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Microwave Spectrum, Structure, and Dipole Moment of Diazoacetonitrile

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The microwave spectra of the normal species and of three isotopic species of diazoacetonitrile, $N_2:CH\cdot CN$, have been investigated between 14 and 31 kMc/sec. The following parameters have been obtained: $r_s(C\equiv N)=1.165\pm0.005$, $r_0(C\text{–}H)=1.082\pm0.004$ (assumed), $r_0(C\text{–}C)=1.424\pm0.006$, $r_0(C{=}N)=1.280\mp0.010$, $r_0(N\equiv N)=1.132\pm0.010$ Å; $\angle HCC=117°\pm1°30'$, $\angle CCN=119°32'\pm30'$. The data are consistent with a planar model. The spectra of molecules in the first and second excited states of a low-frequency in-plane bending vibration have been observed ($\nu=150\pm30$ cm^{-1}). Least-squares analysis of the spectrum of the normal species yields the centrifugal-distortion constants $D_J=1.55\pm0.5$ kc/sec, $D_{JK}=-89.73\pm2$ kc/sec. The dipole-moment components obtained are $\mu_a=2.75\pm0.06$, $\mu_b=2.08\pm0.04$ D giving a resultant dipole moment of 3.45 ± 0.07 D at an angle of $37°6'\pm30'$ to the a axis.

I. INTRODUCTION

THE only molecule containing a diazo group so far studied by the microwave technique is diazomethane, CH_2N_2.[1,2] The technique is, however, particularly well suited to the study of simple (unstable) diazo compounds because of the small quantities needed. Diazoacetonitrile, $N_2:CH\cdot CN$, which differs from diazomethane in that one hydrogen atom has been replaced by a nitrile group, is a typical molecule of this type. Its preparation and properties were first investigated by Curtius[3] who found it to be an orange-yellow oily liquid boiling at 46.5°C (15 mm of Hg). He found that when isolated it is liable to explode violently.

Since it contains both a cyano group and a diazo group, diazoacetonitrile is expected to have a dipole moment somewhere between that of diazomethane (1.5 D, Ref. 2) and that of vinyl cyanide (3.89 D, Ref. 4). A strong spectrum was therefore expected provided that sufficient material could be kept in the cell without decomposition. Since no dipole-moment measurements have been made for this molecule, the Stark effects are of some importance. From a structural point of view it would be interesting to compare the various bond lengths and angles with those obtained in similar molecules. Such comparisons may yield information regarding the interaction, if any, of the $C\equiv N$ and $C{=}N\equiv N$ groups and the effect of such interaction on the C–H bond.

II. EXPERIMENTAL

The diazoacetonitrile was prepared at these laboratories by Merer and Travis for a flash-photolysis study[5] using the method of Dewar and Petit.[6]

Methylene aminoacetonitrile, $CH_2:N\cdot CH_2CN$, prepared from formaldehyde, potassium cyanide, and ammonium chloride, was agitated for three hours with HCl to give aminoacetonitrile hydrochloride, $NH_3^+\cdot CH_2\cdot CN\cdot Cl^-$. This material was then diazotized to give diazoacetonitrile which was extracted from its aqueous solution using a suitable solvent, washed with sodium bicarbonate solution and dried over sodium sulfate. For the microwave studies, dibutylphthalate was used as a solvent because of its very low vapor pressure. The ^{13}C and ^{15}N isotropic modifications were prepared (also by Merer and Travis) using $K^{13}CN$ and $KC^{15}N$ as starting materials. The deuterated species was easily made by shaking up the normal species in dibutylphthalate with a solution of NaOD in D_2O. About 50%–60% exchange was effected in this way.

No attempt was made to separate the diazoacetonitrile from the solvent. Instead a flow system was employed in which the diazoacetonitrile was pumped directly out of the solution into the cell. The solution was cooled to about −10°C to reduce the vapor pressure of the solvent. The best spectrum was obtained at cell temperatures between about −30° and −40°C. At room temperature, decomposition was rapid while at dry-ice temperature the vapor pressure was insufficient for the spectrum to be detected.

The spectrometer used was a conventional, 85-kc/sec Stark-modulated instrument described previously.[7] Because of line broadening due to quadrupole effects, frequencies could only be measured to within ±0.1 Mc/sec. Stark voltage measurements were made using a potentiometric dc voltmeter and the Stark cell was calibrated using the $J=2\leftarrow1$ line of $^{16}O^{12}C^{32}S$.

III. OBSERVED SPECTRA

Lines between 14 and 31 kMc/sec have been observed comprising a- and b-type transitions for the normal species and for three isotopic species, viz.,

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Table I. Lines observed in the spectrum of diazoacetonitrile.

Transition	N$_2$CHCN $v=0$	N$_2$CHCN Obs−calc	N$_2$CHCN $v=1$	N$_2$CHCN $v=2$	N$_2$CDCN	N$_2$CHC^{15}N	N$_2$CH^{13}CN
			($^aR_{0,1}$ Lines).				
$3_{13}\leftarrow 2_{12}$	16 845.0	(−0.10)	16 891.8	16 938.2			
$3_{03}\leftarrow 2_{02}$	17 270.0	(−0.06)	17 329.2	17 385.3			
$3_{21}\leftarrow 2_{20}$	17 290.7	(−0.63)	17 348.1	17 407.7			
$3_{22}\leftarrow 2_{21}$	17 282.5	(0.73)	17 340.8	17 398.7			
$3_{12}\leftarrow 2_{11}$	17 712.3	(0.07)	17 781.8	17 850.8			
$4_{14}\leftarrow 3_{13}$	22 456.9	(−0.27)	22 519.7	22 581.2	22 156.9	21 844.7	22 278.3
$4_{04}\leftarrow 3_{03}$	23 015.3	(−0.13)	23 091.9	⋯	⋯	⋯	22 827.9
$4_{23}\leftarrow 3_{22}$	23 040.4	(0.07)	23 118.0	23 195.2	22 840.5	22 402.0	22 852.6
$4_{31}\leftarrow 3_{30}$ $4_{32}\leftarrow 3_{31}$	23 051.2	(0.64)	23 128.5	23 206.0	22 854.8	⋯	22 862.7
$4_{22}\leftarrow 3_{21}$	23 064.2	(−0.02)	23 142.6	23 220.6	22 880.6	22 424.0	22 875.4
$4_{13}\leftarrow 3_{12}$	23 613.2	(−0.15)	23 705.5	23 798.3	23 511.2	22 949.9	23 416.4
$5_{15}\leftarrow 4_{14}$	28 066.7	(−0.04)	28 144.5	⋯			
$5_{05}\leftarrow 4_{04}$	28 750.9	(−0.23)	⋯	⋯			
$5_{24}\leftarrow 4_{23}$	28 797.4	(0.25)	28 894.3	⋯		27 999.6	
$5_{23}\leftarrow 4_{22}$	28 845.1	(0.20)	28 943.5	⋯		28 043.6	
$5_{32}\leftarrow 4_{31}$ $5_{33}\leftarrow 4_{32}$	28 814.9	(−0.26)	⋯	⋯			
$5_{42}\leftarrow 4_{41}$ $5_{41}\leftarrow 4_{40}$	28 818.3	(−0.24)	⋯	⋯			
$5_{14}\leftarrow 4_{13}$	29 512.1	(0.22)	29 627.4	⋯			
			(^bQ and ^bR Lines)				
$1_{10}\leftarrow 1_{01}$	26 365.4	(−0.15)	26 759.6	27 149.6	21 644.5	26 111.3	26 373.0
$2_{11}\leftarrow 2_{02}$	26 656.9	(−0.44)	27 059.8	⋯	21 987.5	26 390.7	⋯
$3_{12}\leftarrow 3_{03}$	27 099.5	(0.00)	27 513.6	27 922.7	22 508.4	26 812.7	27 095.0
$4_{13}\leftarrow 4_{04}$	27 697.9	(0.48)	28 127.0	⋯			27 682.8
$5_{14}\leftarrow 5_{05}$	28 458.6	(0.43)	⋯	⋯			
$7_{16}\leftarrow 7_{07}$	30 504.5	(−0.41)	⋯	⋯			
$1_{11}\leftarrow 2_{02}$	14 559.2	(0.11)	⋯	⋯			
$7_{07}\leftarrow 6_{16}$	16 863.0	(0.00)	⋯	⋯			

N_2:CD·CN, N_2:CH·^{13}CN, and N_2:CH·C^{15}N. The measured lines are given in Table I.

Lines due to molecules in the first and second excited states of a low-frequency deformation mode have been observed for the normal species. Although by comparison with the work on $CH_2(CN)_2$[8] and $S(CN)_2$[9] it was thought that several other low-lying vibrational levels should exist in such a molecule, no other vibrational satellites were definitely identified. Such lines were difficult to observe because of the rich background spectrum of weak dibutylphthalate lines. Further, the temperature variation method of identifying vibrational satellites was inapplicable because of the relatively unstable nature of the material.

A search for lines due to the species N_2:^{13}CH·CN in natural abundance also proved fruitless.

The quadrupole-coupling pattern is complicated since there are three nitrogen atoms present in the molecule. As expected, none of these patterns were resolved.

The μ_a and μ_b lines in the spectrum were found to be roughly equal intensity for the same J quantum numbers. The two dipole-moment components must therefore be of about the same magnitude.

Table II. Summary of rigid-rotor constants obtained for diazoacetonitrile.[a]

Species	Vibrational state	A_0 (Mc/sec)	B_0 (Mc/sec)	C_0 (Mc/sec)	$I_A{}^0$ (u·Å^2)	$I_B{}^0$ (u·Å^2)	$I_C{}^0$ (u·Å^2)	Δ (u·Å^2)
N_2:CH·CN	$v=0$	29 100.8	3 024.53	2 735.43	17.3664	167.0923	184.7515	0.293
	$v=1$	29 501.1	3 038.92	2 741.47	17.1307	166.3559	184.3449	0.859
	$v=2$	29 896.8	3 051.50	2 747.23	16.9040	165.6152	183.9583	1.439
N_2:CD·CN	$v=0$	24 330.5	3 024.56	2 685.95	20.7713	167.0901	188.1551	0.294
N_2:CH·^{13}CN	$v=0$	29 087.2	2 998.77	2 714.23	17.3745	168.5276	186.1950	0.293
N_2:CH·C^{15}N	$v=0$	28 773.4	2 938.37	2 662.05	17.5640	171.9916	189.8443	0.289

[a] Conversion factor $B\times I=505\ 375$ Mc/sec·u·Å^2, based on ^{12}C=12.000000 u [unified atomic mass unit, Phys. Today **17**, No. 2, 48 (1964)].

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IV. ROTATIONAL CONSTANTS AND CENTRIFUGAL DISTORTION

Rotational constants B_0 and C_0 in the ground state were determined for all four species from the $J=4\leftarrow3$, $K_{-1}=1$ transitions assuming a rigid-rotor model. A_0 was subsequently obtained from the μ_b transition $1_{10}\leftarrow1_{01}$ which for a rigid rotor is given simply by $\Delta W=A_0-C_0$. For the $v=1$ and $v=2$ levels of the low-frequency bending vibration the constants were calculated in the same manner. In Table II the rotational constants, moments of inertia, and inertial defects so obtained are given. The rotational constants for the normal species differ by up to 0.05 Mc/sec from those obtained when centrifugal distortion is included (next paragraph), but for the determination of the structure it is important to use a consistent set of values.

Insufficient data are available from the observed spectrum for the determination of the asymmetric-rotor centrifugal-distortion constants. Further, because of the large value of A_0 (Table II) no $K_{-1}=2\leftarrow1$ transitions could be observed and the determination of D_K is impossible. The constants D_J and D_{JK} have, however, been determined by a least-squares fit of the spectrum to the asymmetric-rotor expression containing only these two distortion constants. This process has been adapted for computation using the IBM 360 computer by J. E. Parkin. The constants obtained for the normal species were $D_J=1.55\pm0.5$ kc/sec and $D_{JK}=-89.73\pm2$ kc/sec and the corrected rotational constants were $A_0=29\,100.8$, $B_0=3024.48$, and $C_0=2735.45$ Mc/sec. Using these constants, the observed line frequencies were reproduced with a rms deviation of 0.31 Mc/sec. The observed − calculated values are listed in Table I. For the isotopically modified species, insufficient transitions were measured for D_J and D_{JK} to be computed. For this reason the uncorrected rotational constants given in Table II have been used to calculate the molecular structure. It should be emphasized that, although the constants given above improve the fit to the observed frequencies, the symmetric-top approximation with regard to the centrifugal distortion is not strictly justified.

TABLE III. Stark coefficients and dipole-moment components for diazoacetonitrile.

(Ground state, normal species)

Transition	Component	$(\Delta\nu/E^2)[\text{Mc/sec}(\text{V/cm})^{-2}]\times10^4$	
		Observed	Calculated
$1_{10}\leftarrow1_{01}$	$M=0$	···	−1.2573
	$M=1$	15.77	15.8046
$2_{11}\leftarrow2_{02}$	$M=0$	···	0.2646
	$M=1$	0.7120	0.8753
	$M=2$	2.7419	2.7023
$3_{12}\leftarrow3_{03}$	$M=0$	···	0.0932
	$M=1$	0.2467	0.1879
	$M=2$	0.4934	0.4720
	$M=3$	0.9559	0.9455
$4_{13}\leftarrow3_{12}$	$M=0$	···	−0.0098
	$M=1$	−0.0862	−0.0693
	$M=2$	−0.2265	−0.2477
	$M=3$	−0.4624	−0.5450
$4_{14}\leftarrow3_{13}$	$M=0$	−0.6276	−0.6494
	$M=1$	···	−0.5525
	$M=2$	−0.2985	−0.2617
	$M=3$	···	0.2227

$\mu_a=2.75\pm0.06$ D
$\mu_b=2.08\pm0.04$ D
$\mu=3.45\pm0.07$ D

V. STARK EFFECTS AND DIPOLE MOMENT

Most of the lines examined showed large second-order Stark effects. For transitions of low J the effects were large enough to make them very useful when searching for the identifying weak vibrational satellites since the underlying solvent lines did not have large Stark effects. The Stark coefficients for the lines considered are given in Table III. These coefficients were used to obtain the dipole-moment components, $\mu_a=2.75\pm0.06$, $\mu_b=2.08\pm0.04$, $\mu=3.45\pm0.07$ D using an IBM 1620 program written by Brooks of Ohio University.[10] The calculated Stark coefficients are given for comparison in Table III.

An interesting Stark effect was found for the $4_{14}\leftarrow3_{13}$ line at 22 456.9 Mc/sec in the normal species. Although one would expect the $K_{-1}=1$ lines of a near prolate top to have Stark coefficients of opposite signs, it was found that for the $J=4\leftarrow3$ branch both the lines had negative coefficients (see Table III). The Stark coefficients for the $4_{14}\leftarrow3_{13}$ line are negative (except for $M=3$) because the 3_{13} and 4_{04} levels and the 4_{14} and 5_{05} levels are nearly degenerate. These pairs of levels are connected by μ_b elements in the Stark energy matrix although the line itself arises through μ_a selection rules. A similar situation is found for the ^{13}C and ^{15}N species but in the deuterated species there is a large drop in A_0 and therefore the degeneracy no longer occurs.

Figure 1 shows the direction of the resultant dipole moment.

VI. DETERMINATION OF THE STRUCTURE

Unlike the problem of a nonplanar structure, which can be proved, a planar structure can only be deduced from evidence consistent with a planar structure, and from the absence of any contrary evidence. For all species of diazoacetonitrile investigated, the inertial defect, $\Delta=I_C{}^0-I_B{}^0-I_A{}^0$, is positive and there is little variation with isotopic modification, (Table II). These observations are all consistent with a strictly planar structure.

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[10] W. V. F. Brooks, Proc. Intern. Symp. Mol. Struct. Spectry., State University of Ohio, Columbus, Ohio, 1965, Paper (Y12) (to be published).

TABLE IV. Comparison of parameters for N_2CHCN with those in similar molecules.

Molecule	r(C–H)	r(C–C)	r(C≡N)	r(C=N)	r(N≡N)	∠HCC	∠HCN	Ref.
CH_2N_2	1.078	···	···	1.300	1.139	···	116°54′	2, a
CH_2CHCN	1.086_8	1.425_6	1.163_7	···	···	115°39′	···	7
N_2CHCN	1.082±0.004	1.424±0.006	1.165±0.005	1.280∓0.010	1.132±0.010	117°±1°30′	123°28′±30′	···

[a] A. P. Cox (private communication).

The coordinates of the three atoms for which isotopic substitutions have been made can be determined by using Kraitchman's equations[11] for a rigid planar molecule. In the present study the fairly common difficulty arises of determining the coordinates of atoms near a principal axis (more correctly, near a principal plane). The **b** coordinate of the $C_{(2)}$ atom in the C≡N group is found to be 0.091 Å, and the **a** coordinate of the H atom is imaginary with $\Delta I_B{}^0 = -0.0021$ u·Å². The errors in these coordinates can only be estimated by comparison of known errors in simple molecules, and the results for the substitution of ^{15}N on the central atom of N_2O provide a useful calibration.[12] These results predict an error of 0.012 Å in the **b** coordinate of the $C_{(2)}$ atom, but it is thought best to use this value as a measure of the uncertainty and not as a correction.

The errors in N_2O arise from a zero-point "defect" in $\Delta I_B{}^0$ of -0.0024 u·Å² for the ^{15}N substitution, and there are many examples of a similar decrease in I^0 when the substitution is known from symmetry to be on a principal axis. For the H atom it is thought that realistic limits on the **a** coordinate would be $a_H = 0.025 \pm 0.025$ Å.

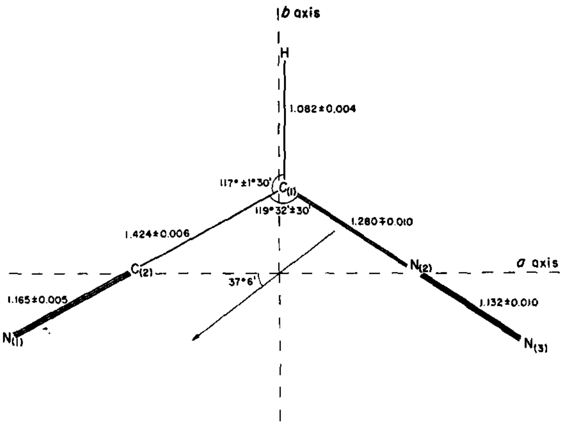

FIG. 1. The structure of diazoacetonitrile showing the principal axes.

Six equations are required to solve for the six coordinates of the three remaining atoms. Since the central atom, $C_{(1)}$, will be very close to the B axis, it is best not to use the equation for $I_B{}^0$. This leaves the equations $\sum m_i a_i = 0$, $\sum m_i b_i = 0$, $\sum m_i b_i = 0$, $I_A{}^0 = \sum m_i b_i^2$. In addition, it would seem resonable to assume the linearity of the C=N≡N chain. Further, this constraint is useful in that it reduces the uncertainty in the small **b** coordinate of the $N_{(2)}$ atom (see Fig. 1). The large deviation from linearity found for $S(CN)_2$[9] and $CH_2(CN)_2$[8] makes it inadvisable to impose a linearity constraint on the C–C≡N chain. Instead, the sixth equation was obtained by the assumption of a C–H bond-length intermediate between those found in diazomethane (1.078 Å) and vinyl cyanide (1.086 Å). Thus taking r_0(C–H) = 1.082±0.004 Å and r_s(C≡N) = 1.165 Å and using the coordinates and equations above, the following parameters are obtained:

$$r_0(\mathrm{C{-}C}) = 1.424 \pm 0.006\ \text{Å},$$

$$r_0(\mathrm{C{=}N}) = 1.280 \mp 0.021\ \text{Å},$$

$$r_0(\mathrm{N{\equiv}N}) = 1.132 \pm 0.020\ \text{Å},$$

$$\angle \mathrm{CCN} = 119°32' \pm 30',$$

$$\angle \mathrm{HCC} = 117° \pm 1°30'.$$

The bend in the C–C≡N chain is less than 1° and therefore little physical significance may be attached to it.

Comparison of the bond lengths obtained here with those obtained for diazomethane[2] shows that a variation in the N≡N bond length between 1.112 and 1.152 Å is unreasonable. The uncertainties in the N≡N and C=N bond lengths were therefore reduced to ±0.010 Å and the final structure is given in Table IV. The relevant parameters for diazomethane and vinyl cyanide are included for comparison purposes.

Substitution of a $^{13}C_1$ atom (Fig. 1) would give a unique value to the **b** coordinate of this atom, but since $\Delta I_B{}^0$ would be very small (~0.003 u·Å²), the rather large uncertainties in the r_0(C=N) and r_0(N≡N) values would remain.

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[11] J. Kraitchman, Am. J. Phys. 21, 17 (1953).
[12] C. C. Costain, J. Chem. Phys. 29, 864 (1958).

VII. DISCUSSION

Although the errors are too great to enable detailed conclusions with respect to the individual C=N and N≡N bond lengths, it is evident from Table IV that the C=N≡N chain length is shorter than that found in CH_2N_2. Further, the ∠HCN(123.5°) is larger than the corresponding ∠HCN in CH_2N_2(117°) by much more than could be accounted for by the experimental uncertainty. It is apparent therefore that there is considerable interaction between the C≡N and the C=N≡N groups.

There is the question as to whether the C≡N bond length reflects this interaction. The experimental value is only slightly more than the vinyl cyanide value, but it is at least 0.006 Å longer than the "normal" r_s(C≡N) bond, for which 1.157 Å for CH_3CN[12] and 1.159 Å for $(CH_3)_3CN$[13] are typical examples. A strong interaction from the C≡N bond is therefore possible, particularly since Mulliken[14] estimates that a 0.005 Å elongation of triple bond can make significant contributions to the bonding in the rest of the molecule.

In $S(CN)_2$ where the ∠CSC angle[9] is about 98° it is found that the S–C≡N chains are bent by some 5°. However, in $CH_2(CN)_2$ where the ∠CCC angle[15] is about 110° the C–C≡N chains are bent by approximately 3°. Assuming that such bending is caused by interaction of the two π-electron systems, then the 1° bend found in N_2:CH·CN is consistent with a ∠CCN angle of 119°32′.

As mentioned previously, the evidence available indicates that the molecule is planar. The central carbon $C_{(1)}$ must be approximately sp^2 hybridized and thus must have coplanar-bonding molecular orbitals associated with it.

The problem of assigning the low-frequency deformation mode is a considerable one, especially in the absence of any other identified levels, and since no infrared or Raman spectra have so far been published. Because of the background of solvent lines there is considerable uncertainty involved in the determination of the frequency of this mode. A value of 150±30 cm^{-1} is obtained from the relative-intensity data obtained for 11 transitions. The value of 2ν is 280±50 cm^{-1}.

From the α_A, α_B, and α_C values of -400.3, -13.7, -6.1, and -395.9, -13.4, -5.9 (all in megacycles per second) obtained from the first and second excited states it is evident that the vibration is nearly harmonic. The large positive Δ for the normal species in the excited states of this lowest frequency vibration indicates that this vibration is "in-plane."[16] By analogy with the results obtained for $S(CN)_2$[9] and $CH_2(CN)_2$[8] it seems reasonable to assign the level at 150±30 cm^{-1} to a mode involving the bending of the NNCCN chain.

Since the measured I_B^0 values could not be used in order to solve for the unknown coordinates one would not expect the coordinates obtained to reproduce exactly the measured moments of inertia. Using r_0(C–H) = 1.082 Å the I_B^0 values calculated for the four isotopic species N_2CHCN, N_2CDCN, $N_2CH^{13}CN$, and $N_2CHC^{15}N$ are 166.2910, 166.2937, 167.7655, and 171.2590 u·Å^2, respectively. These may be compared with the measured values quoted in Table II.

ACKNOWLEDGMENTS

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