperfine splittings.

Because of the similarity between the orbital containing the unpaired electron in pentacyanopyridine and the antisymmetric orbital of the tricyano-*s*-triazine anion, there is little doubt that the antisymmetric orbital does not give rise to the observed nitrogen splittings from the reduction product of tricyano-*s*-triazine as only five nitrogens are expected to yield observable splittings. The cyano nitrogen in the nodal plane will not yield a hyperfine splitting.

With respect to the symmetic orbital, the calculations predict hyperfine splittings by four sets of nitrogens, two sets each containing two nitrogen atoms, and the remaining two each containing one. This is also contrary to experiment. There does not appear to be any way that one might average the two orbital spin density distributions so that one could reproduce even grossly the observed spectrum obtained upon reduction of tricyano-*s*-triazine.

Thus our results, while not completely unambiguous, favor some sort of molecular rearrangement rather than a static Jahn–Teller distortion as an explanation of the resonance spectrum of the reduction product of tricyano-*s*-triazine.

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