The Relative Orientation of the Total Dipole Moment in the N-cis Lone-Electron-Pair-Trans Isomer of Allylamine

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The dipole moment of the doubly deuterated species ($CH_2{=}CH{-}CH_2{-}ND_2$) of N-cis Lone-electron-pair isomer of allylamine has been measured. The "isotope pulling effect" has been used to determine the relative orientation of the total dipole moment with respect to the principal axes in the normal species. The possible effects of large amplitude motions on the observed effective dipole moments are discussed.

Introduction

The molecule allylamine ($CH_2{=}CH\text{-}CH_2\text{-}NH_2$) has been observed with high resolution spectroscopy in four different rotameric forms. Three rotamers possess no symmetry [1 – 4], and only one the N-cis Lone-electron-pair *-trans isomer [2, 5] has a C_s symmetry. In the latter the heavy atoms are coplanar and the out-of-plane hydrogens are symmetrical to the heavy atom plane (see Fig. 1), thus the rotamer has only two non-zero dipole moment components (μ_a and μ_b).

In the course of an investigation of the isotopic species of the molecule [6] the dipole moment of the amine deuterated species (ND_2) of the N-cis Lep-trans rotamer was considered of sufficient interest to merit a separate investigation. It was hoped that the results would allow the determination of the orientation of the dipole moment in the normal species and the influence of deuteration on the total dipole moment.

Orientation of the Total Dipole Moment

The spectrum of the N-cis Lep-trans rotamer (ND_2 species) was assigned and the Stark effect of several transitions measured and the dipole moment components fitted as given in Table 1. The isotope pulling effect can be applied when the geometry of the considered molecule is fairly well known, which in the case of the N-cis Lep-trans rotamer can be assumed with relative certainty.

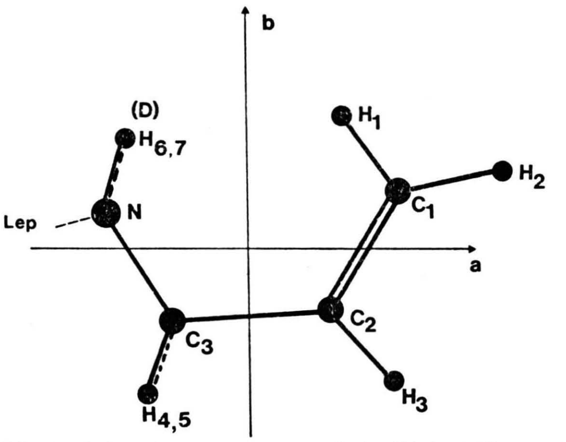

Fig. 1. Approximate structure of the N-cis, N-lone-pair-trans rotamer of allylamine based on a composition of propylene and methylamine.

Assumed structural parameters (Å, degrees)

Taken from propylene [7]			
C_1C_2	1.336	$C_1\hat{C}_2C_3$ *	124.3
C_2C_3	1.501	$C_2\hat{C}_1H_1$	120.5
C_1H_1	1.091	$C_2\hat{C}_1H_2$	121.5
C_1H_2	1.081	$C_1\hat{C}_2H_3$	119.0
C_2H_3	1.090	$H_1\hat{C}_1H_2$	118.0
Taken from methylamine [8]			
C_3N	1.474	$C_2\hat{C}_3N$ *	113.0
$C_3H_{4,5}$	1.093	$C_2\hat{C}_3H_{4,5}$	109.5
N_6H_7,	1.014	$H_4\hat{C}_3H_5$	109.5
		$C_3\hat{N}H_{6,7}$	112.0
		$H_6\hat{N}H_7$	106.0
		$C_3\hat{N}$ (LEP)	108.9

* By fitting the angle C_2C_3N to the experimental rotational constants and assuming $C_1C_2C_3 = 126.1°$ (taken from cis-butene-1 [9]) the value 117.6° was obtained.

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* Lone-electron-pair will be abbreviated as Lep.

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Table 1. Transitions of N-cis Lep-trans doubly deuterated allylamine ($-ND_2$) used for the fitting of the dipole moment components. Error shown twice standard errors.

Transition	M	Measured $(\Delta\nu/E^2)\cdot 10^5$ MHz/(V/cm)^2	Calculated $(\Delta\nu/E^2)\cdot 10^5$ MHz/(V/cm)^2
$3_{13}-2_{12}$	0	-0.0174	-0.0181
	1	0.151	0.154
$3_{12}-2_{11}$	1	-0.134	-0.134
	2	-0.531	-0.497
$3_{03}-2_{02}$	0	-0.0588	-0.0576
	1	-0.0149	-0.0152
	2	0.111	0.112

Measured dipole components	$-ND_2$ [a]	$-NH_2$(5)
μ_a	0.921 ± 0.005 D	0.893 ± 0.004 D
μ_b	0.12 ± 0.02 D	0.06 ± 0.02 D
μ_t	0.928 ± 0.006 D	0.895 ± 0.006 D

[a] This work.

The most probable structure of N-cis Lep-trans allylamine (NH_2) was assumed in [5] to be a combination of that of methylamine [7] and that of propene [8], with the exception of the $C\hat{C}C$ angle (fixed to 126.1° as in butene-1 [9] and the $C\hat{C}C$ angle which was fitted to 117.6°. The actual increase with respect to the equivalent angle in methylamine (113°) was explained through the strong steric repulsion between the amine hydrogens and the allyl proton.

This structure is given in Fig. 1 and provided a rather good prediction for the rotational constants of the $-ND_2$ species showing that it describes fairly well the actual geometry, see Table 2.

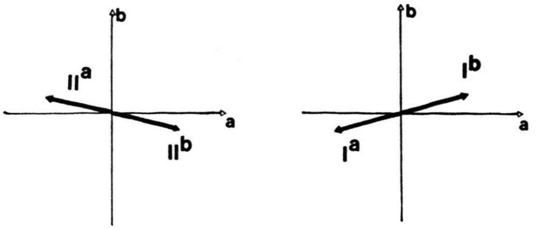

Fig. 2. The four possible orientations of the total dipole moment in the NCLT isomer of allylamine (the arrows are pointing in the negative direction).

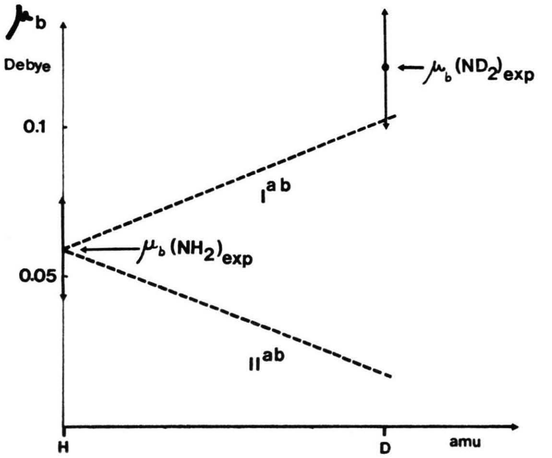

Fig. 3. Comparison of the experimentally determined μ_b dipole moment component for the $-ND_2$ species with the predicted values. The measured μ_b component of the normal species, $\mu_b = 0.06$ D, was placed in orientations $I^{(a,b)}$ and $II^{(a,b)}$ and then the mass of the amine hydrogens increased till complete deuteration.

The previously measured total dipole moment in the $-NH_2$ species can have four possible orientations with respect to the principal axis system but with microwave spectroscopy only two pairs are distinguishable, the two pairs are given in Fig. 2 as orientation $I^{(a,b)}$ and $II^{(a,b)}$. The measured total dipole moment of the normal species (NH_2) was rigidly placed in the orientation I and II in the fitted structure. The rotation of the principal axis system through deuteration gives different predictions for case I and II which can be compared with the experimentally found value, see Figure 3. The isotope pulling effect can be best visualized by gradually increasing the mass of the amine hydrogens and calculating μ_b dipole moment component for each value, see Figure 3. The results point undoubtedly to the case $I^{(a,b)}$ as being the correct orientation. The electronegativity of the electron pair leaves on the other hand little doubt that the true orientation must be with the negative end pointing towards the Lone-electron-pair, namely $I^{(a)}$.

	Meas	Pred [a]
A	14 433.8	14 400
B	5 414.8	5 402
C	4 213.3	4 206

[a] Using the geometry of Figure 1.

Table 2. Measured and predicted rotational constants allylamine NCLT$-ND_2$ species. (MHz)

Influence of the Large Amplitude Motions

The absolute values of the total dipole moments as measured for the $-NH_2$ and $-ND_2$ species, see Table 1, differ by about 3% and merit special attention. Both measurements were made using the same

Table 3. Normal frequencies and G matrix terms corresponding to the CC and CN torsions for NCLT-isomer of allylamine (NH_2- and ND_2-species).

(amu Å²/rad²)	NH_2	ND_2
G_{CC}^{-1}	5.159 [a]	5.716 [a]
G_{CN}^{-1}	1.663 [a]	3.146 [a]
(cm^{-1})		
ν_{CC}	144 [b]	136.8 [c]
ν_{CN}	240 [b]	173.9 [c]

[a] Calculated with the structure of Figure 1.

[b] Experimental result [2, 5].

[c] Derived from the NH_2 values with the formula: $\partial^2 V(\theta)/\partial\theta^2 = 4\pi\,\nu^2 G_{\tau\tau}^{-1}$.

experimental apparatus and calibrating procedure, thus the observed discrepancy can hardly be only due to experimental errors. On the other hand the difference cannot be caused only by a change in the bond moments of C-H and C-D as this effect would account for no more than 0.002 D [10].

A tentative explanation for the increase of the effective total dipole moment due to deuteration can be made by taking into consideration the large amplitude motions of the molecule. Allylamine has two low lying torsional vibrations: the C-C and C-N torsions which were exhaustively described in previous papers [1 – 3]. The corresponding G^{-1} matrix elements [11] and the corresponding normal frequency are given for both species in Table 3. The electron clouds restricting the torsions can be considered as being quite independent of the deuteration in contrast to the effective masses involved ($G^{1-}_{\tau\tau}$ terms).

It should be remarked that in the course of the CN and CC internal torsion, the Lone-electron-pair, which is the largest single contribution to the total dipole moment, is also rotated. Thus even if no exact numerical calculations are possible it can be argued that the effective "in-plane" contribution of the Lep moment should depend inversely on the amplitude of the "out-of-plane" oscillation. Furthermore the amplitude of the oscillation is smaller when the corresponding G_{CC}^{-1} matrix element increases. Observation of the values given in Table 3 and the previous argumentation lead to the qualitative prediction that the relation $\mu_t(ND_2) > \mu_t(NH_2)$ is in fact to be expected, as it has been observed experimentally, even if no quantitative analysis can be made.

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