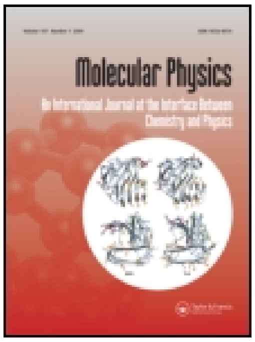


Molecular Physics

ISSN: 0026-8976 (Print) 1362-3028 (Online) Journal homepage: http://www.tandfonline.com/loi/tmph20

Electron spin resonance and bond structure of H_2CN

Donald Banks & Walter Gordy

To cite this article: Donald Banks & Walter Gordy (1973) Electron spin resonance and bond structure of H_2CN, Molecular Physics, 26:6, 1555-1559, DOI: 10.1080/00268977300102721

To link to this article: http://dx.doi.org/10.1080/00268977300102721

Published online: 23 Aug 2006.

Submit your article to this journal

Article views: 7

View related articles

Citing articles: 16 View citing articles

Full Terms & Conditions of access and use can be found at
http://www.tandfonline.com/action/journalInformation?journalCode=tmph20

Download by: [RMIT University Library] **Date:** 15 June 2016, At: 00:55

Molecular Physics, 1973, Vol. 26, No. 6, 1555–1559

Electron spin resonance and bond structure of H_2CN

by DONALD BANKS and WALTER GORDY
Department of Physics, Duke University, Durham, North Carolina 27706

(*Received* 21 *May* 1973)

Downloaded by [RMIT University Library] at 00:55 15 June 2016

E.S.R. evidence for the H_2CN radical has been obtained previously by Cochran, Adrian, and Bowers [1] in photolysed mixtures of HI and HCN in a rare gas matrix at low temperature. We have obtained confirming evidence by producing the radicals in a more direct manner and by observing E.S.R. patterns for D_2CN and HDCN which conform to those expected from CH_2CN. We also provide a more complete description of the molecular orbital of the unpaired electron.

The radicals were produced when gaseous hydrogen atoms (or those of the D isotope) at thermal velocities were allowed to impinge upon successive layers of solid HCN at 77 K. The sample was frozen on the quartz tip of a liquid air flask which without warming or exposure to air or other gases could be inserted into the resonance cavity of an X-band (9·3 GHz) E.S.R. spectrometer. The atoms were produced by an electric discharge through hydrogen gas at a flow pressure of approximately 0·1 torr. Both H and D isotopes were employed. A description of the apparatus will be given elsewhere.

Hydrogen atoms were found to add directly to the carbon of the hydrogen cyanide to produce the H_2CN radical. The top curve of figure 1 is the second derivative of its E.S.R. absorption. The splitting of the resonance into a prominent triplet having component spacing of 91 G is due to the nuclear coupling of the two hydrogens. The triplet pattern with intensity ratios 1 : 2 : 1, approximately, proves that the couplings of the two hydrogens are equivalent. The sharpness of the triplet peaks indicates that the proton coupling is essentially isotropic. That this splitting is due to proton coupling is confirmed by the alternate bombardment with D atoms to produce HDCN and also some D_2CN radicals. The observed changes in the pattern were exactly those expected for the change in spin and magnetic moment of D from those of H. Figure 2 shows the second derivative E.S.R. for the deuterium-bombarded HCN samples with theoretical patterns for D and H hyperfine structure. The strong D_2CN component indicates appreciable substitution of D for H in the sample.

The E.S.R. of H_2CN was found also to have hyperfine structure arising from the ^{14}N nucleus. Because it is strongly anisotropic, this structure could not be resolved for the poly-oriented radicals in the samples. Nevertheless, values of the ^{14}N coupling were derived from the characteristic bend points in the unresolved patterns. The features of the ^{14}N hyperfine structure are most clearly revealed in the first-derivative presentation of the E.S.R. given in figure 1 (middle curve). Analysis of these features, described below, revealed that the coupling is axially symmetric, as would be expected from the *p*-orbital spin density on the nitrogen.

Downloaded by [RMIT University Library] at 00:55 15 June 2016

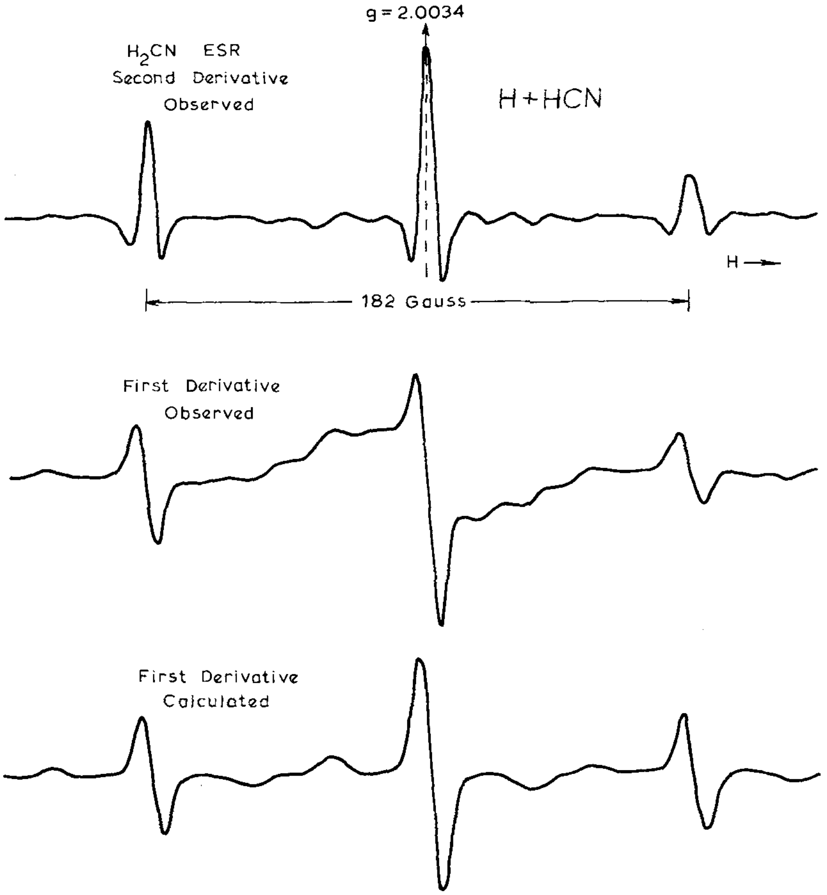


Figure 1. First and second derivative E.S.R. curves of the H_2CN observed at $\nu_0 = 9257$ MHz and 77 K in the HCN matrix.

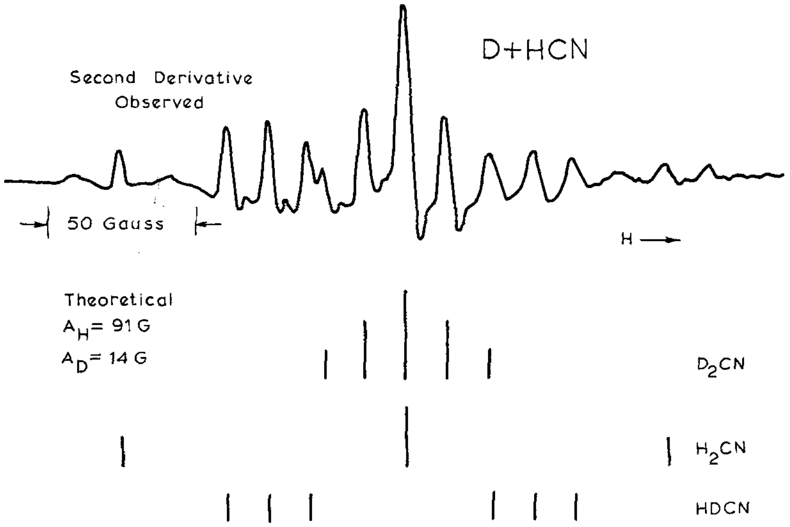


Figure 2. Second derivative E.S.R. of radicals produced by interaction of D atoms with HCN at 77 K.

From the shape and spread of the ^{14}N hyperfine structure we can obtain the coupling constants and spin density on the ^{14}N. For an orientation θ of the applied magnetic field with the axis of the coupling p orbital, the shift in magnetic field units at constant frequency caused by the ^{14}N coupling is expressed adequately by the formula :

$$\Delta B = M_I \sqrt{[(A_{\parallel}^2 - A_{\perp}^2)\cos^2\theta + A_{\perp}^2]}, \qquad (1)$$

where for $I=1$ for ^{14}N, $M_I=0, \pm 1$. In this formula the coupling constants A are expressed in magnetic field units ; if A^* denotes the corresponding constant in frequency units, then $A = hA^*/g\mu_B$, where g is observed to have the nearly isotropic value 2·003. The ^{14}N has an isotropic A_f component caused by a slight s orbital spin density and an anisotropic component B caused by a large p orbital spin density on the N. It is easy to show that

$$A_{\parallel} = A_f + 2B, \qquad (2)$$

$$A_{\perp} = A_f - B, \qquad (3)$$

where $A_{\parallel}$ represents the principal element of the coupling tensor (in field units) for the symmetry axis and where $A_{\perp}$ represents that perpendicular to this axis. Structural considerations described below indicate that the coupling symmetry axis is in the molecular plane and perpendicular to the CN bond.

For the polycrystalline sample, the shape of the ^{14}N hyperfine pattern caused by anisotropy in the coupling tensor alone is obtained from a plot of the relative numbers of radicals with orientation in different elements of solid angle represented by $2\pi r \sin\theta(r\,d\theta)$ as a function of the corresponding change in ΔB with θ. This shape function can be expressed in the form :

$$S(\Delta B) = M_I K / \sqrt{\{(A_{\parallel}^2 - A_{\perp}^2)[1 - (A_{\perp}/\Delta B)^2]\}} \qquad (4)$$

where K is a constant. It gives the spread of the different M_I components exclusive of the normal line shape caused by other factors. It is evident that the central component corresponding to $M_I=0$ will have no distortion or spread due to the coupling anisotropy. This component has the normal line shape and width of approximately 6 G as measured for the strong central component. The heights of the $M_I = \pm 1$ components were determined by equalization of the area of each to that for the central $M_I=0$ component.

The bottom curve of figure 1 represents the first derivative of the resulting E.S.R. with the g factor and proton hyperfine structure assumed to be isotropic and with the shape of the ^{14}N hyperfine multiplets determined in the manner described. The agreement with the observed first-derivative curve is satisfactory except for the central region where there is apparently a weak absorption by a second radical, probably CN. The various coupling constants and spin densities resulting from the analysis are listed in the table. The couplings obtained in the earlier work [1], 87·4 G for H and $A_f = B = 11{\cdot}4$ G for ^{14}N, agree well with these values obtained in a different matrix and at a different temperature.

The spin densities are obtained from division of the coupling for a particular orbital by the known atomic coupling for a spin density of unity in that orbital. The following atomic couplings [2] were employed : for H, $A_s = 508$ G ; for ^{14}N, $A_{2s} = 549$ G and $B_{2p} = 17{\cdot}1$ G It is interesting that the spin densities on the two hydrogens, 0·18 on each, and that on the nitrogen, 0·64, add to unity. This

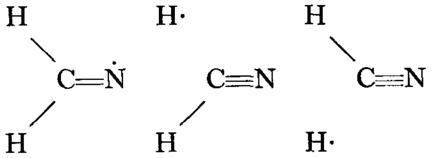
Downloaded by [RMIT University Library] at 00:55 15 June 2016

indicates that the carbon has a very small spin density, if any at all. A small amount of negative spin density is expected on the carbon from spin polarization of the σ bond by the π orbital spin density on N. Although this spin polarization does not diminish the spin density of the π orbital, it is believed to account mostly for the small, 0·02, positive s spin density on the N which gives rise to the observed A_f for ^{14}N.

	Coupling constant					
	A_f		B			
Atom	G	MHz	G	MHz	Spin density	
H	91	255	~0		0·18	1s
D	14	39	~0		0·18	1s
^{14}N	11	31	11	31	0·02	2s
					0·64	2p

Nuclear couplings and electron spin densities in the H_2CN radical.

From the spin density distribution of the unpaired electron and reasonable assumptions about the bonding, the molecular symmetry and bond structure of the radical can be obtained. The very large equivalent hyperconjugative coupling to the protons indicates that the two CH bonds must be in the same, or very nearly the same, plane as the π orbital of the unpaired electron. A π electron would not hyperconjugate with a CH bond in an orthogonal plane. This means that the radical must be planar, or approximately so, and that the p orbital of the N having the electron spin density must be in this plane, with its axis perpendicular to the CN bond, if there is to be equivalent coupling to the two protons. These considerations indicate that the radical has C_{2v} symmetry. The C forms three σ bonds with sp_2 hybrids in the molecular plane, which we shall designate as the yz plane with z along the CN bond. The remaining valence orbital of C, a p_x orbital, is employed for forming a π_x bond with the p_x orbital of N. The orbital of the unpaired electron is a π_y orbital in the molecular plane formed by hyperconjugation of the p_y of N with the two σ CH bonds. The hyperconjugation gives appreciable π_y bonding to CN while reducing the bond order of the CH bonds below unity. In valence bond parlance, the radical can be regarded as a hybrid of the structures :



64 per cent 18 per cent 18 per cent

The CN bond thus has approximately $0{\cdot}36\pi_y$ character with a total π bond character $(\pi_x+\pi_y)$ of about 1·36.

The amount of hyperconjugation in H_2CN is exceptionally large. Proton couplings by π electrons, of which there are now many known examples, are

Downloaded by [RMIT University Library] at 00:55 15 June 2016

usually in the range of 20 to 40 G, or less. We are not aware of any other observed π orbital coupling to protons as large as that in H_2CN. The comparably large proton coupling found in HCO and in $HCCH_2$ occur with the unpaired electrons in σ orbitals [2].

From its symmetrical structure and large amount of π bonding achieved by the unpaired electron, one would conclude that the H_2CN radical should be sufficiently stable to be observed in the gaseous state. The radical might be detectable in interstellar space. Attempts will be made in this laboratory to observe its microwave rotational spectrum.

This work was supported by a grant from the U.S. Army Research Office (Durham), No. DA-ARO-D-31-124-72-G96.

Downloaded by [RMIT University Library] at 00:55 15 June 2016

REFERENCES

[1] COCHRAN, E. L., ADRIAN, F. J., and BOWERS, V. A., 1962, *J. chem. Phys.*, **36**, 1938.

[2] WERTZ, JOHN E., and BOLTON, JAMES R., 1972, *Electron Spin Resonance : Elementary Theory and Practical Applications* (McGraw-Hill).