The Microwave Spectrum of Aminoacetonitrile

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Summary Microwave-spectroscopic studies on NH_2CH_2CN, $NHDCH_2CN$, and ND_2CH_2CN indicate that the amino and methylene groups adopt the *trans*-orientation with respect to each other.

SHERIDAN and his co-workers[1] have established that in the gas phase the predominant conformation of prop-2-ynylamine is that in which the amino and methylene groups adopt the relative *trans*-configuration (see Figure). Microwavespectroscopic evidence for a similar situation existing for the related molecule aminoacetonitrile is presented here. We have measured μ_a, R-branch transitions for the species NH_2CH_2CN, $NHDCH_2CN$, and ND_2CH_2CN, and for the first two μ_b, Q-branch series (Table 1). All measurements were made in a Stark modulation spectrometer at room temperatures. Samples of NH_2CH_2CN were prepared by the method outlined by Adams and Langley[2] and the deuteriated substances formed directly in the waveguide cell by exchange with D_2O vapour.

TABLE 1. *Measured line frequencies for aminoacetonitrile* (MHz)

	NH_2CH_2CN	$NHDCH_2CN$	ND_2CH_2CN
$1_{01} \leftarrow 0_{00}$	9071·87	8820·17	
$2_{02} \leftarrow 1_{01}$	18137·61	17633·58	
$2_{12} \leftarrow 1_{11}$	17693·57		
$2_{11} \leftarrow 1_{10}$		18082·69	
$3_{03} \leftarrow 2_{02}$	27191·56	26434·43	25736·18
$3_{13} \leftarrow 2_{12}$	26536·60	25792·01	25123·09
$3_{12} \leftarrow 2_{11}$	27887·14	27120·16	26391·95
[a]$3_{22} \leftarrow 2_{21}$	27217·06	26462·46	25764·82
[a]$3_{21} \leftarrow 2_{20}$	27238·67	26484·87	25786·43
$4_{04} \leftarrow 3_{03}$	37227·27	35215·92	34284·97
$4_{14} \leftarrow 3_{13}$	35374·63	34382·06	33490·31
$4_{13} \leftarrow 3_{12}$	37175·21	36152·11	35181·19
$4_{23} \leftarrow 3_{22}$	36283·73	35276·37	34344·91
$4_{22} \leftarrow 3_{21}$	36324·37	35339·12	34408·59
$4_{32} \leftarrow 3_{31}$ $4_{31} \leftarrow 3_{30}$	36302·17		34364·97
$1_{10} \leftarrow 1_{01}$	25935·46	23391·83	
$2_{11} \leftarrow 2_{02}$	26391·53	23841·41	
$3_{12} \leftarrow 3_{03}$	27087·14	24526·46	
$4_{13} \leftarrow 4_{04}$	28035·21	25462·45	
$5_{14} \leftarrow 5_{05}$	29252·73	26667·65	
$6_{15} \leftarrow 6_{06}$	30760·84	28163·63	
$7_{16} \leftarrow 7_{07}$	32583·51	29976·84	
$8_{17} \leftarrow 8_{08}$	34747·95	32134·23	

[a] These line frequencies for all the species are the least well fitted by the constants of Table 2. Their measurement may be uncertain to *ca.* ±2 MHz as a result of inexact zero-basing of the Stark modulation voltage.

All three rotational constants are obtainable to good precision for NH_2CH_2CN and $NHDCH_2CN$, but only the B and C constants are well determined for ND_2CH_2CN from the lines measured. In deriving values for the rotational constants, allowance has been made for centrifugal distortion, but the parameters describing this phenomenon are not well determined in this case. Consequently the values D_J, D_{JK}, and δ_J quoted in Table 2 with the rotational constants should only be taken to indicate their orders of magnitude.

TABLE 2. *Rotational constants and centrifugal distortion constants* (MHz).

	NH_2CH_2CN	$NHDCH_2CN$	ND_2CH_2CN
A	30245·98	27580·45	
B	4761·04	4631·34	4505·17
C	4310·77	4188·68	4082·09
D_J	$0{\cdot}00_3$	$0{\cdot}00_3$	$0{\cdot}00_4$
D_{JK}	$-0{\cdot}05_4$	$-0{\cdot}05_2$	$-0{\cdot}06_4$
δ_J	$0{\cdot}00_1$	$0{\cdot}00_1$	$0{\cdot}00_2$

The observation of only one spectral species for $NHDCH_2CN$ and the substitution co-ordinates of the amine hydrogen atoms ($a = 1{\cdot}541$ Å, $b = 1{\cdot}006$ Å, $c = 0{\cdot}814$ Å) provide clear evidence that the preferred conformation here is that with the amino group in a *trans*-orientation with respect to the methylene group. This conclusion is strengthened by the observation of the ^{14}N quadrupole fine structure pattern for the $1_{01} \leftarrow 0_{00}$ transition of NH_2CH_2CN. This pattern is very similar to that observed[3] in $HOCH_2CN$ where χ_{aa} is negative and is consistant with the χ_{aa} values for both nitrogen atoms in NH_2CH_2CN being negative as would be expected for the *trans*-conformation. In contrast to the case of $HOCH_2CN$, no very strong vibrational satellites associated with internal motions of the NH_2 group in this case are found to accompany the ground-state lines. Stark-effect measurements on selected transitions yield the following dipole moment components in NH_2CH_2CN: $\mu_a = 2{\cdot}55 \pm 0{\cdot}02D$, $\mu_b = 0{\cdot}30 \pm 0{\cdot}02D$, and the total dipole moment as $2{\cdot}57 \pm 0{\cdot}03D$.

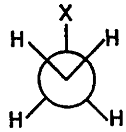

FIGURE. trans-*Form viewed along the amino* N–C *bond:* X = C≡C–H *or* C≡N

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[3] J. K. Tyler and D. G. Lister, *Chem. Comm.*, 1971, 1350.