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THEORETICAL DETERMINATION OF MOLECULAR STRUCTURE AND CONFORMATION

Part X. Geometry and puckering potential of azetidine, $(CH_2)_3NH$, combination of electron diffraction and ab initio studies*

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ABSTRACT

Restricted Hartree—Fock calculations on 21 planar and puckered conformers of azetidine have been done employing a split valence basis augmented by *d* functions. Complete geometry optimizations have been performed for eight conformers. In this way the puckering potential of azetidine is explored over the range $-40° < \phi$ (puckering angle) $< 40°$, for both sp^3 and sp^2 hybridization of the nitrogen atom. In its equatorial form, azetidine is slightly more puckered than cyclobutane. This is because of a decrease of van der Waals' repulsion between H atoms. Charge effects lead to destabilization of the axial forms. There is only moderate coupling between puckering and methylene group rocking. Previously published electron diffraction (ED) data are reinvestigated using vibrational corrections and information from the ab initio calculations. On the basis of this MO constrained ED (MOCED) analysis a puckering angle $\phi = 35.1(1.8)°$ is found. Observed r_g and r_e bond distances are compared with ab initio values.

INTRODUCTION

Recent studies of azetidine have revealed that the accurate determination of its structure and conformation poses a challenge to both experimentalists and theoreticians [1—6]. IR [1], Raman [2], and electron diffraction studies [3] have shown that the molecule is puckered with the N—H bond preferring the equatorial site. Ab initio calculations confirm these experimental results [5, 6]. Differing observations, however, have been reported with regard to (i) the degree of puckering, (ii) the coupling between ring puckering and methylene group rocking and (iii) the shape of the puckering potential.

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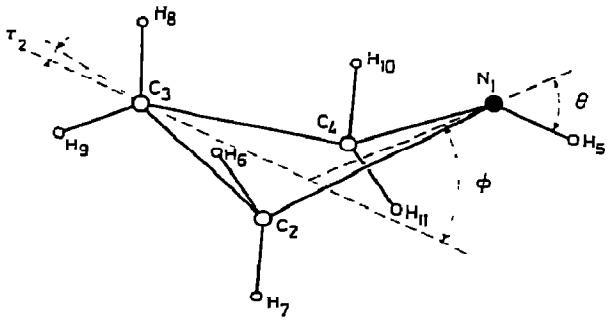


Fig. 1. Molecular model of azetidine (conformer I). Puckering (ϕ), rocking (τ_2) and pyramidalization angle (θ) are indicated. Rocking angle τ_1 is associated with the methylene groups at C_2 and C_4.

Degree of puckering

Employing electron diffraction (ED) Mastryukov et al. [3] found a puckering angle ϕ_a (see Fig. 1) of 33.1°. No other structure determination in the vapor phase has been reported so far but there is evidence from the IR study of Carreira and Lord [1] that supports a relatively large ϕ_a value. If, for example, the geometrical parameters of ref. 3 (Table 1, model II) are combined with the spectroscopically determined puckering coordinate x of about 0.16 Å [1], a puckering angle of about 34° is evaluated for the equatorial conformer of azetidine. On the other hand, this value seems to be quite high in view of the puckering angles reported for cyclobutane [7—10] and oxetane [11—14], the carbon and oxygen analogues of azetidine (see Table 1).

Ab initio data are not very helpful in solving this contradiction. From Table 1 it becomes obvious that minimal basis set calculations suggest that ϕ_e is significantly increased upon going from cyclobutane (13° [15]) to azetidine (23.5° [5]). Extended basis set results, however, predict the opposite trend; namely a decrease of 7° from 21.3° [15] to 14.7° [6].

Coupling between ring puckering and methylene group rocking

In a recent ab initio study on azetidine Catalán et al. [5] analyzed the coupling between ring puckering and rocking displacement. In the light of their results they argued that the high ED value of ϕ_a can be ascribed to the neglect of methylene group rocking in the experimental work [3]*. This argument is worth considering, especially when recalling the observations made for cyclobutane. Early ED work based on a molecular model

*Actually, the reasoning of Catalán et al. [5] is confusing. The authors report an STO—3G value of ϕ_e almost twice as large as the corresponding value calculated for cyclobutane [15]. Since the minimal STO—3G basis severely underestimates ring puckering [15], an experimental ϕ significantly larger than the one observed for cyclobutane is suggested by the STO—3G results of Catalán et al. [5].

TABLE 1

Puckering and rocking angles ϕ and τ (in degrees) for cyclobutane, azetidine, and oxetane (figures in parentheses give uncertainty)

Molecule	Parameter	Method			ED reinvest.	Ref.
		ED	IR	NMR		
	ϕ	35	29—37	27	26(3)	8, 9
	τ			4	6(3)	10, 17
	ϕ	33.1(2.4)	34[a]	15—20		3, 1, 4
	ϕ		14[b]	0		11, 13
		RHF/ STO—3G	RHF/ 4—31G	RHF/ 6—31G*	Correlation corrected	
	ϕ_e	13.0	21.3	24.4	26.7[c]	15
	τ_e	2.1	3.8	4.4	5.1[c]	
	ϕ_e	23.5	14.3[d]			5, 6
	τ_e	4.3	2.5[d]			
	ϕ_e	0	0	0	0	23

[a]Derived from the data of refs. 1 and 3, see text. [b]ϕ value which corresponds to the amplitude of puckering vibration; energy of zero-point vibration is above the top of the potential maximum at $\phi = 0°$, [c]D. Cremer, unpublished results. [d]Calculated with a 4—21G basis.

with $\tau = 0°$ yielded a relatively large ϕ_a of 35° [8] (Table 1). Subsequent ab initio [16] and NMR studies [10] on cyclobutane indicated that the methylene groups are tilted upon ring puckering. Tilting occurs in such a way that the axial hydrogen atoms in the 1,3 position come closer together, thus diminishing torsional strain but still keeping the H atoms in the attractive range of the van der Waals potential. Elaborate ab initio calculations with an augmented basis suggest a puckering angle of 24.4° and a rocking angle of 4.4° [15]. These predictions have been confirmed by Kuchitsu and co-workers [17] who reinvestigated cyclobutane by ED. These authors found a substantially lower ϕ_z value of 26(3)° accompanied by a rocking angle τ of 6(3)°.

Shape of the puckering potential

Finally, it should be pointed out that the reported ED value of ϕ_a might be affected by the assumption that equatorial and axial conformers of azetidine are about equally populated [3]. This possibility stems from IR spectroscopy results that led to the proposal of an asymmetric double-well potential function with a difference in energy of the two well minima of 0.27 kcal mol^{-1} and a barrier to planarity of 1.26 kcal mol^{-1} [1]. This energy

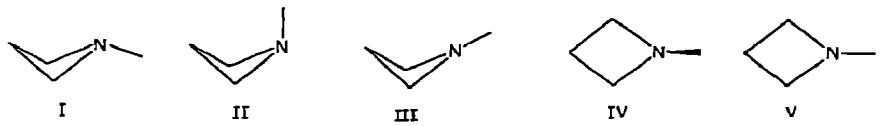
difference suggests an equatorial:axial ratio of about 60:40. Calculations with both minimal and split valence basis sets, however, suggest that the axial conformer is unstable [5, 6]. With the minimal STO—3G basis, an asymmetric single-well puckering potential was calculated [5]. Thus, a reinvestigation of the ED data giving 100% weight to the equatorial conformation might lead to a change in ϕ.

In this work, we present a detailed theoretical analysis of questions (i), (ii) and (iii). For this purpose, 21 different conformers of azetidine have been calculated at the restricted Hartree—Fock (RHF) level [18]. This has been done with an augmented basis set, since minimal and extended basis sets have been found to be insufficient for an accurate description of cyclobutane [15]. From the computed geometrical data we derive an average rocking angle τ_{av} that can be used in the reinvestigation of the ED data. Since ED is not very sensitive to variations in the position of the imine hydrogen, we will reconsider experimental measurements by utilizing theoretical data with regard to both the angle θ (Fig. 1) and the equatorial: axial ratio of azetidine conformers.

COMPUTATIONAL DETAILS

In this work single determinant RHF theory has been used throughout [18]. Energy minimization with regard to the internal parameters of azetidine has been performed with an improved version of the complementary Davidon—Fletcher—Powell (CDFP) method [19] which employs a finite-difference technique for the calculation of energy derivatives. Convergence was achieved when changes in energy were less than 0.01 kcal mol^{-1}, and the reduced norm of the gradient was lower than 0.001 [20]. Geometrical parameters thus obtained are accurate to 0.001 Å and 0.1°.

In a first step, STO—3G basis set [21] calculations were carried out for the conformers I—IV, namely the most stable equatorial form I, its axial counterpart II, then a puckered form III with a trigonal, sp^2 hybridized N, and the planar rings IV and V with pyramidal and planar N.



I II III IV V

The purpose of these calculations is twofold. First, they are aimed at resolving some of the inconsistencies of the STO—3G ab initio work of Catalán et al. [5]. Secondly, they provide reasonable starting geometries for the augmented basis set calculations. The latter were carried out with Hariharan and Pople's 6—31G* basis [22] in order to obtain data which could be compared with the related work on cyclobutane [15] and oxetane [23]. All internal parameters of forms I—V have been optimized within C_s (I—IV) and C_{2v} (V) symmetry constraints and using ϕ(I) for II and III. Thus 16 (I), 15 (II), 14 (III), 15 (IV), and 9 (V) geometrical parameters had

TABLE 2

RHF/STO—3G energies (kcal/mol^{-1}) of azetidine conformers I—V relative to the energy minimum at —170.00663 hartree compared with STO—3G results of ref. 5[a]

Form	This work		Ref. 5	
	ϕ	E_{rel}	ϕ	E_{rel}[b]
I	13.9	0	23.5	0
II	—10.0	1.12	—10	~1.9
III	10.0	11.36		
IV	0	0.53	0	~0.9
V	0	10.76	0	~14.6

[a]Minimal energy, —170.00576 hartree. [b]Estimated from Figs. 2 and 3 of ref. 5.

to be varied until the corresponding stationary points on the azetidine potential hypersurface were reached. In order to explore the potential in the ϕ direction three additional forms at ϕ = —12.45, 8.72 and 34.87° have been optimized in the same way. Geometries of intermediate forms for sp^3 and sp^2 hybridized N have been derived from computed parameters by applying linear interpolation techniques. Thus, the relative energies of 21 forms of azetidine have been evaluated at the RHF/6—31G* level.

THEORETICAL RESULTS

RHF/STO—3G and RHF/6—31G* energies of azetidine are summarized in Tables 2 and 3. The corresponding geometrical parameters are given in Tables 4 and 5.

TABLE 3

RHF/6—31G* energies (kcal mol^{-1}) of azetidine conformers given relative to the energy minimum at —172.07876 hartree[a]

Pyramidal N				Planar N	
Equatorial		Axial		ϕ(deg.)	E_{rel}
ϕ(deg.)	E_{rel}	ϕ(deg.)	E_{rel}		
0(IV)	1.65			0(V)	6.54
6.23	1.41	—6.23	2.08	4.98	6.63
8.72(*)	1.15				
12.45	0.79	—12.45(*)	2.45	12.45	7.09
18.68	0.25	—18.68	2.84	19.92	8.00
24.90(I)	0	—24.90(II)	3.45	24.90(III)	9.00
29.89	0.18			29.89	10.47
34.87(*)	0.90			34.87	12.59
37.36	1.51	—37.36	6.82		

[a]Forms that have been optimized completely are indicated by roman figures or (*).

TABLE 4

RHF/STO—3G geometrical parameters of forms I—V (distances in Å, angles in degrees)

r_e Parameter	I	II	III	IV	V
R(CN)	1.504	1.512	1.455	1.508	1.455
R(CC)	1.550	1.550	1.558	1.551	1.558
R(NH)	1.036	1.038	1.014	1.037	1.014
$R(C_2H_6)$	1.091	1.090	1.095	1.091	1.095
$R(C_2H_7)$	1.092	1.090	1.096	1.091	
$R(C_3H_8)$	1.086	1.086	1.086	1.086	1.086
$R(C_3H_9)$	1.087	1.086	1.086	1.086	
∠CNC	90.9	89.9	96.4	90.7	96.6
∠CCN	90.0	91.0	87.3	90.8	87.5
∠CCC	87.5	87.1	88.2	87.6	88.5
$\angle CNH_5$	111.2	107.8	131.8	109.4	131.7
$\angle NC_2H_6$	113.2	114.8	115.8	114.5	115.4
$\angle NC_2H_7$	114.2	111.2	115.3	112.1	
$\angle C_3C_2H_6$	116.1	116.0	115.2	114.9	114.6
$\angle C_3C_2H_7$	113.6	113.9	114.2	114.9	
$\angle C_2C_3H_8$	113.8	113.6	113.5	114.5	114.4
$\angle C_2C_3H_9$	115.6	115.9	115.4	114.9	
$\angle HC_2H$	108.8	109.0	108.2	108.8	108.3
$\angle HC_3H$	109.4	109.3	109.5	109.2	109.5
∠CNCC	10.0	7.2	7.2	0	0
∠NCCC	9.7	7.1	6.6	0	0
$\angle H_5NCH_6$	118.2	18.0	56.1	7.1	63.8
$\angle H_5NCH_7$	7.1	142.3	71.7	131.7	
$\angle H_6C_2C_3H_8$	10.8	10.9	9.0	1.8	126.8
$\angle H_6C_2C_3H_9$	117.0	117.0	118.6	125.8	0.6
$\angle H_7C_2C_3H_8$	138.1	138.6	135.1	129.1	
$\angle H_7C_2C_3H_9$	10.3	10.7	7.6	1.5	
ϕ	13.9	10.0	10.0	0	0
θ	59.0	64.4	0	61.8	0
τ_1	0.7	2.3	0.6	0.5	0
β	1.2	2.1	1.0	1.4	—0.9
ω	1.4	0.7	0.2	1.2	0
τ_2	1.4	1.7	1.5	0.4	0

Comparison of STO—3G results with those of Catalán et al. [5] reveals that the latter do not correspond to the most stable azetidine forms in STO—3G space. Thus, our absolute energy of I is 0.5 kcal mol^{-1} lower than the one given in ref. 5. Relative energies of forms II, IV and V are overestimated in ref. 5 by 0.4—3.8 kcal mol^{-1} (Table 2). This indicates that the puckering potential and the barrier to N inversion given in ref. 5 are only of qualitative value. More interesting is the fact that the puckering angle ϕ_e at the true STO—3G minimum is about 10° lower (Table 4) than has been found by Catalán et al. [5]. Relatively large deviations are also calculated for the C—N bond length (1.504 Å vs. 1.486 Å [5]), the internal ring angles, the rocking angle τ_2 and the angle θ. We conclude that the optimization pro-

TABLE 5

RHF/6—31G* geometrical parameters of forms I—V (distances in A, angles in degrees)

r_e Parameter	I	II	III	IV	V
R(CN)	1.467	1.481	1.441	1.473	1.438
R(CC)	1.541	1.540	1.547	1.543	1.551
R(NH)	1.001	1.003	0.991	1.000	0.991
$R(C_2H_6)$	1.084	1.085	1.087	1.086	1.089
$R(C_2H_7)$	1.089	1.084	1.091	1.084	
$R(C_3H_8)$	1.083	1.085	1.082	1.083	1.082
$R(C_3H_9)$	1.082	1.084	1.084	1.083	
∠CNC	91.2	88.8	94.8	91.9	96.8
∠NCC	88.8	90.5	86.7	90.8	87.7
∠CCC	85.7	84.6	86.5	86.6	87.8
$\angle CNH_5$	116.3	109.7	132.6	114.3	131.6
$\angle NC_2H_6$	114.5	115.5	116.1	114.7	115.4
$\angle NC_2H_7$	114.0	110.0	114.5	112.5	
$\angle C_3C_2H_6$	117.7	118.2	116.5	114.7	114.7
$\angle C_3C_2H_7$	112.1	112.9	113.5	115.3	
$\angle C_2C_3H_8$	112.7	112.0	111.6	114.6	114.7
$\angle C_2C_3H_9$	117.4	118.6	117.7	115.6	
$\angle HC_2H$	108.7	108.7	108.5	108.2	108.0
$\angle HC_3H$	109.3	109.2	109.9	108.7	109.0
∠CNCC	18.0	18.1	17.9	0	0
∠NCCC	17.1	17.5	16.6	0	0
$\angle H_5NCH_6$	101.6	29.4	44.1	0	63.6
$\angle H_5NCH_7$	24.5	152.9	83.6	124.2	
$\angle H_6C_2C_3C_8$	21.5	25.4	22.3	2.2	0.7
$\angle H_6C_2C_3H_9$	106.9	103.3	106.2	125.4	126.7
$\angle H_7C_2C_3H_8$	148.7	153.9	149.3	129.0	
$\angle H_7C_2C_3H_9$	20.4	25.1	20.8	1.3	
ϕ	24.9	24.9	24.9	0	0
θ	50.7	61.8	0	53.7	0
τ_1	2.4	4.2	1.7	0.6	0
β	0.7	3.1	0.4	1.6	—0.7
ω	2.0	0.4	0.6	1.1	0
τ_2	3.5	4.9	4.6	0.7	0

cedure applied in ref. 5 is insufficient to provide accurate geometrical parameters for azetidine.

Our STO—3G energies and geometries confirm what one would expect in view of the results found for cyclobutane [15]. Basis sets without polarization functions, especially minimal basis sets, severely underestimate the puckering in small rings. They are not suited for deriving a reasonable description of the degree of puckering and the puckering potential. It is, of course, possible to obtain some qualitative results by comparing STO—3G parameters of cyclobutane [15] with those of azetidine. For example, the STO—3G values of ϕ_e (cyclobutane, 13.0°; I, 13.9°) give support to the argument that azetidine is strongly puckered.

A reliable puckering angle is provided by our 6—31G* calculations. For I, we find $\phi_e = 24.9°$ (Table 5). Again, this is in accord with the cyclobutane value of 24.4° (Table 1). By employing correlation corrections, ϕ_e increases to 28° [23], which is somewhat larger than the corresponding cyclobutane value of 26.7° (Table 1). Thus it is safe to say that azetidine is slightly more puckered than cyclobutane.

The theoretical r_e parameters shown in Table 5 provide an idea of how bond lengths and angles change with changes in either ϕ (puckering) or θ (pyramidalization). Thus, it is obvious that the CN and NH bonds become shorter when the *s* character of the nitrogen valences increases. At the same time the CC and CH bond lengths become slightly longer.

If N adopts a trigonal structure, the CNC angle has to widen, thus increasing angle strain of the ring. Angle strain is lowered when the ring becomes planar. Therefore nitrogen inversion of azetidine should be facilitated by a decrease of ϕ. We calculate 6.5 kcal mol^{-1} for the most favorable path to N inversion, namely I → IV → V → IV′ → I′ where IV′ and I′ stand for the inverted forms. An inversion via form III requires 9 kcal mol^{-1}. These barrier values can be compared with experimental barriers of 5.8 and 9.0 kcal mol^{-1} observed for NH_3 and 1,3,3-trimethylazetidine [24].

The planar ring IV is destabilized by 1.6 kcal mol^{-1} with regard to form I. A ring inversion I → IV → II leads to an increase in energy of 3.5 kcal mol^{-1}. There exists no stable axial form as is indicated by the puckering potential shown in Fig. 2. RHF/6—31G* calculations clearly show that the puckering potential of azetidine must be regarded as an asymmetric single-well function. Its shape can be described as resulting from a superposition of two symmetric single-well potentials, one relatively narrow, centered at $\phi = 24.9°$ and describing the puckering of the equatorial form I, the other relatively broad,

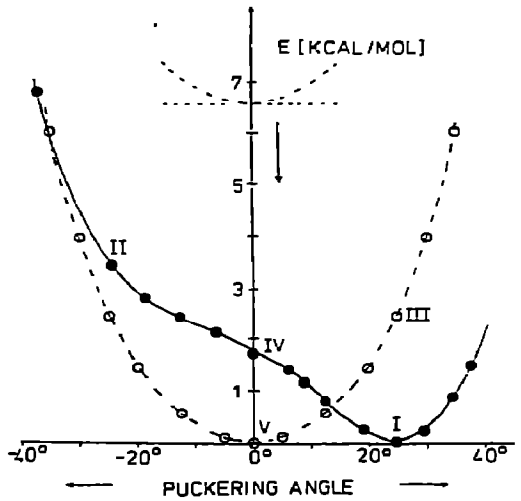


Fig. 2. RHF/6—31G* puckering potential of azetidine. (The dashed line corresponds to the potential of azetidine with a trigonal N, shifted by 6.54 kcal mol^{-1} along the energy axis as indicated.)

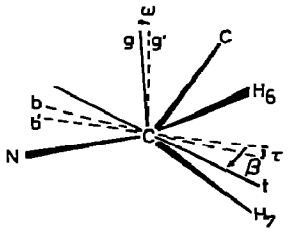


Fig. 3. Definition of rocking (τ), wagging (β) and twisting angle (ω). (t is the bisector of ∠NCC, b the bisector of ∠HCH, b' its projection into the plane containing N and the two C atoms; g' is perpendicular to b' and lies in the plane of the CH_2 group; its projection into the plane containing t and being perpendicular to the NCC plane is designated by g. Arrows indicate positive values of distortion angles.)

centered at $\phi = 0°$, $E = +1.65$ kcal mol^{-1} and describing the puckering of the axial form. It may be interesting to check whether the spectroscopically observed frequencies [1] can be fitted to the potential of Fig. 2.*

Puckering of the ring leads to a decrease of torsional strain. Strain can be further diminished by distortion of the methylene groups. We have described these distortions by a rocking angle τ,** a wagging angle β and a twisting angle ω, which are defined in Fig. 3. Ideal C_{2v} symmetry of the CH_2 groups is lowered to C_s for $\tau \neq 0°$ and to C_1 for $\tau, \beta, \omega \neq 0°$.

As can be seen from the data of Tables 1 and 5, methylene group rocking is somewhat lower in azetidine ($\tau_1 = 2.4°$, $\tau_2 = 3.5°$) than in cyclobutane ($\tau = 4.4°$). This has certainly to do with the fact that CH bond eclipsing can be further lowered by twisting and wagging of the CH_2 groups next to the N atom. We note that the dihedral angles between axial and equatorial CH (NH) bonds of azetidine and cyclobutane are of comparable magnitude, namely all larger than 20°.

To test the reliability of theoretical rocking angles, we have repeated some of the calculations correcting for the correlation error of the RHF ansatz [23]. We obtained rocking angles of 2.51° (τ_1) and 4.07° (τ_2). These were used when reinvestigating ED data.

STRUCTURAL ANALYSIS

We took the final form of the $sM(s)$ function without any modification from the previous ED study [3]. In ref. 3 the puckering angle ϕ_a was determined by assuming I and II to be equally populated and by keeping all τ, β and ω angles at 0°. In view of the ab initio results these assumptions are no longer appropriate. It is necessary to examine whether the experimental puckering angle changes significantly upon dropping the restriction $\tau = 0°$ and the equal weighting of I and II.

*This problem is currently being investigated by J. R. Durig.

**Naturally, τ is defined in the same way for all CH_2 groups of azetidine. Catalán et al. [5], however, used different definitions for the rocking angles which leads to some confusion. In particular, these authors discuss "a noticeable rocking angle β (= 13.1°) for the methylene groups attached to the nitrogen atom".

In addition, we have investigated the influence of vibrational effects by deriving an r_α structure of azetidine, which provides a more reliable value of the puckering angle than the r_a structure of ref. 3. (For definition of these structures, see ref. 25.)

The final subsection concerns a rough reduction of thermally averaged r_g parameters, derived from ED, to the equilibrium distances r_e which are obtained in ab initio calculations.

The rocking movement

In addition to the eight independent parameters chosen in the previous analysis, namely R(CC), R(CN), $R(\mathrm{CH})_{av}$, R(NH), $\angle$CNC, $\angle(\mathrm{HCH})_{av}$, θ and ϕ, an average rocking angle $\tau_{av} = (2\tau_1 + \tau_2)/3$ was introduced. In order to facilitate the least-squares refinement, R(NH) and θ were kept fixed at the values of ref. 3. In subsequent refinements their ab initio values were used.

Because of the relatively weak scattering power of the hydrogen atoms bonded to carbon, it was doubtful at the outset whether conclusive evidence could be obtained on the magnitude of the rocking angle. In fact, it became rapidly apparent that this parameter is ill-determined. With this in mind, our attention was primarily called to the influence of the rocking movement on the puckering angle of azetidine.

First, a series of refinements were carried out at fixed values of τ_{av}. The corresponding plot of Hamilton's "R-factor ratio" [26] versus τ_{av} is depicted in Fig. 4 together with refined values of the puckering angles ϕ_a. The best value of τ_{av} (2°) corresponds to a puckering angle of 31.5(2.5)°, which is only slightly different from the previous value of 33.1(2.4)° [3] obtained for $\tau_1 = \tau_2 = 0°$. By application of Hamilton's criterion for the R ratios, the 95% confidence interval is confined to the limits −2 and 7°.

When the rocking angle is also allowed to vary, the values collected in column I of Table 6 are obtained. Values of τ_{av} and ϕ are given in Table 6.

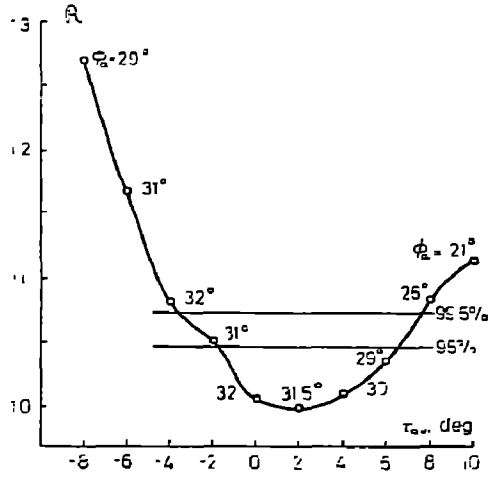


Fig. 4. Hamilton test for the rocking angle τ_{av} with refined values of ϕ_a.

TABLE 6

Puckering (ϕ) and rocking (τ_{av}) angles (deg.) for different conditions in the structural analysis of electron diffraction data on azetidine[a]

Parameter	Previous study[b] ϕ_a	Present reinvestigation					
		r_a			r_α		
		I[c]	II[d]	III[e]	IV[c]	V[d]	VI[e]
ϕ	33.1(2.4)	31.5(2.5)	30.7(3.3)	28.4(2.0)	33.9(1.8)	34.3(1.7)	29.9(1.9)
τ_{av}	—[f]	2.0(3.0)	3.7(3.0)[g]	6.3	−1.0(2.4)	−0.63(2.5)[h]	6.9
R factor	0.069	0.068	0.069	0.071	0.063	0.063	0.077

[a]Parenthesized quantities are three times the computed standard deviations. [b]Ref. 3. [c]ϕ and τ_{av} independent. [d]$\tau_{av} = k \cdot \phi$. [e]$\tau_{av} = 0.23\ \phi$. [f]Neglected in the analysis. [g]This result and its estimated standard deviation are calculated from the refined value of the coefficient $k = 0.12(10)$. [h]See footnote g with $k = -0.018(73)$.

All other parameters were found to be nearly insensitive to the conditions of the refinements.

Malloy and Lafferty [9], reexamining the IR and Raman data on cyclobutane, suggested that the puckering and the rocking motions are linearly dependent

$$\tau = k \cdot \phi \qquad (1)$$

They reported values of 0.22 and 0.25 for the coefficient k. A value of $k = 0.23$ has been used by Kuchitsu and co-workers [17] in their reinvestigation of cyclobutane by ED. We formally applied eqn. (1) and tested two possibilities, once refining ϕ and k and once refining ϕ alone at a fixed value of k. These results are shown in columns II and III of Table 6. Obviously $k = 0.23$ is too large when used for azetidine.

The r_α structure

So far no force field has been reported for azetidine. Therefore, we decided to transfer the force field used by Yokozeki and Kuchitsu in their ED study of piperazine [27]. Vibrational amplitudes (u) calculated as described by Stølevik et al. [28] should be reasonably reliable as these quantities are known to be only moderately sensitive to rather large variations in the molecular force field. The calculated u and $D = u^2/r - K$ parameters are listed in Table 7.

Dependent distances were calculated from the r_α values of the independent parameters and subsequently converted to the r_a values required for intensity calculation ($r_\alpha = r_a + D$). Resulting values of τ_{av} and ϕ_α based on the r_0 structure are given in column IV of Table 6. Although the relatively low R-factor indicates that a reasonable ϕ_α is obtained, the negative value of τ_{av} is unacceptable in view of the ab initio results. No significant improvements of τ_{av} are gained when applying the relationship $\tau = k \cdot \phi$, as can be seen from columns V and VI of Table 6.

TABLE 7

Molecular force field and calculated vibrational parameters[a]

K(N—C) = 5.5	F(N···H) = 0.52	H(CCC) = 0.32
K(C—C) = 2.3	F(C_2···H_5) = 0.46	H(NCH) = 0.28
K(N—H) = 5.6	F(C_2···H_8) = 0.48	H(CNH) = 0.32
K(C—H) = 4.1	F(H···H) = 0.07	H(CCH) = 0.22
F(N···C) = 0.7	H(CNC) = 0.35	H(HCH) = 0.44
F(C···C) = 0.25	H(CCN) = 0.30	Y = 0.11

Distance	u	D	Distance	u	D
N—C	442	—9	C_3···H_5	1296	20
C—C	524	—4	C_3···H_6	1069	—29
N—H	739	—102	C_3···H_7	1080	—25
C—H_{av}	789	—103	H_5···H_6	1669	9
N···C	625	12	H_5···H_7	1280	—51
C···C	515	5	H_5···H_8	1984	71
N_1···H_6	1025	—34	H_5···H_9	1431	—10
N_1···H_7	1037	—29	H_6···H_7	1282	—88
N_1···H_8	1241	6	H_6···H_8	1766	20
N_1···H_9	987	—15	H_6···H_9	1541	—20
C_2···H_5	1053	—21	H_6···H_{10}	1431	—11
C_2···H_8	1084	—23	H_6···H_{11}	1342	—20
C_2···H_9	1073	—25	H_7···H_8	1352	—39
C_2···H_{10}	955	—17	H_7···H_9	1761	20
C_2···H_{11}	1184	2	H_7···H_{11}	1914	48

[a]Force constants K and F in mdyn · Å^{-1}, H and Y (torsion) in mdyn · Å; amplitudes and vibrational corrections in 10^4 Å.

Attempts to compute a more reasonable rocking angle by using RHF/6--31G* values of R(NH) and θ also failed: τ_{av} was found to be more negative while ϕ_α slightly increased. Thus, it seemed more prudent to take τ_{av} = (2·2.5° + 4.1°)/3 = 3.0° and from ab initio results and give 100% weight to the equatorial form. With these constraints the remaining parameters have been refined. We note that this procedure of improving the ED analysis is in accord with the recently published MO constrained ED (MOCED) study on 1-butene [29].

Table 8 contains the most probable set of molecular parameters of azetidine derived from ED with recourse to the auxiliary information: spectroscopy (vibrational quantities) and ab initio calculations. For comparison, the r_a parameters of ref. 3 are also listed in Table 8.

Equilibrium geometry

Customarily, the distance and angle parameters derived from ED (r_a or r_g) are directly compared with the corresponding r_e parameters of ab initio calculations (see e.g., refs. 5 and 6). However, the r_g and r_e parameters for

TABLE 8

Experimental and theoretical parameters of azetidine (distances in Å, angles in degrees)

Parameter	r_a[a]	r_g[b]	r_e(expt.)	r_e(theo.)
R(CN)	1.482(6)	1.484(3)	1.478	1.467
R(CC)	1.553(9)	1.553(4)	1.545	1.541
$R(CH)_{av}$	1.107(3)	1.110(6)	1.092	1.085
R(NH)	1.022(14)	1.027[c]	1.003	1.001
∠CNC	92.2(0.4)	92.3(0.6)	92.3	91.2
$\angle(HCH)_{av}$	110.0(0.7)	111.3(2.8)	111.3	109.0
θ	67.0(3.4)	50.7[d]		50.7
ϕ	33.1(2.4)	35.1(1.8)	35.1	28.0[e]
τ_{av}	0[c]	3.0[e]		3.0[e]
R-factor	0.069	0.070		

[a]Ref. 3. [b]Angles are taken from the r_α structure. [c]Assumed. [d]RHF/6—31G* value of θ used in refinement. [e]Correlation corrected ab initio value.

the same internuclear distance may differ by more than 0.01 Å, which exceeds the limit of error of the ED parameter. At the same time, it is difficult to reduce correctly the r_g parameters to the equilibrium geometry. Therefore a simple scheme has been used.

For a Morse oscillator in its ground state it can be shown [30] that the ED parameter r_a and the equilibrium bond length r_e are related by

$$r_e \approx r_g - \frac{3}{2}au^2 = r_a + \frac{u^2}{r} - \frac{3}{2}au^2 \qquad (2)$$

where a is the Morse asymmetry constant. The terms u^2/r and $3/2\ au^2$ represent harmonic and anharmonic corrections, respectively. More sophisticated calculations in terms of normal coordinates [31, 32] lead to essentially the same conclusion. This gives support to the idea that the r_e values of bonded distances of polyatomic molecules can be roughly estimated from eqn. (2)*.

The asymmetry parameter a was approximately fixed at 2 $Å^{-1}$ for bonds not involving hydrogen and at 3 $Å^{-1}$ for bonds involving hydrogen [33, 35]. Utilizing the amplitudes of vibration u of Table 7, the experimental r_e parameters shown in Table 8 have been determined. The bond angles of the r_α structure are believed to be fairly close to the equilibrium values since the differences may be as small as a few tenths of a degree [36]. Accordingly they have been transferred to the r_e structure. A similar procedure, however, is questionable in the case of the puckering angle ϕ_α since ϕ_α might differ substantially from the equilibrium angle ϕ_e.

*The case of methane [31, 33] is of particular concern in view of recent ab initio work [34].

DISCUSSION

In ref. 3 two geometrical models of conformation I have been found which provided nearly equal fits of the experimental data. Preference was given to model II on the basis of primitive molecular mechanics calculations and a comparison with related data of cyclobutane and oxetane. Our ab initio calculations fully confirm this choice.

Although it cannot be established by the ED data alone whether the CH_2 groups are tilted or not, the ab initio results clearly indicate that methylene group rocking is almost as important as in the case of cyclobutane [9—10, 15]. On the other hand, it is quite obvious that consideration of an additional parameter τ_{av} does not change the experimental puckering angle. This is in accord with theory*.

The experimental puckering angle is hardly influenced by the different conditions of the various refinements: rocking or shrinkage corrections lead to essentially the same ϕ within the limits of computed uncertainties (Table 6).

While ϕ_a and ϕ_α are almost identical, our best ab initio results suggest a somewhat lower ϕ_e of 28° (correlation corrected results [23]), which is slightly outside the margin of experimental error. Future studies have to show whether the relatively large difference $\phi_\alpha - \phi_e$ is real or an artefact of the applied methods and techniques.

Nevertheless, the agreement between experimental and theoretical puckering angles is satisfying. The relatively strong puckering of azetidine has been confirmed by our work. This seems to be a result of the topology of the molecule: while bond eclipsing between the NH and the adjacent CH_2 groups adds to the forces that cause out-of-plane puckering, one of the forces cushioning puckering is missing, namely van der Waals' repulsion between axial hydrogen atoms at N and C_3. We note that an imine hydrogen in the axial position of I would be located just 2.2 Å away from H_8, i.e. within the range of van der Waals' repulsion. Thus ring puckering of I arises from H,H repulsions but these are definitely less than in cyclobutane.

A large ϕ is certainly supported by the attractive interactions between the nitrogen lone pair and the positively charged H_8. Charge effects are probably responsible for the instability of the axial forms. The computed gross atomic charges suggest that the axially positioned hydrogen atoms H_7 and H_{11} become more positively charged in II than in I owing to stabilizing interactions with the nitrogen lone pair that reside on the same side of the ring. As a consequence, negative charge is accumulated at C_2 and C_4 leading to destabilizing charge repulsions with N which are definitely higher than in I.

It is certainly an oversimplification to attribute the stability of I to any single effect. Inspection of the MOs shows that orbital mixing and orbital

*A statement to the contrary was made by Catalán et al. [5]. In recent calculations of the same authors [37], however, a value of 23.0° was found for $\tau = 0°$, thus confirming the moderate coupling between ϕ and τ. We note that the new ϕ value is still in error by almost 10° (see Table 4).

I II

Fig. 5. Bond eclipsing between NH and the adjacent CH_2 groups.

reorientation enhance stabilizing interactions in I [23]. Pyramidalization at the nitrogen also plays an important role as is indicated by the θ angles of Table 5. Figure 5 shows that bond eclipsing is lowered in I when θ decreases, i.e. when the *s* character of the N hybrid orbitals increases. The nitrogen bonds become stronger. In II, the opposite is true (Fig. 5). A relatively large value of θ, however, causes enhanced H,H repulsion and a weakening of the nitrogen bonds.

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