Microwave Structure of Cyclopropylamine: Substituent Effect of the Amino Group

Martha Rall,[†] Marlin D. Harmony,*[†] David A. Cassada,[‡] and Stuart W. Staley*[‡]

Contribution from the Departments of Chemistry, University of Kansas, Lawrence, Kansas 66045, and University of Nebraska, Lincoln, Nebraska 68588. *Received March 17, 1986*

Abstract: A complete heavy-atom microwave structure and fully geometry-optimized structures at the ab initio 6-31G* and MP2/6-31G* levels are presented for cyclopropylamine. The experimental C_2C_3 bond length (1.512 Å) is essentially unchanged relative to cyclopropane whereas there is a small but distinct shortening of C_1C_2 (1.499 Å). The latter effect is attributed primarily to hybridization changes at C_1. Amino group parameters are discussed in terms of four-electron repulsive interactions between filled amino and cyclopropyl orbitals, and previous analyses of the cyclopropylamine structure are evaluated.

Some years ago we reported microwave structural results for cyclopropylamine (Figure 1) based on studies of the normal, ^{13}C, NHD, and ND_2 isotopic species.[2] Although useful results were obtained, the lack of ^{15}N data and the occurrence of several small r_s coordinates left some uncertainties in the structure. In this work we report ^{15}N data and extensive computations which lead to a structure of enhanced reliability and precision for the ring and the amino group. We also present an analysis of the influence of electronic interactions between the cyclopropyl ring and the amino group on the molecular structure.

Several thermodynamic studies have been conducted on cyclopropylamino systems, and current evidence indicates that the thermodynamic effect of an amino group on cyclopropane is approximately equivalent to that of an alkyl group.[3] More recently, ab initio quantum mechanical investigations have been reported for cyclopropylamine.[4] Two of the studies present rather extensive discussions of the σ and π conjugation effects of the NH_2 group and related substituents.[4b,c] Our own experimental and theoretical efforts have recently been concentrated upon strong π-electron acceptor substituents,[5] but we felt it was important to refine our understanding of the structural effects of the amino substituent, which functions primarily as a π-electron donor in conjugated systems.

Experimental Section

Materials. Cyclopropylcarboxamide-^{15}N, prepared from cyclopropanecarbonyl chloride (Aldrich) and ammonium-^{15}N chloride (5 atom %, Prochem), was (after rotary evaporation of the solvent) separated from the reaction mixture by Soxhlet extraction with ethyl acetate and then converted to cyclopropylamine-^{15}N hydrochloride.[6] The latter compound (5.2 g, 55.6 mmol) was mixed with 8 mL of concentrated sodium hydroxide and 10 mL of ethylene glycol and the mixture was distilled through a Vigreux column. Cyclopropylamine-^{15}N (1.44 g, 25.3 mmol, 43%) was collected in the range of 48–53 °C) (lit.[7] 50 °C).

Microwave Spectroscopy. Microwave spectra were obtained by employing both Stark modulation and radio-frequency–microwave double resonance methods, and were assigned easily by analogy to our earlier studies.[2] We have made a more extensive assignment in the present case, however, and report in Table I a total of 24 measured transitions. These have been analyzed by utilizing a Hamiltonian which includes centrifugal distortion terms through P^4.[8] Table II lists the resulting rotational and distortion constants. The quality of the fit is very good as can be seen by observing the frequency derivations listed in Table I.

In our previous studies of the normal, ^{13}C, NHD, and ND_2 isotopic species, we did not measure enough transitions to perform centrifugal distortion analyses. In order to make the results of our earlier studies more consistent in quality with the present work, we have reanalyzed the previous data by making corrections for centrifugal distortion. This has been accomplished by using the distortion constants of Table II along with the assumption that the distortion contributions for the various isotopic frequencies scale according to the transition frequency. For completeness then, we list in Table III the slightly revised rotational constants obtained by this procedure. The Table III results differ little from the earlier published values,[2] but they provide us with confidence that differing spectral analysis methods do not affect the structural calculations presented in the next section. In all cases, the Table III results have a better precision than the earlier published results.

[†] University of Kansas.
[‡] University of Nebraska.

Table I. Microwave Spectrum of Cyclopropylamine-^{15}N[a]

transition	obsd[b]	obsd − calcd[c]
$2_{11} \leftarrow 1_{01}$	35 861.19	0.00
$2_{20} \leftarrow 2_{12}$	31 812.03	0.04
$2_{11} \leftarrow 2_{21}$	29 121.53	−0.02
$3_{22} \leftarrow 2_{21}$	36 597.16	0.02
$3_{13} \leftarrow 2_{12}$	35 245.97	−0.03
$3_{12} \leftarrow 2_{11}$	37 877.21	0.00
$3_{21} \leftarrow 2_{20}$	36 823.08	−0.01
$3_{21} \leftarrow 3_{13}$	33 389.09	0.00
$3_{22} \leftarrow 3_{12}$	27 841.47	−0.01
$4_{04} \leftarrow 3_{12}$	35 215.39	0.02
$4_{22} \leftarrow 4_{14}$	35 762.38	0.00
$5_{14} \leftarrow 4_{22}$	35 915.11	−0.01
$5_{23} \leftarrow 5_{15}$	39 127.47	0.00
$6_{16} \leftarrow 5_{24}$	32 946.55	0.00
$7_{26} \leftarrow 6_{34}$	33 230.38	−0.01
$8_{36} \leftarrow 7_{44}$	27 254.47	0.00
$8_{35} \leftarrow 7_{43}$	28 257.97	−0.01
$10_{47} \leftarrow 9_{55}$	31 849.37	0.01
$10_{46} \leftarrow 9_{54}$	32 071.81	0.02
$10_{38} \leftarrow 10_{28}$	37 421.24	0.00
$11_{39} \leftarrow 11_{29}$	33 624.08	0.00
$12_{58} \leftarrow 11_{66}$	36 182.71	0.03
$12_{57} \leftarrow 11_{65}$	36 226.66	−0.04
$12_{3,10} \leftarrow 12_{2,10}$	29 571.91	0.00

[a] Frequencies in megahertz. [b] Frequency accuracy better than ±0.05 MHz. [c] Computed with the data of Table II.

Table II. Rotational Constants for Cyclopropylamine-^{15}N[a]

A	16 245.767 ± 0.005[b]
B	6 538.515 ± 0.002
C	5 660.657 ± 0.002
τ'_{aaaa}	−0.062 ± 0.002
τ'_{bbbb}	−0.0121 ± 0.0002
τ'_{cccc}	−0.0080 ± 0.0002
τ'_{bbcc}	−0.0083 ± 0.0002
$\tau'_{aacc} + \tau'_{aabb}$	−0.0402 ± 0.0007

[a] Values in megahertz. [b] Uncertainties represent the standard deviations.

Table III. Revised Rotational Constants for Normal Cyclopropylamine and Various Isotopic Species[a]

	normal	1-^{13}C	2-^{13}C
A	16 270.083 (19)	16 144.522 (9)	15 976.907 (22)
B	6 723.024 (8)	6 698.487 (4)	6 645.077 (10)
C	5 795.349 (6)	5 793.174 (2)	5 702.537 (6)
	NHD		ND_2
A	15 957.277 (45)		15 592.725 (34)
B	6 382.021 (20)		6 091.393 (15)
C	5 504.049 (14)		5 246.555 (11)

[a] All values in MHz; uncertainties in parentheses represent standard deviations. See ref 2 for the original data.

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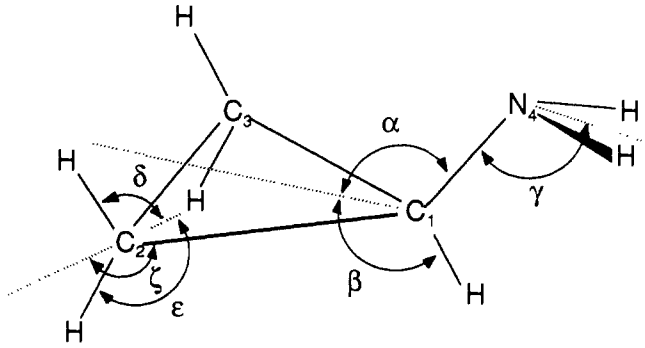

Figure 1. Cyclopropylamine structure.

Table IV. Cyclopropylamine Coordinates

	method I[a]			method II[b]		
	a	*b*	*c*	*a*	*b*	*c*
C_1	0.1833	0	−0.4957	0.1987	0	−0.4960
C_2	−0.9309	−0.7562	0.1322	−0.9283	−0.7568	0.1372
C_3	−0.9309	0.7562	0.1322	−0.9283	0.7568	0.1372
N	1.4545	0	0.2215	1.4536	0	0.2332
H_1	2.0002	−0.8162	−0.0761	2.0009	−0.8158	−0.0647
H_2	2.0002	0.8162	−0.0761	2.0009	0.8158	−0.0647

[a] Computed from Kraitchman's equations. [b] Computed by least-squares fit of isotope shifts in moments of inertia.

Quantum Mechanical Methods. Ab initio calculations were performed with Pople's GAUSSIAN 76[9a] or GAUSSIAN 82[9b] series of programs which employed the STO-3G[10] minimal and the 4-31G[11] and 6-31G*[12] split-valence basis sets. Electron correlation effects were included at the MP2/6-31G* level by the use of analytical second-derivative techniques.[13] Geometry optimizations were performed by employing analytically evaluated atomic forces in a Berny multiparameter search routine.[9b]

Results

Microwave Structural Analysis. In our most recently published structural results for cyclopropylamine,[2c] the lack of ^{15}N isotopic data meant that a complete heavy atom *substitution* (r_s) structure could not be obtained. With the new data it is now possible to compute the substitution coordinates for all heavy atoms plus the amino hydrogens according to the Costain–Kraitchman procedure.[14] These coordinates, listed under "method I" in Table IV, lead immediately to the pure r_s structure in the method I column of Table V. It is clear that the several small coordinates in Table IV lead to rather large Costain uncertainties,[15] and indeed the sign of the hydrogen *c* coordinate is perhaps not unambiguous.

It is well known that the Costain substitution procedure suffers from an inherent potential problem in that it forces certain rotation–vibration contributions to the moments of inertia (or planar second moments) to have a large impact on a single coordinate.[15] Moreover, the method does not generally permit a balanced structural averaging over all available isotopic data. On the other hand, the least-squares structural procedure of Nösberger et al.[16] effectively produces a structure in which the resulting parameters are the best average values over *all* the data. Used judiciously, the method compels one to believe that it leads to a cancellation of vibration–rotation effects in such a way that the resulting structure has the same general validity as a pure r_s (substitution) structure.

The key factor in applying this method to obtain an r_s-type structure is to use *only* isotopic differences of the moments of inertia as the experimental observations in the least-squares equations. (That is, $I_a(^{15}N) - I_a(\text{normal})$, etc.) On using this procedure with equal weighting of all fifteen isotope shift values, the seven independent structural parameters listed in the method II column of Table V are obtained, along with the corresponding method II coordinates in Table IV. It is important to point out that although this least-squares procedure requires that one assume values for the CH_2 and CH parameters, the use of isotope differences (only) leads to a very high degree of insensitivity to the assumptions. In our fit we have assumed all CH distances to be 1.084 Å, ∠HCH to be 116.2° (with local C_{2v} symmetry), and the angle between the C_1H bond and the ring plane to be 123.2°. If, for example, we increase all four methylene CH bond lengths by 0.01 Å, a rather extreme assumption, no least-squares computed bond length changes by as much as 0.001 Å. By extensive variations in our assumed parameters, we estimate that the Table V computed parameters of column two cannot be in error by more than 0.3% (e.g., 0.005 Å), and most likely incur much less error than this.

It is interesting and important to note that the method II and method I coordinates differ by less than 0.002 Å for coordinates whose magnitude is greater than 0.3 Å. The *small* coordinates, on the other hand, differ rather widely; for example, $a(C_1)$ differs by 0.015 Å. Because these small coordinates are poorly determined by the Costain–Kraitchman procedure, and because the least-squares method yields parameters whose values are balanced averages over all the isotopic data, we believe the least-squares (method II) values are more reliable. Indeed our present feeling, based on extensive calculations for several related cyclopropyl molecules, is that large differences in small coordinates computed by methods I and II are symptomatic of serious uncancelled vibration–rotation effects on the pure r_s coordinates.

Thus, the method II structure of Table V should be superior to that of method I. It is apparent, in fact, that the two structure calculations are very similar except for the C_1C_2 and C_1N bond lengths, whose differences arise primarily because of the 0.015-Å shift in the small *a* coordinate of C_1 (see Table IV). Except for the parameters whose precision is degraded by small coordinates, the r_s structure retains its validity. Since such structures are widely computed and, in the absence of small coordinates, are generally

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Table V. Microwave and ab Initio Geometry-Optimized Structures for Cyclopropylamine[a]

parameter	microwave			theory	
	method I[b]	method II[c]	method III[d]	6-31G*	MP2/6-31G*
C_1C_2	1.486	1.498	1.499 ± 0.008	1.494	1.499
C_2C_3	1.512	1.514	1.512 ± 0.003	1.500	1.504
C_1N_4	1.460	1.451	1.452 ± 0.007	1.435	1.442
NH	1.026	1.026	1.026 ± 0.007	1.002	1.019
C_1H				1.081	1.092
C_2H				1.075	1.084
C_2H'[e]				1.076	1.085
$\angle C_2C_1N$	116.5	116.0	116.1 ± 0.4	117.1	116.2
$\angle C_1NH$	108.7	108.4	108.3 ± 0.8	111.0	110.0
$\angle HNH$	105.4	105.2	105.4 ± 0.7	107.7	106.9
$\angle C_2C_1C_3$	61.2	60.7	60.6 ± 0.2	60.3	60.2
$\angle\alpha$	121.2	120.5	120.6 ± 0.5	121.7	120.7
$\angle\beta$				120.6	120.5
$\angle\gamma$	122.0	121.3	121.2 ± 2.0	127.3	125.0
$\angle\delta$				58.2	58.8
$\angle\epsilon$				56.7	56.5
$\angle\zeta$				149.8	149.6

[a] See Figure 1 for definitions; distances in Å, angles in degrees. Three parameters are redundant. [b] Computed from the method I coordinates of Table IV. [c] Computed from the method II coordinates of Table IV. [d] Computed from the method I coordinates of Table IV, except coordinates smaller than 0.3 Å are replaced by the method II coordinates. [e] H′ is anti to the substituent.

considered to be reliable approximations to equilibrium structures,[15b] it seems desirable to stay within this framework. We propose then a third structure calculation, listed as method III in Table V, which we term a "modified r_s" structure. This structure is computed by using all r_s (method I) coordinates except those whose magnitude is less than 0.3 Å, which are replaced by the least-squares (method II) coordinates. This procedure is entirely analogous in spirit to the common procedure of replacing small r_s coordinates with values computed from first moment or from product of inertia equations.[14b,15b] The result is a hybrid structure which retains all the "good" r_s parameter values but replaces the questionable values with results which utilize the more reliable least-squares coordinates. It is clear, as can be seen from Table V, that the modified r_s (method III) structure computed in this fashion differs very little from the least-squares (method II) structure. We accept this as the most reliable structure and report conservative uncertainties according to the Costain procedure.[15]

Geometry-Optimized Structures. Geometry optimizations were performed at the 6-31G* and MP2/6-31G* levels and the results are given in Table V. C_s symmetry was assumed in the former calculation but no symmetry constraints were placed on the MP2/6-31G* optimization. Nevertheless, the optimized structure had effective C_s symmetry.

Discussion

In Table VI we present a comparison of the heavy-atom bond distances obtained in the present and previous experimental and theoretical studies. There is now a somewhat better level of agreement between experiment and the various theoretical values for the ring distances. In particular, the new experimental data analysis now indicates that the ring asymmetry is not as large as previously reported, although both experiment and theory continue to agree that the C_1C_2 bond length ($r(C_1C_2)$) is smaller than $r(C_2C_3)$. The experimental results indicate that $r(C_2C_3)$ is essentially identical with the cyclopropane r_z value of 1.513 Å,[15] while C_1C_2 is slightly but distinctly shorter.

The following are the key structural features and changes in cyclopropylamine relative to cyclopropane and ammonia or methylamine. (a) A pyramidal amino group assumes a perpendicular conformation in which the lone pair and NH bonds are staggered with regard to the cyclopropyl CC and CH bonds at C_1. (b) The cyclopropyl C_1C_2 and C_1C_3 bonds are shortened by 0.014 Å relative to cyclopropane (1.513 Å),[17] whereas C_2C_3 is essentially unchanged. (c) The C_1N bond is shortened slightly relative to the corresponding distances in methylamine (1.471 Å)[19] and dimethylamine (1.464 Å).[20] (d) The angle α is 120.6°, somewhat less than the corresponding angles in cyclopropylsilane (124.2°),[21] cyclopropylacetylene (124.2°),[5c] cyanocyclopropane (123.4°),[5c] isocyanocyclopropane (123.4°),[5d] and cyclopropane (122.7°),[17] the other simple cyclopropanes for which microwave data are available. (e) The NH_2 group parameters differ somewhat from the corresponding values for simple amines. Thus, the NH bond lengths in NH_3, CH_3NH_2, and $(CH_3)_2NH$ are 1.014,[22] 1.010,[9] and 1.022 Å,[20] respectively, all somewhat shorter than the 1.026-Å value reported here. In addition, $\angle HNH$ has a value of 107.1° in both NH_3[22] and CH_3NH_2,[19] slightly larger than the 105.4° value reported here.

In summary, the structure which emerges for cyclopropylamine is of a perpendicular NH_2 conformation with slightly shortened vicinal cyclopropyl bonds (relative to cyclopropane) and with an amino group which is more pyramidal than in ammonia and tilted slightly toward the cyclopropyl ring (relative to the CH bonds in cyclopropane). How can this structure be understood?

Table VI. Comparison of Various Cyclopropane and Cyclopropylamine Structure Results[a]

experimental	cyclopropane	cyclopropylamine		
	C_1C_2	C_1C_2	C_2C_3	C_1N
previous	1.513 (r_z)[b] 1.501 (r_e)[b]	1.486[c]	1.513[c]	1.462[c]
this work (modified r_s)		1.499	1.512	1.452
theory (r_e)				
MINDO/3[d]	1.504	1.510	1.494	1.408
MNDO[d]	1.525	1.537	1.525	1.445
STO-3G	1.502	1.506	1.502	1.472
(7,3) contracted[e,f]		1.508	1.512	1.451
(7,3) contracted[f,g]	1.513	1.500	1.518	1.452
3-21G[h]	1.513	1.508	1.514	1.443
4-31G[f,i]	1.502	1.496	1.502	
4-31G[j]	1.502	1.500	1.503	1.428
6-31G*	1.497[k]	1.494	1.500	1.435
MP2/6-31G*	1.502[k]	1.499	1.504	1.442

[a] Values in Å; this work unless indicated otherwise. [b] Reference 17. [c] r_s; reference 2c. [d] Reference 4g. [e] Reference 4a. [f] Partial optimization. [g] Reference 4b. [h] Reference 4h. [i] Reference 4f. [j] Reference 4c. [k] Reference 18.

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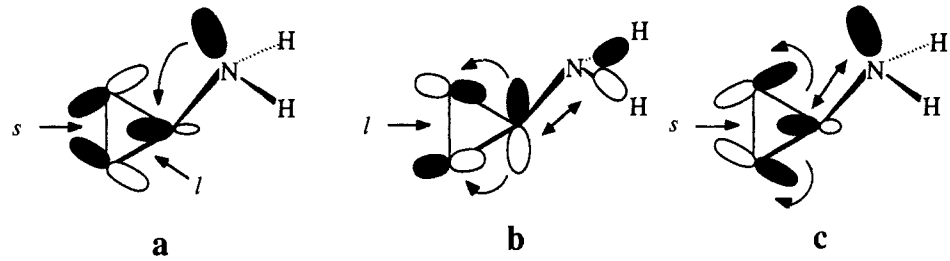


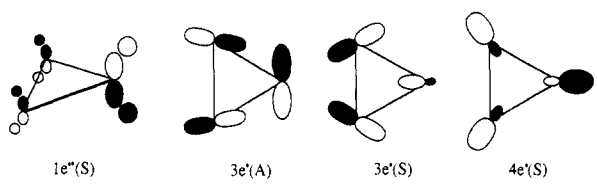
Figure 2. (a) π'-Electron donation into the cyclopropyl 4e'(S) orbital. (b) π-Electron repulsion between a filled orbital and the cyclopropyl 3e'(A) orbital. (c) π'-Electron repulsion between a filled orbital and the cyclopropyl 3e'(S) orbital. Double-headed arrows represent electron repulsion whereas single-headed arrows represent shifts of electron density. The corresponding structural changes are represented by an *s* (bond shortening) or an *l* (bond lengthening).

Various theoretical workers have addressed the question of the origin of the stability of the s-trans amino conformation and the small ring asymmetry.[4a-c,f,g] Arguments in terms of σ/π orbital interactions have not yielded an unambiguous interpretation. It seems clear that the small asymmetry indicates that a single strong orbital interaction is not operative as in the case of strong π-acceptor substituents.[5,23]

Our complete 6-31G* and MP2/6-31G* geometry optimizations for cyclopropane and cyclopropylamine are compared in Table VI with previous calculations at smaller basis set levels. The semiempirical calculations show a lengthening of C_1C_2 and a shortening of C_2C_3, neither of which is observed experimentally. We believe this to be an artifact of these calculations, which place σ^* levels at too low an energy and thus overemphasize the cyclopropyl 3e'(A) → amino σ^* two-electron interaction.

With the exception of the minimal basis set (STO-3G) results, the ab initio calculations almost all agree that the cyclopropyl bonds adjacent to the amino substituent are shortened, whereas the opposite bond is unchanged or only slightly lengthened. Thus theory and experiment are in general agreement with regard to *relative bond lengths*, although the MP2/6-31G* differential between $r(C_1C_2)$ and $r(C_2C_3)$ is not as great as the experimental value. Also, except for $r(C_2C_3)$, the MP2/6-31G* bond lengths are less than the experimental r_z[17] and "modified r_s" values, as expected, although it is difficult at this time to state what difference is most appropriate. However, we do note that there is excellent agreement between the experimental[17] and MP2/6-31G* theoretical r_e values for cyclopropane, the only case in which a direct comparison can be made.

In order to analyze this system, we consider two-electron interactions between an occupied and an unoccupied orbital in which partial electron transfer occurs (π-electron donation, π-electron withdrawal), four-electron interactions between two occupied σ or π orbitals (polarization or repulsion), σ inductive effects, and hybridization effects. We shall furthermore find it useful to subdivide π interactions into those involving antisymmetric cyclopropyl orbitals, such as 3e'(A), and symmetric cyclopropyl orbitals, such as 3e'(S) and 4e'(S). We refer to these interactions as π-electron donation or withdrawal and π'-electron donation or withdrawal, respectively.



We can ignore both σ-electron donation and π- or π'-electron withdrawal in the case of cyclopropylamine because the amino group is σ-electron withdrawing and has no low-lying vacant π or π' orbitals. π-Electron donation can also be ignored since the amino group has no lone pairs of π-type symmetry. The effects of other interactions are discussed below.

(a) π'-Electron Donation. As shown in Figure 2a, π' donation of electron density from the amino lone pair into the symmetric unoccupied 4e'(S) orbital of cyclopropane would result in a lengthening of C_1C_2 and C_1C_3 and a shortening of C_2C_3.[2b] Clark, Schleyer, and co-workers have stated that the s-trans pyramidal conformation of cyclopropylamine confirms that the most effective acceptor orbital of cyclopropane is the 4e'(S) orbital.[4c] However, the observed bond-length changes in the three-membered ring are not what are predicted by this model. Furthermore, this orbital is calculated to lie over 1.5 eV above the LUMO of cyclopropane at both the 6-31G[24] and MP2/6-31G* levels.

(b) π- and π'-Electron Repulsion. The π interaction of two filled orbitals will lead to a net polarization of electron density away from the point of interaction (Figure 2b).[25] As shown by Allen and co-workers in the case of fluoro- and 1,1-difluorocyclopropane[26] and by us in the case of isocyanocyclopropane,[5d] this effect is primarily evidenced by a polarization of the cyclopropane 3e'(A) orbital on interaction with π electrons of the substituent and will lead to a lengthening of C_2C_3. In contrast, π'-electron repulsion between a filled substituent orbital and the 3e'(S) cyclopropyl orbital is expected to cause a shortening of C_2C_3 (Figure 2c).

Cremer and Kraka[4f] have, following Bader and co-workers,[27] examined the Laplacian of the one-electron density distribution ($\Delta^2\rho(r)$) for substituted cyclopropanes and have concluded that σ-attractor and π-repeller substituents (such as amino) cause a shortening of the vicinal and a lengthening of the opposite bond. We believe this approach has considerable value. It correctly predicts the shortening of the vicinal bonds in cyclopropylamine, but does not predict the unchanged C_2C_3 bond length, although the discrepancy may be minor or within experimental error.

(c) σ-Electron Withdrawal. Skancke and Boggs[4a] pointed out that the amino group can effect σ-electron withdrawal from the symmetric orbitals of the cyclopropyl ring, and Clark, Schleyer, et al.[4c] concluded that the symmetric 1e"(S) orbital, which is antibonding at C_1C_2 and bonding at C_2C_3, is the most effective σ-electron donor orbital. This appears to be reasonable based on a Mulliken population analysis, although the structural consequences are likely to be rather small because the latter orbital is primarily CH bonding in character and contributes only π-type bonding at the cyclopropyl CC bonds.

(d) Hybridization. The effect of electronegative substituents on the cyclopropyl ring structure can be predicted on the basis of the Walsh/Bent model;[28] that is, an electronegative substituent will reduce the p character and increase the s character of the adjacent ring CC bonds. Jason and Ibers[29] have, following Bernett,[30] recognized that this will cause a shortening of C_1C_2. Durmaz and Kollmar have disputed this view and have instead postulated that such substitution will increase the ring strain and that this strain will be accommodated by simultaneously lengthening the opposite and shortening the adjacent bonds.[4b] However,

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force constants for stretching and compressing CC bonds are generally regarded as too large for these structural changes to serve as a mechanism for relieving bond angle strain, such as that caused by substitution.

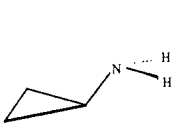
Durmaz and Kollmar have concluded that hybridization changes lead to bond differentiation in substituted cyclopropanes. They have further argued, based on geometry-optimized structures for, among others, cyclopropylamine and cyclopropylammonium ion, that substituent electronegativity *does not* seem to be an important factor in the determination of cyclopropyl ring structure.[4b] However, we have found that their geometry-optimized structure for cyclopropylammonium ion was influenced by an unrecognized π-type electron donation from the cyclopropyl 3e'(A) orbital to a low-lying σ_π* substituent orbital which causes a change in $r(C_1C_2)$ opposite to that arising from electronegativity effects and therefore serves to mask structural changes caused by the latter.

The complexity of the cyclopropylamine problem is increased by the relatively small structural changes which are observed relative to cyclopropane. It is not unreasonable to expect that several factors, possibly working in opposite directions, might be required for a full understanding.

C_2C_3 Bond. One's first impulse might be to ignore any electronic effects of the amino group on this bond since its length is unchanged relative to cyclopropane. However, all geometry-optimized ab initio calculations in the literature clearly indicate that this bond is lengthened by methyl substitution (as in methylcyclopropane).[4a,f,31] This is consistent with a small electron repulsion between the occupied methyl σ_π orbitals and the 3e'(A) cyclopropyl orbital.

In contrast, Zil'berg et al. have calculated a shortening of C_2C_3 in methylcyclopropane by MINDO/3 and have attributed this to π-electron donation from cyclopropyl to the π* CH_3 orbital and especially to the polarization which accompanies this two-electron interaction.[32] However, as in the case of cyclopropylamine, we believe this result to be an artifact of the MINDO/3 method, which places methyl antibonding orbitals at too low an energy and consequently overemphasizes π-electron donation from the cyclopropyl 3e'(A) orbital.

The amino group should also cause a small lengthening of C_2C_3 on the basis of the above repulsion effect alone (Figure 2b). This view is supported (a) by a slight lengthening of C_2C_3 calculated for cyclopropylamine relative to cyclopropane; (b) by a small lengthening of C_2C_3 (relative to geometry-optimized **1**) which is calculated for perpendicular cyclopropylamine with a planar amino group (**2**), where the NH bonds can overlap better with the 3e'(A) orbital; and (c) by the significant lengthening of C_2C_3 calculated for bisected cyclopropylamine with a planar amino group (**3**), where the nitrogen lone pair can overlap strongly with the 3e'(A) orbital.[4c]



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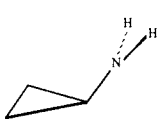

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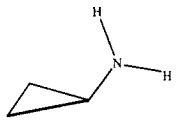

3

The fact that C_2C_3 in cyclopropylamine is not lengthened (experimentally) relative to cyclopropane can be attributed to experimental uncertainty or to counterbalancing effects not present in methylcyclopropane. Thus π'-electron donation of the amino lone pair to the 4e'(S) cyclopropyl orbital (Figure 2a) and π'-electron repulsion between the lone pair and the 3e'(S) orbital (Figure 2c) will both serve to shorten C_2C_3 and one or both effects may be operative.

Support for at least one of the effects in Figure 2 is provided by the MP2/6-31G* total electron density on C_2 which increases by 0.0044 electron on going from cyclopropane to **1**, even though the density on the cyclopropyl moiety *decreases* by 0.3431 electron. Analysis of the C_2 orbital populations indicates that this increase occurs almost exclusively in the $2p_y$ and $3p_y$ orbitals, where the y axis lies at the intersection of cyclopropyl ring plane and the molecular symmetry plane. These orbitals constitute the major components of the 3e'(A) orbital at C_2 and C_3, and support our contention that the four-electron repulsion in Figure 2b is the major effect. The electron shifts depicted in Figure 2a,c would primarily increase the C_2 and C_3 electron density in the $2p_x$ and $3p_x$ orbitals (where x lies in the cyclopropyl ring plane). However, the latter orbitals are calculated to lose 0.1313 electron on going from cyclopropane to **1**.

Table VII. Ab Initio Geometry-Optimized Bond Angles at C_1[a] for Selected Monosubstituted Cyclopropanes

substituent	$\angle\alpha$,[b] deg	$\angle\beta$,[b] deg	Δ,[c] deg	σ_1[d]
SiH_3	125.2[e]	118.5[e]	6.7	
CH_3	126.0[f]	119.7[f]	6.3	−0.04
	124.2	120.8	3.4	
H	122.9[g]	122.9[g]	0	0
	122.6	122.6	0	
NH_2	120.7[h]	120.5[h]	0.2	0.12
	120.0	121.2	−1.2	
F	122.3[i]	125.9[i]	−3.6	0.50
	122.5	125.3	−2.8	

[a] See Figure 1. [b] The lower values are from 3-21G optimizations; ref 4h. [c] $\Delta = \angle\alpha - \angle\beta$. [d] Hammett inductive constant; ref 33. [e] 4-21 (3-3-21 for Si) optimization; ref 21b. [f] 4-31G optimization; ref 31. [g] MP2/6-31G* optimization; ref 18. [h] MP2/6-31G* optimization; this work. [i] 4-21 optimization; ref 34.

C_1C_2 Bond. Of the various potential influences on C_1C_2, only σ-electron withdrawal and hybridization effects can lead to a shortening of this bond. A dominant σ-electron withdrawal would cause a lengthening of C_2C_3 as well as a shortening of C_1C_2. As noted above, the former change is not observed, even though π-electron repulsion (Figure 2b) would *also* serve to effect a change in this direction.

On the other hand, theoretical and structural arguments suggest that rehybridization at C_1 is a primary cause of C_1C_2 bond shortening in cyclopropylamine. Rehybridization and σ-electron withdrawal are necessarily linked, but are not identical. Hybridization changes are more or less localized at C_1 and are expected to be reflected by changes in $\angle\alpha$ and $\angle\beta$ (Figure 1).

Since the total MP2/6-31G* Mulliken overlap populations for CC in cyclopropane and for C_1C_2 and C_2C_3 in cyclopropylamine (0.4956, 0.5409, and 0.4623, respectively), approximately inversely parallel the corresponding bond lengths (Table VI), it is of interest to consider the *partial* populations for C_1C_2 relative to CC in cyclopropane. Thus the C_1C_2 π population increases by 0.0186 in **1** whereas the population associated with the 2s and 3s orbitals at C_1 increases by 0.0222. Since the former is primarily associated with σ-electron withdrawal from the 1e''(S) orbital whereas the latter must reflect rehybridization (it is opposite to what is expected on the basis of σ-electron withdrawal), both effects appear to be important. However, rehybridization at C_1 has the effect of enhancing σ-electron withdrawal from the 1e''(S) orbital because it causes the substituent to move closer to the C_1 p_z axis (which is perpendicular to the cyclopropyl ring plane).

We suggest that a key parameter is the value of $\Delta = \angle\alpha - \angle\beta$ as obtained from geometry-optimized ab initio calculations. As seen in Table VII, the value of Δ for substituents which do not possess low-lying vacant orbitals closely reflects the substituent electronegativity as reflected by the corresponding Hammett σ_1 values. These data are highly suggestive of the influence of hybridization effects on the C_1C_2 bond length.

Parameters Associated with the Amino Group. We have previously noted that the bond-length changes in cyclopropylamine are not consistent with donation from the amino lone pair to the 4e'(S) orbital. However, is this interaction required to explain why **1** is the minimum energy conformation? We believe that four-electron repulsive interactions, although significant in **1**, are nevertheless minimized in this conformation owing to the stag-

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gering of the amino lone pair and CH bonds with the cyclopropyl CH and CC bonds.

The shortening of C_1N relative to methylamine and dimethylamine is consistent with a higher degree of s character in the exocyclic cyclopropyl orbital compared to the corresponding methyl orbital. The longer NH bond is cyclopropylamine relative to other simple amines can be understood on the basis of a greater degree of pyramidalization of the amino group in the former compound (more p character in the NH bond). This increased pyramidalization is also consistent with a minimization of π'-electron repulsion between the amino lone pair and NH bonds and the cyclopropyl 3e'(S) and 3e'(A) orbitals, respectively, as discussed above.

Finally, we note that our conclusion that there is little evidence for π'-electron donation into the cyclopropyl 4e'(S) orbital (Figure 2a) is in accord with those of Boggs and co-workers,[35] who showed that the total electron density on nitrogen in cyclopropylamine indicates little dependence of charge on rotation angle, and of Compton et al.,[36] who rejected such an interaction on the basis of the similar magnitudes of the trans → gauche barriers in cyclopropylamine and isopropylamine. Interestingly, the greater enthalpy difference between the gauche conformation and the more stable s-trans conformation in cyclopropylamine relative to isopropylamine is fully consistent with a four-electron repulsion between the nitrogen lone pair and the cyclopropyl 3e'(A) orbital in the gauche conformation of the former compound.

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Summary

A complete heavy-atom microwave structure of cyclopropylamine and full 6-31G* and MP2/6-31G* geometry-optimized structures are reported. The three-membered ring structure is similar to that of cyclopropane, but there is a small but distinct shortening of C_1C_2. We attribute this primarily to hybridization changes at C_1 caused by the increased electronegativity of the amino group relative to hydrogen. Other features of the structure, such as a relatively highly pyramidal amino group which adopts a staggered perpendicular conformation with respect to the cyclopropyl ring, can be attributed to four-electron repulsive interactions between filled amino and cyclopropyl orbitals. In contrast to the key roles of hybridization and π repulsion/polarization effects, we conclude that σ-electron withdrawal from the 1e''(S) cyclopropyl orbital is of less importance and find little or no evidence for a significant role for π'-electron donation from the lone pair to the 4e'(S) cyclopropyl orbital.

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Registry No. Cyclopropylamine, 765-30-0; cyclopropylamine-^{15}N, 103851-60-1.

Comparative Stabilities of Cationic and Anionic Hydrogen-Bonded Networks. Mixed Clusters of Water–Methanol

Michael Meot-Ner (Mautner)

Contribution from the Chemical Kinetics Division, Center for Chemical Physics, National Bureau of Standards, Gaithersburg, Maryland 20899. *Received April 14, 1986*

Abstract: The thermochemistry of the mixed water–methanol cationic clusters $(H_2O)_n(CH_3OH)_mH^+$ and anionic clusters $[(H_2O)_n(CH_3OH)_m - H]^-$ (i.e., clusters containing OH^- or CH_3O^-) was measured. The stability of the total hydrogen-bonded network in each positive cluster is greater by 3–6 kcal/mol than in the corresponding negative cluster. The variation of the stabilities of the cationic and anionic clusters with composition shows remarkable similarities. (1) Both $H_3O^+ \cdot nH_2O$ and $OH^- \cdot nH_2O$ show effects of solvent shell filling at $n = 3$. (2) Both for anions and cations, neat methanol clusters are more stable than neat water clusters. (3) Both $CH_3OH_2^+$ and CH_3O^- are solvated more strongly by methanol than by water. (4) Stepwise ion solvation compresses the differences between the gas-phase acidities of H_2O and CH_3OH and also between the gas-phase basicities. The compression effect with increasing solvation is somewhat larger in the positive than in the negative ions. (5) Both for anions and cations, stepwise replacement of H_2O by CH_3OH is exoergic for every step from neat water to neat methanol. The results indicate that in the water–methanol clusters, the favored topology places methanol molecules near the charged centers and water molecules at the periphery. This is in contrast to blocked clusters such as water–acetonitrile, where hydrogen-bonding requirements place water at the protonated center and acetonitrile at the periphery. In general, the observed trends show the significance of the formation of unlimited O–H···O hydrogen-bonded networks in both the cationic and anionic water–methanol clusters.

The stepwise clustering of neutral solvent molecules onto an ionic moiety constitutes a transition between isolated ions and electrolyte solutions. Electrolyte solutions often involve mixtures of solvents, and it is therefore important to extend clustering studies to systems which involve a mixture of components. Multicomponent clusters are also found in radiation environments such as the Earth's ionosphere. In a present series of papers we are investigating clusters of components that are used in mixed solvents and/or are found in the atmosphere such as H_2O, CH_3OH, CH_3CN, HCN, and NH_3.

In this paper, we examine the thermochemistry of hydrogen-bonded clusters containing methanol and water. These clusters

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