1199. *Unstable Intermediates. Part XXXII.*[1] *An Electron Spin Resonance Study of the Radicals* $N_2H_4^+$, $C_2(CN)_4^-$, *and* 1,1-*Diphenyl*-2-*picrylhydrazyl*

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The structures of the radicals $N_2H_4^+$, $C_2(CN)_4^-$, and 1,1-diphenyl-2-picrylhydrazyl in the solid state are discussed and compared in the light of information obtained from electron spin resonance data.

The radicals $N_2H_4^+$ and $C_2(CN)_4^-$ have been studied extensively in solution by electron spin resonance spectroscopy,[2-4] and molecular-orbital treatments of the latter have been reported.[3,5] The stable radical 1,1-diphenyl-2-picrylhydrazyl has been studied both in solution and in the solid state [6-8] and some consequences of the extra structural information derived from the solid have been discussed.[8]

The radical $N_2H_4^+$ is of interest because it has three π-electrons and might be expected to have an unusual geometry. The other radicals are structurally related but are almost certainly planar and hence a comparison between them and $N_2H_4^+$ might be informative. Also, since $C_2(CN)_4^-$ and 1,1-diphenyl-2-picrylhydrazyl can be prepared unambiguously, their solid-state electron spin resonance spectra can be used as an aid in the interpretation of spectra thought to be due to $N_2H_4^+$. Accordingly, solid-state spectra for all three species have been recorded both at *X*- and *Q*-band wavelengths.

Experimental and Results

Materials.—Tetrahydrofuran (B.D.H. laboratory reagent) was refluxed over calcium hydride for 24 hr. and then fractionated through a heated 40 cm. Vigreaux column. The fraction with b. p. 65·0° ± 0·5° was degassed on a vacuum line and used immediately.

Tetracyanoethylene (B.D.H. laboratory reagent) was recrystallised twice from benzene.

Sodium iodide, ceric sulphate (low in other rare earths), hydrazine sulphate, and hydrazine hydrate (B.D.H. laboratory reagents) were used without further purification.

Preparation of Radicals.—Addition of sodium iodide to a solution of tetracyanoethylene in tetrahydrofuran gave the straw-coloured solution characteristic of the anion $C_2(CN)_4^-$.

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[1] Part XXXI, R. Catterall and M. C. R. Symons, *J.*, 1965, 3763.
[2] J. Q. Adams and J. R. Thomas, *J. Chem. Phys.*, 1963, **39**, 1904.
[3] W. D. Phillips, J. C. Rowell, and S. I. Weissman, *J. Chem. Phys.*, 1960, **33**, 626.
[4] P. H. Rieger, I. Bernal, and G. K. Fraenkel, *J. Amer. Chem. Soc.*, 1961, **83**, 3918.
[5] P. H. Rieger and G. K. Fraenkel, *J. Chem. Phys.*, 1962, **37**, 2795.
[6] R. W. Holmberg, R. Livingston, and W. T. Smith, *J. Chem. Phys.*, 1960, **33**, 541.
[7] N. W. Lord and S. M. Blinder, *J. Chem. Phys.*, 1961, **34**, 1693.
[8] R. Lefebvre, J. Maruani, and R. Marx, *J. Chem. Phys.*, 1964, **41**, 585.

Tetrahydrofuran was used as solvent because it forms a good glass when rapidly cooled to 77°K. A 0·05M-solution of 1,1-diphenyl-2-picrylhydrazyl in tetrahydrofuran was glassified in the same way.

The radicals $N_2H_4^+$ and $N_2D_4^+$ were prepared from finely powdered hydrazine sulphate and perdeuterated hydrazine sulphate by irradiation at room temperature with γ-rays from a ^{60}Co source in a Gammacell 200. The radical $N_2H_4^+$ was also prepared in solution as an unstable intermediate in the reaction between ceric ions and hydrazine in dilute sulphuric acid. The method used was that of Adams and Thomas [2] in which a stream of hydrazine solution was mixed with a stream of ceric sulphate solution in a Varian aqueous-solution sample cell. By employment of continuous flow of the reactants a steady concentration of radicals was maintained in the microwave cavity of the electron spin resonance spectrometer.

Electron Spin Resonance.—*X*-Band measurements at room temperature and at 77°K were made with a high-resolution spectrometer previously described [9] and a Varian V-4502-03 spectrometer with a variable-temperature accessory.

Q-Band measurements at room temperature and at 77°K were made with a balanced-bridge reflection spectrometer which employed a high-frequency alternating magnetic field to sample the slope of the electron resonance absorption line. Phase-sensitive detection was used, giving an absolute sensitivity of $10^{12} \times \Delta H$ spins, where ΔH is the width of the absorption line.

The rectangular cavity was made from a WG20 wave-guide and oscillated in the HO24 mode. The sides of the cavity were milled down to 0·1 mm. in thickness and modulation was achieved by fixing to them ten-turn coils supplied with 100-kc./sec. current from a transistorised power amplifer driven by a crystal oscillator. The cavity was contained in a copper bath insulated with polystyrene foam. For measurements at 77°K the bath was filled with liquid nitrogen, and dry oxygen-free nitrogen gas was passed slowly through the cavity to prevent condensation of oxygen or moisture.

The d.c. magnetic field was provided by an electromagnet with 8-in. pole pieces fitted with conical pole tips of 5-in. diameter to give a 2·5-cm. gap. The stability of the magnetic field was ± 1 in 10^5, with an a.c. ripple less than 20 milligauss in amplitude and a homogeneity over the sample of 2 in 10^5. Slow linear sweep of the field for phase-sensitive detection was obtained by feeding the output from a modified Miller sweep generator into the control amplifier of the power unit, giving a sweep with a maximum amplitude of 1000 gauss and a maximum duration of 20 min. Because of saturation of the magnetic yoke, linear current sweep did not produce linear field sweep. To overcome this a variable positive feed-back was applied to the Miller sweep generator to increase its rate of sweep with time. The field was always increased during a sweep, so that adjustment of the positive feed-back produced linear field sweep.

The magnetic field was measured with a marginal oscillator proton resonance magnetometer. The microwave frequency was measured with a Hilger and Watts cylindrical wavemeter of type W871. The *g*-values thus obtained were accurate to $\pm 0{\cdot}0004$ in 2·0000, the accuracy being checked against charred dextrose.[10]

Interpretation of Electron Spin Resonance Spectra.—Differentiation between "peaks" (perpendicular features) and shoulders (parallel features) in the spectra of powders and glasses is often unambiguous,[11] but in the cases under consideration this is not so and each possible assignment has to be tested. This testing is aided by the following factors. Suitable isotopic substitution can help in the assignment of hyperfine coupling data to the various magnetic nuclei. Measurement at two frequencies (*X*- and *Q*-band) can help to distinguish between the effect of hyperfine coupling (frequency-independent) and that of *g*-value variation (frequency-dependent). The spectrum of a radical in liquid solution gives unambiguously the magnitudes of the isotropic hyperfine coupling constants. This information, coupled with reasonable structural expectations, generally leads to a single set of self-consistent parameters. Thus, the tetracyanoethylene anion is known to be planar and to have the unpaired electron in a π^*-orbital delocalised over all nuclei. This symmetry requires that the *g*-tensor and the nitrogen hyperfine coupling tensors be axially symmetric and have the same principal directions. The four equivalent nitrogen nuclei should give rise to nine parallel and nine perpendicular features. However, the *X*-band spectrum (Figure 1) reveals only one set of nine features, so that either the two sets almost coincide (*i.e.*, $A_{\parallel} \approx A_{\perp}$) or else one set is concealed in the central feature.

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[9] J. A. Brivati, N. Keen, and M. C. R. Symons, *J.*, 1962, 237.

[10] R. H. Hoskins and R. C. Pastor, *J. Appl. Phys.*, 1960, **31**, 1506.

[11] M. C. R. Symons, *Adv. Phys. Org. Chem.*, 1963, **1**, 283.

The possibility of near coincidence is ruled out by the *Q*-band spectrum (Figure 2) because it shows no splitting of the hyperfine features despite the greater effect of the *g*-anisotropy, as indicated by the displacement of the central feature relative to the others. If one set of hyperfine features is hidden, then either $A_\perp \approx 0$ and $A_\parallel = \pm x$, where x is the observed hyperfine splitting, or *vice versa*. Of these four possibilities only the two with $A_\perp \approx 0$ give a value for A_{iso} in good agreement with the solution value. The remaining ambiguity of sign can be resolved by considering the anisotropic coupling between the unpaired electron and a nitrogen nucleus. This coupling is too large to be due to an electron in a molecular orbital that is not delocalised over the nitrogen nucleus. Such delocalisation must involve the nitrogen $2p\pi$-orbital, giving an anisotropic coupling tensor of the form $(2B, -B, -B)$. Since $A_\perp \approx 0$, A_{iso} must be positive. Use of the solution value of A_{iso} and the value of $A_\parallel$ obtained from the powder spectrum gives the value of $A_\perp$ quoted in Table 1.

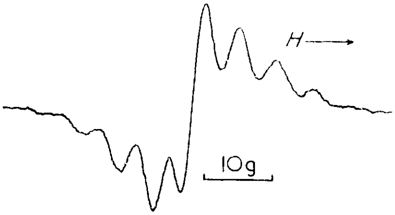

FIGURE 1. *X*-Band electron spin resonance spectrum of $C_2(CN)_4^-$

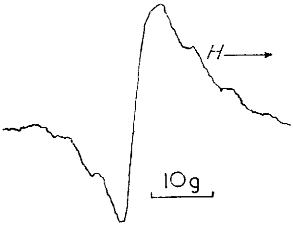

FIGURE 2. *Q*-Band electron spin resonance spectrum of $C_2(CN)_4^-$

Our interpretation of the *X*- and *Q*-band spectra of glasses of 1,1-diphenyl-2-picrylhydrazyl is similar to that of the tetracyanoethylene anion and is in accord with the conclusions of Lord and Blinder.[7]

As far as the nitrogen hyperfine structure of the $N_2H_4^+$ spectra is concerned, our interpretation again follows closely that for $C_2(CN)_4^-$, but the situation is complicated by the presence of a second set of magnetic nuclei. The thirteen hyperfine features of the *X*-band spectrum (Figure 3) are as expected for two equivalent nitrogen nuclei and four equivalent protons if one assumes that the nitrogen hyperfine splitting is about twice that of the protons. Only by taking these splittings to be parallel can one obtain a value of A^{N}_{iso} in agreement with the solution value obtained by Adams and Thomas [2] and confirmed by us.

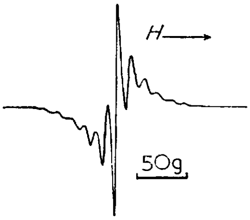

FIGURE 3. *X*-Band electron spin resonance spectrum of $N_2H_4^+$

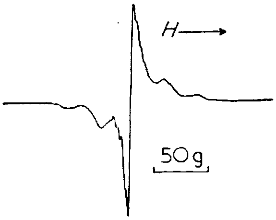

FIGURE 4. *X*-Band electron spin resonance spectrum of $N_2D_4^+$

The anisotropy of the *g*-tensor shows up more clearly in the *Q*-band spectrum and indeed only from the *Q*-band spectrum can accurate *g*-values be obtained. The central part of the spectrum has the shape expected if there were an axially symmetric *g*-tensor and no hyperfine splitting.[11] In agreement with our assignment, the thirteen hyperfine features are centred on the $g_\parallel$-shoulder. To confirm the interpretation and to obtain accurate *g*- and *A*-tensors, the *X*-band spectrum (Figure 4) and the *Q*-band spectrum of $N_2D_4^+$ were examined. As expected these exhibit five hyperfine features due to the nitrogen nuclei, and the central one of these carries nine hyperfine features from the four deuterons.

The small value of A^{N}_{iso} obtained from the solution spectrum and the small value calculated from $A^{N}_\parallel$ assuming that $A^{N}_\perp \approx 0$ show that the radical is planar both in solution and in the solid state. We are therefore justified in taking these values of A^{N}_{iso} and $A^{N}_\parallel$ together to calculate the value of $A^{N}_\perp$ shown in Table 1. Since the radical is planar the unpaired electron must be in a

TABLE 1

Experimental results

Radical	Wave-length band	Temp. (°K)	$g_{\parallel}$	$g_{\perp}$	g_{iso}	Hyperfine coupling constants (gauss) Nucleus	$A_{\parallel}$	$A_{\perp}$	A_{iso}
$N_2H_4^+$	*Q*	300	2·0020	2·0035	2·0030	N	+28·1	(+3·2)	+11·5
						H			−11·0
$N_2D_4^+$	*Q*	300	2·0022	2·0041	2·0035	N	+28·3	(+3·1)	
						D	−1·7		
$C_2(CN)_4^-$	*X*	77	2·0015	2·0028	2·0024	N	+5·44	(−0·37)	+1·57
	Q	77	2·0019	2·0030	2·0026	N	+5·48	(−0·38)	+1·57
DPPH	*X*	77	2·0024	2·0033	2·0030	N-1	+21·0	(+1·25)	+7·85[a]
						N-2	+21·0	(+3·53)	+9·35[a]

[a] Ref. 7.

π*-orbital and the anisotropic coupling between the electron and the protons will be approximately of the form $(0, C, -C)$. Thus $A^{H}_{\parallel}$ should be approximately equal to A^{H}_{iso} and $A^{H}_{\perp}$ should have the continuous range of values from $A^{H}_{iso} + C$ to $A^{H}_{iso} - C$. The subscripts $\parallel$ and $\perp$ refer to the principle directions of the *g*-tensor. One principal direction of each proton hyperfine coupling tensor coincides with the parallel axis of the *g*-tensor. The in-plane principle directions for each proton tensor lie along and perpendicular to the corresponding N–H bond and are therefore the same for protons *trans*, but different for protons *cis*, to one another. By analogy with other π-radicals containing α-protons, *C* is expected to be about 5·5 gauss. Thus, to the single values of $A^{N}_{\perp}$ and $g_{\perp}$ there corresponds a range of values of $A^{H}_{\perp}$ from about −8·5 to −16·5 gauss. This resuts in a blurring of all but one of the perpendicular features and explains why they do not stand out sharply like the parallel features. The parallel deuteron splitting, $A^{D}_{\parallel} = 1{\cdot}7$ gauss, corresponds to a parallel proton splitting, $A^{H}_{\parallel} = 11{\cdot}1$ gauss, which is in excellent agreement with the solution value, $A^{H}_{iso} = 11{\cdot}1$ gauss.

Derivation of Spin Populations.—If an LCAO-MO approximation is used and overlap of atomic orbitals is neglected, then

$$| A^{N}_{iso} | = a_{2s}^{2}(8\pi/3)g_{n}\beta_{n} \, | \psi_{2s}(0) |^{2}$$

$$\text{and } B = a_{2p}^{2}(2/5)g_{n}\beta_{n} < r^{-3} >_{2p}$$

where a_{2s}^2 and a_{2p}^2 are the spin populations of the nitrogen 2*s*- and 2*p*-orbitals. The spin populations quoted in Table 2 were obtained using values of $| \psi_{2s}(0) |^{2}$ and $< r^{-3} >_{2p}$ calculated from self-consistent-field atomic wave-functions derived by Mayers and by Roothaan and Clementi.[12]

DISCUSSION

Identification of $N_2H_4^+$.—Our identification of the radical detected in γ-irradiated hydrazinium sulphate, $N_2H_5^+HSO_4^-$, rests upon the following factors. (i) Fission of an N–H bond in the hydrazinium cation, $N_2H_5^+$, is the reaction most likely to occur. This mode of decomposition was observed for ammonium salts [13] and C–H bond fission is the normal decomposition for a wide range of organic molecules.[11] (ii) There is a set of features in the electron spin resonance spectrum centred on one *g*-value, and this is in accord with expectation for two equivalent nitrogen nuclei and four equivalent protons. A comparison with the spectrum of the perdeuterated material confirms this analysis. (iii) It was possible to interpret the spectrum completely in terms of the formulation $N_2H_4^+$, taking the resolved features as the parallel components of the hyperfine tensors and using the known isotropic parameters derived from the solution spectrum (Table 1).

In the following discussion this identification is presumed to be correct.

Structure of $N_2H_4^+$.—Although a planar configuration is most probable for this three-π-electron radical, nevertheless two other structures are worthy of consideration. One involves a twisted configuration such as is predicted for the first excited singlet and triplet states of ethylene; [14] the other has a pyramidal arrangement of bonds about each nitrogen

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[12] D. H. Whiffen, personal communication.

[13] T. Cole, *J. Chem. Phys.*, 1961, **35**, 1169.

[14] A. D. Walsh, *J.*, 1953, 2325.

atom, the deviation from planarity being somewhat less than that found for hydrazine itself. Our results are sufficient to eliminate these other possibilities. The high p/s ratio of 23·4 for the two nitrogen atoms shows clearly that the unpaired electron is located in a molecular orbital composed almost entirely of nitrogen $2p\pi$-atomic orbitals. The equal coupling found for the two nitrogen nuclei also rules out the hydrazine-like possibility. The fact that the two nitrogen tensors are parallel demonstrates that the radical is planar overall and this is confirmed by the equivalence of all four protons when the applied magnetic field is parallel to the axes of the nitrogen $2p\pi$-orbitals.

Spin Densities for $N_2H_4^+$.—The parameters listed in Table 2 show that the unpaired electron is adequately described as being located in the π^*-molecular orbital. Indeed, the summation (98%) is remarkably good in view of the fact that values for nitrogen radicals often appear to be slightly low.[15] The isotropic proton hyperfine coupling is nearly half that found for NH_3^+ (25·9 gauss) giving a Q-value for α-protons attached to nitrogen of (—)22 gauss, which is, within experimental error, identical with that for α-protons attached to carbon [approx. (—)23 gauss].

Spin Densities for $C_2(CN)_4^-$.—Our spin density for the four equivalent nitrogen atoms of 11% each is somewhat greater than that calculated by Fraenkal *et al.*[5] of 7—8% each but equal to that calculated by Weissman *et al.*[3] This experimental value gives the large net value of 44% spin density on the nitrogen atoms.

Little can be said of the isotropic coupling of (+)1·57 gauss which is a normal value for a spin density of 0·11, except that it must be taken as positive in order that a reasonable anisotropic coupling tensor be obtained. Fraenkal and his co-workers [16] reached the same conclusion by analysing trends in the widths of the nitrogen hyperfine lines and so did Carrington and Luckhurst [17] by studying radicals partially aligned in the magnetic field using a liquid-crystal medium.[18] This latter conclusion, however, was based on Fraenkal's calculated value [5] for the spin density on nitrogen. It is of interest that the liquid-crystal experiment gave a ^{14}N hyperfine coupling constant which, in the limit of complete alignment, would be equal to the perpendicular component, (A_{iso}–B). The result of (—)0·62 gauss is somewhat greater than our value calculated from $A_{\parallel}$ for the solid-state spectrum, but the agreement is satisfactory in view of the fact that the radicals in the liquid-crystal are not expected to be completely aligned.

Spin Densities for 1,1-*Diphenyl-*2-*picrylhydrazyl*.—Our results for this radical are close to those reported by Lord and Blinder.[7] As stressed by Marx and her co-workers,[8] the results of Holmberg, Livingston, and Smith,[6] which were derived from the study of 1,1-diphenyl-2-picrylhydrazyl in single crystals of the corresponding hydrazine, cannot be fitted to the frozen-solution spectra whichever set of alternative parameters is chosen. We agree with them that this difference probably stems from a distortion of the hydrazyl radical in the crystal resulting in a modification of the isotropic hyperfine coupling to the nitrogen nuclei, rather than from a major change in the spin densities. If this is so, then Livingston's first set of spin densities [6] is to be preferred since it gives a spin density on N-2 which is closer to that derived by Lord *et al.*[7] and by us.

Three structurally interesting aspects emerge from these spin densities. First there is apparently an almost equal distribution of the unpaired electron between the two nitrogen atoms. This must stem in part from the electron-withdrawing effect of the picryl group relative to the two phenyl groups, and, in part, from the fact that such a distribunoit corresponds to an accumulation of charge on the two nitrogen atoms (Figure 5). If charge localisation of this sort is substantial, then the free atom parameters used to calculate the spin densities would require modification, as was shown by Livingston.[6] This would lead to a greater estimated spin density on N-2 and a smaller one on N-1.

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[15] M. C. R. Symons, *J.*, 1963, 570.
[16] J. Gendell, J. H. Freed, and G. K. Fraenkel, *J. Chem. Phys.*, 1964, **41**, 949.
[17] A. Carrington and G. R. Luckhurst, *Mol. Phys.*, 1964, **8**, 401.
[18] A. D. Buckingham and E. G. Lovering, *Trans. Faraday Soc.*, 1962, **58**, 2077.

Secondly, the two nitrogen atoms account for over 70% of the unpaired electron (Table 2). The results are remarkably close to those for $N_2H_4^+$. This will arise in part because of the presence of regions of negative spin density in the three aromatic rings, but it does underline the similarity to the corresponding hydrazine molecule in which, conventionally and reasonably, the two nitogen atoms are depicted as having a major share of the "lone-pair" electrons. The third interesting aspect is that the 1,1-diphenyl-2-picrylhydrazyl radical is clearly a π-radical rather than a σ-radical. That an ambiguity sometimes arises has recently been stressed[19] and is underlined by a consideraton of the electronic rearrangement which occurs when the N–H bond of the corresponding hydrazine is broken. The unpaired electron could remain in the non-bonding σ-orbital, but in this instance one of the π-electrons moves into this orbital and there is a concomitant change of shape.

FIGURE 5. Two resonance structures of 1,1-diphenyl-2-picrylhydrazyl

TABLE 2

Spin populations of nitrogen atomic orbitals

Radical	Atom	a_s^2	a_p^2	a_p^2/a_s^2	Radical	Atom	a_s^2	a_p^2	a_p^2/a_s^2
$N_2H_4^+$	N	0·021	0·489	23·4	DPPH	N-1	0·014	0·387	27·6
$C_2(CN)_4^-$	N	0·0029	0·114	39·3		N-2	0·017	0·341	20·1

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[19] M. C. R. Symons, *J.*, 1963, 1189; 1965, 2276.