Electron Diffraction Investigation of the Molecular Structure of Monocyanocyclobutane

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The molecular structure and conformation of monocyanocyclobutane (MCCB) have been determined by gas-phase electron diffraction. In contrast to previously published MW spectroscopic results[10,11] and in accordance with a recent MW and *ab initio* study,[12] this molecule exists in axial and equatorial forms. The stability of the equatorial conformer (77%) is evidently higher than that of the axial one. Most likely due to simultaneous inductive and mesomeric interactions of the cyano group with the four-membered ring, MCCB does not obey the Jonvik and Boggs relationships, in contrast to a variety of related monosubstituted cyclobutane homologues. As a result of the influence of the cyano group as a substituent and in agreement with data for 1,1-dicyanocyclobutane, the adjacent C−C ring bond distance (1.557 Å) is larger than the distal C−C ring bond distance [1.547 Å(ax) and 1.551 Å(eq)]. The puckering angles are 19.1° and 27.0° for the axial and equatorial conformers, respectively.

Dedicated to Professor Otto Bastiansen on his 70th birthday

One of the main lines of investigation followed by structural chemists is the examination and systemization of the effects of substituents on the electronic configuration, and hence on the reactivity of the remainder of the molecule or at least on a particular group within it. Jonvik and Boggs have recently studied a series of monosubstituted four-membered ring systems by means of computational methods.[1] They derived from these studies some interesting predictions which reflect the correlation found between the electronegativity and some prominent parameters of the ring, including its conformational stability. We recently published two structural studies on cyclobutylsilane[2] and cyclobutylgermane,[3] and the structural parameters for these two molecules can be interpreted as supporting these predictions. Furthermore, with these predictions in mind we investigated most recently the structure of 1,1-dicyanocyclobutane[4] to examine whether or not the effects of substituents in 1,1-disubstituted cyclobutanes are additive. The structural results for this disubstituted system, however, demonstrate a significant deviation from Jonvik and Boggs' rule which correlates the electronegativity of the substituent with the skeleton C−C bond lengths. This rule, however, is the only one which might be applicable to disubstituted cyclobutanes.

The present structural analysis of monocyanocyclobutane (MCCB) has been initiated mainly for three reasons:

(i) to continue our previous efforts to understand the nature of the electronic interchange between the cyano group and the fragment R attached to it. Two main effects should certainly be taken into account when attempting an explanation of the perturbation of bond lengths and bond angles caused by the cyano group. These are firstly the inductive effect of the electrophilic C≡N group and secondly the possibility of the formation of delocalized π-bonding with groups conjugated with the C≡N bond. Depending on the nature of the substituent R and its electronegativity, the

two-way σ and π charge transfer between R and the N atom in the cyano group could be fairly complex.[5,6] Four-membered rings with their puckering capability and the possibility of the formation of two conformers are considered to be sensitive detectors for such effects of substituents.

(ii) The above-mentioned relations between the electronegativity of substituents and the prominent parameters for monosubstituted cyclobutanes were derived on the basis of studies carried out on systems with substituents showing either a purely inductive or a purely mesomeric effect. The cyano group, however, provides both effects simultaneously. This group is known to be an electron acceptor with a pronounced inductive influence, in addition to its readiness for mutual π-interaction with adjacent π or pseudo-π systems.[7,8] More clearly, the cyano group can either accept or donate electrons and these are either of σ- or π-type or both. Consequently, the cyano group can in principle behave as a π-donor or acceptor or a σ-donor or acceptor. Taking this more or less unique two-way charge transfer capability of the cyano group into consideration we may settle the question about the applicability of the Jonvik and Boggs rules (JB-R) to a substituent of such high electronegativity (3.3) and pronounced versatility regarding charge transfer and electrostatic interaction with adjacent groups. In our recent investigation on the molecular structure of 1,1–dicyanocyclobutane[4] we discussed the results in the light of the above-mentioned rules, in so far as they are valid for disubstituted systems. In this particular case the results indicated a distinct deviation from these rules. Since it was not clear whether the source for this incompatibility is the treatment of a disubstituted system or the extraordinary charge transfer effects of the cyano group, we decided to study MCCB. Additionally, it can be anticipated that the aforementioned electronic properties of the cyano group would lead to a substantial change in the geometry of the ring. This will allow for an unequivocal understanding of effects of substituents in monosubstituted four-membered rings in terms of the JB-R. Moreover, a comparison of the structural results for MCCB with those for DCCB may provide some evidence for the additivity of effects of substituents.

(iii) In an earlier far infrared study[9] the potential function for the ring puckering vibration of MCCB was determined to be an asymmetric single-minimum potential. Thereafter, the authors concluded that only one conformer for this molecule should be present. In 1973 two microwave investigations[10,11] led to postulation of the exclusive existence of the equatorial conformer of MCCB. A very recent microwave and *ab initio* investigation by Caminati *et al.*,[12] however, revealed the presence of both equatorial and axial conformers. It should be pointed out that in those previous spectroscopic studies all structural parameters, except the puckering angle[10,11] or the conformational ratio,[12] have been assumed. The main purpose of the present electron diffraction investigation was, therefore, to carry out a complete conformational analysis of MCCB, and to gain information on the electronic distribution between the cyano group and the ring from a critical inspection of the structural results. The electron diffraction method proved to be reliable and efficient for the solution of such conformational problems on numerous occasions. It is worthwhile mentioning that the first demonstration of the coexistence of conformers in the gas phase was presented in 1946 by Bastiansen and Hassel.[13]

Experimental

MCCB was prepared in our laboratory in a manner analogous to the preparation of DCCB.[4] Monoethyl ester of cyclobutanecarboxylic acid was treated for 10 days at room temperature with a concentrated solution of ammonium hydroxide, saturated with NH_3 several times, and the resulting amide was dehydrated with P_2O_5 under reduced pressure (100 Torr). Distillation of the crude sample yielded pure MCCB, b.p. 86–87 °C / 720 Torr. The purity was checked by IR and mass spectroscopy.

The electron diffraction scattering intensities were recorded on Kodak electron image plates, using the Balzers Gas Diffractograph KD-G2 at the University of Tübingen.[14] Data were collected using two camera distances of 50 and 25 cm (nominal). Four photographic plates at each camera distance were selected for the structure determination. The wavelength of the electron beam was calibrated using diffraction patterns for ZnO

Table 1. Experimental conditions for electron diffraction experiments.[a]

Camera distance/mm	Temperature/°C		Camera pressure/Torr	Exposure time/s	Wavelength (λ)/Å	s-Scale/Å^{-1}
	Sample	Nozzle				
500	30	50	1.5×10^{-5}	3.5– 6	0.048646 (16)	1.6–17.8
250	30	50	2.0×10^{-5}	15 –25	0.048686 (23)	6.0–35.0

[a]Accelerating voltage $\cong$ 60 kV.

powder. Details of the experiments are given in Table 1. The diffraction patterns were scanned by a modified ELSCAN 2500 microdensitometer[15] using intervals of $\Delta r = 0.1$ mm. The optical density data were processed by routine methods[16] and reduced to the modified molecular intensities $s \cdot M(s)$ at intervals of $\Delta s = 0.2$ Å^{-1} separately for each photographic plate. The atomic scattering amplitudes and phases given by Haase[17] were used.

Structure determination

Although the available *ab initio* results indicate the existence of two conformers, a single-conformer model involving only the equatorial conformer was first tried following the microwave studies of Durig *et al.*[10] and Fong *et al.*[11] While this model fits the region of the bonded distances of the radial distribution curve fairly well, the discrepancy in the region of the non-bonded distances was, however, evidently high. Consequently, this one-conformer model of MCCB was

abandoned and the *ab initio* geometry of MCCB was used as a starting model for the refinement.

By symmetry there are 51 distinct intramolecular atomic distances. Thus, with the same number of vibrational amplitudes for both conformers and the ratio of conformers, a total of 205 parameters is required for a proper description of the radial distribution curve. In order to facilitate the analysis and to limit variable geometrical parameters to a reasonable number, the following constraints concerning the molecular model were introduced (see Fig. 1 for atom numbering): (1) The intramolecular r_a distances are approximated with a geometrically consistent model. (2) The geometrical parameters for both conformers are equal, except for the most prominent parameters, the dihedral angle θ, and the angle between the bond C_1-C_5 and the plane $C_2C_1C_4$. (3) All C–H bonds have the same length. (4) No twisting or wagging of the CH_2 groups is considered. (5) The difference between the ring C–C distances, $\Delta_{CC} = C_1C_2 - C_2C_3$, was fixed at the value determined by the *ab initio* calculations. (6) Sev-
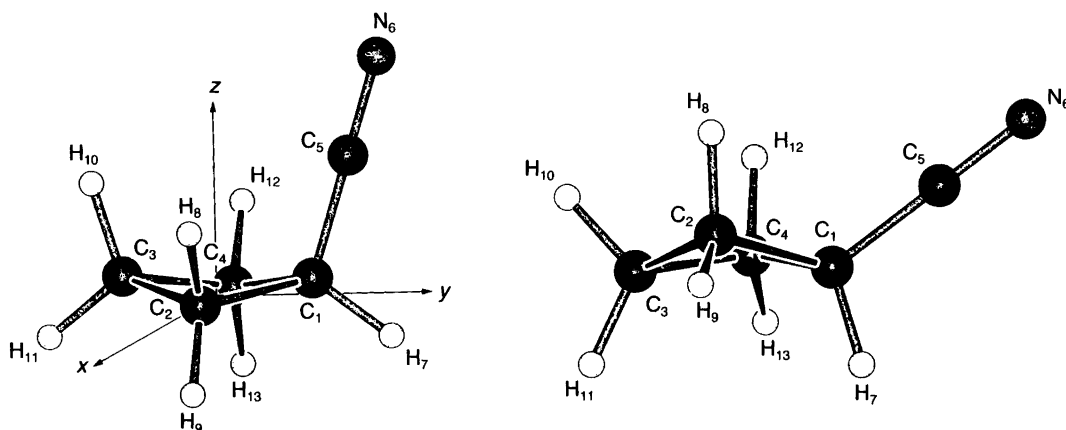

Fig. 1. Molecular model and atom numbering of axial (left) and equatorial (right) conformers of monocyanocyclobutane.
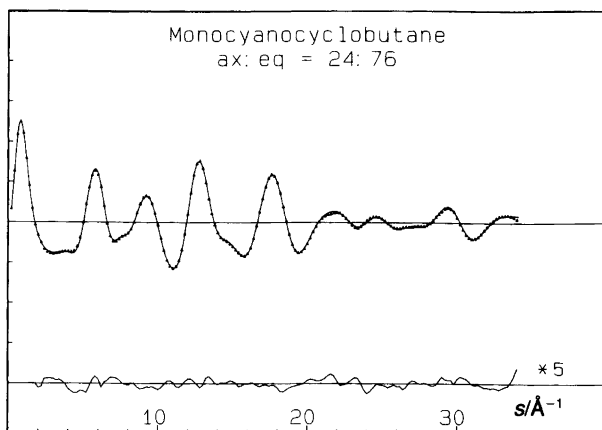
Fig. 2. Experimental (dotted line) and theoretical (solid line) reduced molecular intensities $s \cdot M(s)$ and difference ($\times 5$) for monocyanocyclobutane.

eral vibrational amplitudes of nonbonded distances, $C \cdots H$, $N \cdots H$ and $H \cdots H$, were grouped in a reasonable manner and fixed.

The assumptions (1)–(4) were made without regard to the *ab initio* structure in order to obtain an experimental model that is independent of the quantum mechanical calculations. The constraint (5) concerning the ring $C-C$ bonds had to be introduced due to high correlations: the electron diffraction method does not allow, on the level of the r_a structure, the independent refinement of both ring $C-C$ bond lengths. Taking into account the fact that quantum mechanical calculations usually provide accurate values for differences between bonds, but not necessarily their absolute values, this constraint seems reasonable.

The structural refinements were performed on the basis of the molecular intensities using Mar-quardt's non-linear modification of the least-squares procedure.[18] A diagonal weight matrix was applied. Fig. 2 presents a comparison of the experimental reduced molecular intensity $s \cdot M(s)$ with the intensity function calculated from the final best-fit model. While the first peak in the radial distribution curve (Fig. 3) includes contributions from $C-H$ and $C\equiv N$ bond distances, and the second peak is determined by the contributions of the two ring $C-C$ bond distances and the C_1-C_5 atom pair, more than 35 different contributions from non-bonded atom pairs are included in the two peaks in the range between 2 and 2.8 Å. This elucidates the necessity of grouping vibrational amplitudes of similar non-bonded distances in both conformers and fixing them at reasonable values. In general, most of the vibrational amplitudes of the non-bonded distances

Fig. 3. Experimental (dotted line) and theoretical (solid line) radial distribution curves for monocyanocyclobutane.
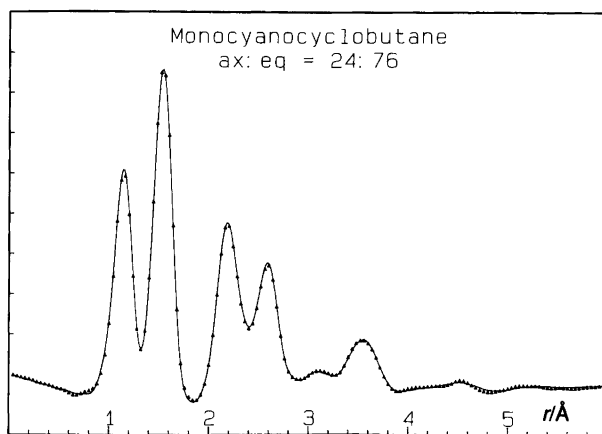
were fixed in the early stages of the fitting procedure. This should be done because of the instability of the least-squares refinements as a result of high correlations between similar distances and their vibrational amplitudes. However, after an acceptable level of refinement was achieved several of these amplitudes were refined in a series of fitting steps, keeping some of them fixed and varying the others. In particular, the amplitudes allotted to the non-bonded distances which define the puckering angle and the ratio of the two conformers have been adjusted. For instance, in order to reduce the discrepancies between the calculated and experimental radial dis-

tribution functions within the range from 2.8 to 4.8 Å, all amplitudes attributed to this range were treated using the successive fitting procedure mentioned above and were then fixed during the final steps of refinements. Only the amplitudes of the non-bonded distances, $(C_2 \cdots C_5)_{ax}$, $(C_3 \cdots C_5)_{ax,eq}$ and $(C_2 \cdots N)_{ax,eq}$, were refined. The introduction of the difference Δ_{CC} between the ring C−C distances, with a fixed value transferred from the ab initio calculations has proved to be helpful during the fitting procedure. In one of the cycles of the refinement this parameter was allowed to vary. It converged to a value of 0.0082 Å. However, since its correlation with the

Table 2. Final structural results for monocyanocyclobutane [distances (r_a) and amplitudes of vibration (l) in Å, angles in degrees]. For atom numbering see Fig. 1. Error limits in parentheses are three times the standard deviation (3σ).

Parameter	Equatorial conformer		Axial conformer	
	r_a	l	r_a	l
(a) Independent parameters				
C1−C2	1.557 (5)	0.054 (2)		
C2−C3	1.551[a]	0.054 (2)	1.547[a]	
C1−C5	1.454 (4)	0.045[b]		
C≡N	1.156 (3)	0.038 (3)		
C−H	1.112 (5)	0.094 (6)		
θ^c	27.0 (1.1)		−19.1 (2.3)	
∠C2−C1−C4	88.7 (1.1)			
∠C5−C1−H7	112.4 (6.8)			
∠H−C2−H	109.1 (4.8)			
∠H−C3−H	112.0[b]			
α_1^d	−7.3 (8.1)		+5.3 (8.9)	
α_2^e	+2.0[b]		−2.0[b]	
α_3^f	−4.0[b]		+4.0[b]	
γ^g	0.0[b]			
Percentage	76.6 (7.6)		23.4 (7.6)	
R_{500}^h	0.038			
R_{250}^h	0.043			
(b) Important nonbonded distances and vibrational amplitudes				
C1···C3	2.157	0.059[b]	2.181	0.059[b]
C1···N6	2.610	0.058[b]	2.610	0.058[b]
C2···C4	2.178	0.059[b]	2.178	0.059[b]
C2···C5	2.583	0.062 (11)	2.467	0.062 (11)
C2···N6	3.614	0.103 (12)	3.466	0.080[b]
C3···C5	3.446	0.125[b]	2.991	0.081 (50)
C3···N6	4.542	0.155[b]	3.910	0.150[b]

[a]Determined from the constrained difference $\Delta_{CC} = C_1C_2 - C_2C_3$ (see text). [b]Not refined. [c]Puckering angle. [d]Tilt angle of the group $C_5-C_1-H_7$. [e]Tilt angles of the groups $H-C_2-H$ and $H-C_4-H$. [f]Tilt angle of the group $H-C_3-H$. [g]$\gamma = 180 - \angle C-C\equiv N$. [h]$R = [\Sigma w_i \Delta_i^2 / \Sigma(w_i s^2 M_i^2(obs))]^{\frac{1}{2}}$, where $\Delta_i = sM_i(obs) - sM_i(calc)$.

C_1–C_2 bond length and other relevant parameters was considerable, it was again fixed at 0.01 Å and 0.006 Å for the axial and equatorial forms, respectively. The final results for the r_a structure of the pseudo-equatorial and pseudo-axial conformers of MCCB are summarized in Table 2. Error limits are based on 3σ values, and systematic errors due to constraints are not included.

One cause of the difficulties in the structure refinements mentioned above is the complete neglect of all linear[19] and non-linear[20] shrinkage effects introduced on applying constraint (1). It is therefore desirable to take these effects into account, and to determine the geometrically consistent r_α representation of the molecular structure. This reduces the number of independent geometry parameters to 20; this number can be reduced reasonably well to 16 on applying constraints (3) and (4). However, with these reductions the structural information provided by the scattering intensities is still insufficient for a reliable determination of all parameters. Therefore, the inclusion of rotational constants as independent observations has proven to be useful. The proper procedure for this kind of joint analysis has been established in the past two decades.[21] It requires the calculation of the harmonic vibrational contributions to both the rotational constants and the electron diffraction patterns. The resulting structure representation is known as the r_{av} structure.

Unfortunately, no force field is as yet available for MCCB. In order to obtain a reasonable basis for the calculation of the harmonic contributions, we tried to transfer the diagonal force field of monochlorocyclobutane[22] for the cyclobutyl part and the diagonal force constants of methyl cyanide[23] for the cyano group. However, the structure calculations based on this assumed force field resulted in unsatisfactory parameters. We attribute this difficulty to the deficiencies of the force field used as well as to the underestimation of the vibrational contributions of the large amplitude puckering motion. This point has been discussed extensively by Jonvik.[22] We must therefore postpone the combined analysis until a more reasonable force field and additional rotational constants are available.

Discussion

Table 3 shows a comparison between some of the principle experimental and ab initio-calculated[12] geometric parameters for both conformers of MCCB. The optimization of all geometrical parameters was performed using Pulay's gradient method.[24] The basis set used was the 4-21G*[25] with d-functions on carbon and nitrogen. Taking into consideration the different sources of both structural determinations, the agreement between the experimental and calculated values appears to be reasonable except for two cases: (i) the calculated C≡N bond length (1.131 Å) is clearly smaller than the experimentally determined value for this bond (1.156 Å), and (ii) the calculated C_1–C_5 bond length (1.468 Å for the axial and 1.466 Å for the equatorial conformer) is greater than the experimentally determined value (1.454 Å).

It is interesting to point out that feature (i) is in line with the repeatedly made observation on triply bonded atom pairs. In order to be more specific, several examples of calculated and experimental C≡N bond distances in some cyclic compounds, as well as their differences, are listed in Table 4. As can be easily seen from this table, the differences between the computed and experimental C≡N bond lengths are remarkably consistent. It may be added that the relatively sub-

Table 3. Comparison between electron diffraction and ab initio results for MCCB (distances in Å, angles in degrees).

	Electron diffraction		Ab initio[a]	
	eq	ax	eq	ax
C1–C2	1.557		1.556	1.559
C2–C3	1.551	1.547	1.550	1.549
C1–C5	1.454		1.466	1.468
C≡N	1.156		1.131	1.131
C–H	1.112		1.084	1.084
∠C2–C1–C4	88.7		88.4	88.1
θ[b]	27.0	−19.1	27.4	−24.4
∠C5–C1–H7	112.4		108.9	108.7
∠H–C2–H	109.1		109.6	109.6
∠H–C3–H	112.0		109.3	109.3
γ[c]	0.0		0.8	0.3
Percentage	76.6	23.4	81.0	19.0

[a]Ref. 12. [b]Puckering angle. [c]γ = 180 − <C–C≡N.

Table 4. Values of experimentally determined and *ab initio*-calculated C≡N bond distances (Å) in some cyclic compounds.

Compound	C≡N (exp)	C≡N (calc)	Difference
MCCP[a]	1.161	1.136	0.025
DCCB[b]	1.162	1.138	0.024
MCCB[c]	1.156	1.131	0.025
3-CNCP[d]	1.162	1.136	0.026

[a]Monocyanocyclopropan, see Ref. 46. [b]Ref. 4. [c]This work. [d]3-Cyanocyclopropene, see Ref. 29.

stantial difference of about 0.025 Å can hardly be explained exclusively by the systematic distinction between the r_e and r_a structures. It is rather more likely that the approximations made in the calculations (exclusion of electron correlation) and the quality of the representation of the wavefunction by the basis set used contribute partially to this value. It is generally known that there are characteristic differences between *ab initio* and experimental parameters, "offset values",[26] which are introduced for different types of bond distances and bond angles individually.[27,28] In some particular cases these empirical corrections may attain relatively high values, for instance for aliphatic C−H bond length $r_g - r_e = 0.034$ Å.[27] Based on this experience, the value of 0.025 Å for the difference between the computed and experimental C≡N bond distances displayed in Table 4 may be considered as an adjustment factor for calculated C≡N bond lengths in saturated cyclic compounds. Analogous argumentation can be applied to the difference in the C−H bond distance of 0.028 Å (Table 5). It is noteworthy that this C−H adjustment factor in cyclic molecules of this type is about 0.006 Å less than that for the same bond distance in aliphatic compounds.

Table 5. Values of experimentally determined and *ab initio*-calculated C−H bond distances (Å) in some cyclic compounds.

Compound	C−H (exp)	C−H (calc)	Difference
Cyclobutane	1.109[a]	1.081[b]	0.028
DCCB	1.106[c]	1.078[c]	0.028
MCCB	1.112[d]	1.084[e]	0.028

[a]Ref. 35. [b]Ref. 37. [c]Ref. 4. [d]This work. [e]Ref. 12.

In contrast, feature (ii) states that the experimentally determined C_1-C_5 bond length (1.454 Å) is shorter than the calculated one (1.468 Å for the axial and 1.466 Å for the equatorial conformer). Regardless of the assumed equality of this bond length for both conformers in the experiment, this means, however, that in this case the r_e value is higher than the r_a value. This surprising feature cannot be rationalized trivially unless we accept that the *ab initio* calculations, at least when the 4-21G∗ basis set is used, fail in the case of the optimization of a C−C bond distance alternating with a triple bond. This conclusion is supported by similar results reported by other groups.[29-32] It is interesting that even the application of extended split-valence basis sets of higher level, as has been demonstrated in some of the latter investigations, did not lead to an inversion of this tendency. This again indicates that this striking feature does not depend on the basis set used.

One of the major aims of this study was to verify the applicability of the JB-R to MCCB. Briefly, these rules describing some aspects of substituent effects on four-membered rings state:

The higher the electronegativity of a substituent: (1) The greater the stability of equatorial conformer. (2) The larger the puckering angle of the equatorial form. (3) The smaller the puckering angle of the axial form. (4) The more the C_1-C_2 bond length decreases by comparison with the C_2-C_3 bond length. In this context we present in Table 6 a comparison between some relevant structural parameters obtained in the present and previous experimental and theoretical studies on several monosubstituted four-membered ring systems. An inspection of this table shows that there is only limited agreement with the JB-R in the case of MCCB. Thus, while the puckering angles of the axial and equatorial conformers fit fairly well within the predicted behavior for these angles, the others show a significant discrepancy. The most striking disagreement, however, is the positive value of Δ_{CC}. This reverse tendency for the difference of the skeletal C−C bond distances in MCCB clearly contradicts relationship (4) of JB-R. It is worthwhile mentioning that a similar discrepancy has been observed for 1,1-dicyanocyclobutane[4] and for cyclobutylacetylene.[33] The values of Δ_{CC} for these compounds were +0.025 Å and $(+0.0113$ Å$)_{ax}$, $(+0.007$ Å$)_{eq}$, re-

Table 6. Electronegativity of substituents, stability of equatorial conformer, and some important structural parameters for a variety of monosubstituted cyclobutanes (angles in degrees).

Compound	EN[a]	Eq-conf (%)	ΔE (ΔG) (kJ/mol)	Δ_{CC} (Å)	θ_{ax}	θ_{eq}	Method
C_4H_7 F	4.10[b]	98	9.1	–	−13.4	26.9	ab initio[d]
C_4H_7 CN	3.3	77 (8)	3.1 (1)	+0.010	−19.1 (2.3)	27.0 (1.1)	ED[j]
C_4H_7 Cl	2.83[b]	85	4.3	−0.016	−20.3	25.1	ab initio[d]
C_4H_7 Br	2.74[b]	84	4.2	−0.008	–	–	IR[e]
C_4H_7 GeH₃	2.32[c]	77 (7)	3.0 (1)	~0.0	−20.4 (3.6)	25.3 (3.1)	ED[f]
C_4H_7 CH₃	2.27[c]	66	1.7	+0.002	−19.7	24.1	ab initio[g]
		89	5.0 (1.0)	0.0	−20.0	31.0 (1.0)	ED[h]
C_4H_7 SiH₃	2.21[c]	54	0.4	+0.016	−20.3	21.8	ab initio[i]
		59 (5)	0.8 (0.4)	+0.016	−23.3 (4.1)	31.8 (3.0)	ED[j]
C_4H_7 Li	0.97[b]	32	−1.8	+0.032	−26.5	23.7	ab initio[d]

[a]Electronegativity of substituent. [b]Ref. 47. [c]Ref. 48. [d]Ref. 1a. [e]Ref. 49. [f]Ref. 3. [g]Ref. 1b. [h]Ref. 50. [i]Ref. 2. [j]This work.

spectively. The electronegativity value for the -C≡C- group is 3.07.[34] Further disagreement with JB-R is displayed by ΔE or the ax:eq ratio (Table 6). From the present point of view, the only conclusion, if any, which can be drawn in this respect is that the effect of substituents including an sp hybridized carbon atom on four-membered rings most likely cannot be explained in terms of relationships found for a variety of monosubstituted cyclobutanes. It appears rather more likely that substituents of this type obey some other criteria of interaction with cyclobutane than those valid for substituents with purely σ inductive effects. Thus, further structural results for additional cyclobutanes with substituents which display a "two-way" charge transfer interaction, similar to the C≡N type, should be awaited for the purpose of comparison. This might reveal specifically systematic behavior for this series.

Table 7 contains a comparison between some prominent structural parameters for cyclobutane, MCCB and DCCB. As mentioned above, one of the main purposes of this study was to investigate whether substituent effects in geminally disubstituted cyclobutanes such as DCCB are in any sense additive. As seen in Table 7, the value of 0.025 Å for the parameter Δ_{CC} for DCCB is approximately twice that for MCCB. This increase in the difference between C_1-C_2 and C_2-C_3 bond distances as a result of the disubstitution can be interpreted as an indication of an enhanced influence of substituents.

It is interesting to note that the C≡N bond in MCCB (1.156 Å) is shorter than the corresponding bond in DCCB (1.162 Å). Furthermore, the C_1-C_5 bond length is about 0.012 Å smaller in MCCB than in DCCB, and in contrast to the C−C≡N groups in DCCB the C−C≡N chain in MCCB is linear. One plausible interpretation for these observations is the following: As has been discussed previously[4] there are several indications of local conjugation between the geminal cyano groups in DCCB due to the participation of the ring orbitals (Walsh-Orbitals). The mutual interplay of electron interactions and the redistribution of the electron density within this coupled π-electron system leads to enhanced higher local charge concentration on the nitrogen atoms in accordance with their relatively high electronegativity. This, however, gives rise to an additional repulsion interaction between these two atoms. In contrast, the cyano group in MCCB interacts exclusively with the ring system. Taking all this into consideration, the above-mentioned distinctions in both related molecules appear (without going in further details) to be rational. Nevertheless, one particular remark should be made concerning the linearity of the C−C≡N group in MCCB: In one of the refinements the bending angle γ was allowed to vary. This attempt led, however, to unreasonable values of some parameters. Moreover, this refinement provided a very small bending angle with large uncertainty (0.4±2.0)°; this angle was subsequently fixed at zero during the final refinements.

Table 7. Comparison of some important experimental structural data for cyclobutane, monocyanocyclobutane (MCCB) and 1,1-dicyanocyclobutane (DCCB) (bond distances in Å, angles in degrees).

Parameter	Cyclobutane[a]	MCCB		DCCB[b]
		eq	ax	
C1−C2	1.554 (1)	1.557 (5)		1.574 (10)
Δ_{CC}	−	+0.006	0.010	+0.025
C1−C5	−	1.454 (4)		1.466 (2)
C≡N	−	1.156 (3)		1.162 (1)
C−H	1.109 (3)	1.112 (5)		1.106 (6)
θ[c]	27.9 (1.6)	27.0 (1.1)	−19.1 (2.3)	21.7 (1.3)
∠C2−C1−C4		88.7 (1.1)		88.1 (3.0)
∠C5−C2C1C4		131.1 (1.3)	118.5 (2.1)	123.2 (2.4)
∠C5−C1−H7	−	112.4 (6.8)		−
∠C5−C1−C6	−	−		110.2 (6)
∠H−C1−H	106.4 (1.3)	−		−
∠H−C2−H		109.1 (4.8)		107.0 (10.0)
∠H−C3−H		112.0		117.7 (12.0)
α_1[d]	6.2 (1.2)	−7.3 (8.1)	+5.3 (8.9)	1.7 (2.4)
α_2[d]		+2.0	−2.0	1.0 (8.0)
α_3[d]		−4.0	+4.0	3.9 (9.5)
γ[e]	−	0.0		3.7 (2.0)
δ_1[f]	0.22	0.27	0.27	0.08
δ_2[f]		0.07	0.10	0.05
δ_3[f]		0.15	0.21	0.18

[a]Ref. 35. [b]Ref. 4. [c]Puckering angle. [d]Tilt angle. [e]$\gamma = 180 - <C-C\equiv N$. [f]Mixing parameter $\delta_i = \alpha_i/\theta$.

Accordingly, we believe that the C−C≡N group in MCCB is linear, although a slight non-linearity below the resolution limits of the ED method cannot be excluded. The *ab initio* calculations, however, indicate a slight non-linearity of the C−C≡N chain (Table 3).

Next, we compare the skeletal geometry parameters for MCCB and DCCB with those for the mother molecule cyclobutane (Table 7). Such a comparison is of importance because it shows to some extent how far the ring geometry is affected by the cyano group as a "versatile" substituent. Very recently, Kuchitsu and his coworkers have published a comprehensive paper on the structure and molecular dynamics of cyclobutane.[35] The comparison presented in Table 7 reveals three interesting features. Firstly, the C−C bonds adjacent to the substituents are longer than the C−C bonds in cyclobutane by about 0.005 Å in MCCB and 0.02 Å in DCCB. This trend in changes of bond lengths resulting from mono- and disubstitution reflects the additivity tendency of substituent effects within this series. Secondly, the puckering angle θ in both MCCB and DCCB is smaller than that in the parent molecule, cyclobutane. This can be interpreted as a result of non-bonded interaction between the C≡N group moiety and the opposite methylene group. The smaller degree of puckering in the axial form of MCCB supports this assumed repulsive interaction.

One more feature which is worthwile mentioning is the change in the three tilt angles α_1, α_2 and α_3, and in the mixing parameter δ which is related to them. The angles α are defined as the angles between the bisectors of the H−C−X (X=H or cyano C) and the C−C−C angles in the ring. The methylene groups (including the H−C−X group) are tilted in such a way that the axial atoms in 1,3 and 2,4 positions come closer together. It may be added that the exclusion of these angles in our model has always led to substantial uncertainties in some of the structural parameters, in particular in the puckering angle. This is not surprising because the cooperative interaction between ring puckering and methylene rocking minimizes the torsional ring-strain (Pitzer strain). This kind of mixing between the vibrational modes of the

methylene groups and the ring puckering in four-membered rings has been the subject of several detailed theoretical[36-40] and experimental investigations.[4,41-43] Malloy and Lafferty[42] have concluded from an analysis of spectroscopic data for cyclobutane that there is an approximately linear relationship between the rocking angle, α, and the puckering angle, θ, of the form $\alpha = \delta \cdot \theta$, where δ is the mixing parameter. The application of this simple linear relationship to cyclobutane gives a value $\delta = 0.22$.[35] It may be noted that the values of δ_3 in MCCB (0.15, 0.21) and DCCB (0.18) are comparable to the mixing parameter in the parent molecule. Naturally, no unambiguous conclusions can be derived from the values of δ_1, δ_2 and δ_3 shown in Table 7, but once more they reflect roughly the degree of coupling of ring puckering/CH_2-rocking, wagging and twisting modes in order to minimize the steric conflict within the strained ring. The relatively large δ_1 angle in both conformers of MCCB may reflect the contribution of the rocking of the $H-C_1-X$ group to the minimization of the destabilizing 1,3 interactions (Dunitz-Schomaker strain), since the magnitude of this strain depends mainly on the puckering and rocking motions in four-membered rings.[44,45] Nevertheless, just to emphasize the exceptional position of the methylene group opposite to the substituent we may interpret the agreement between the values of δ_3 for MCCB, DCCB and cyclobutane in the sense that the deformation motions of this group are little affected by substitution.

Finally, we proceed to compare our results with those obtained from the already mentioned spectroscopic studies.[9-12] Unfortunately, a complete comparison of the structural parameters cannot be performed because all geometrical parameters have been assumed in these studies, except for the puckering angle.[10,11] As apparent from Table 8, the difference between the puckering angle, θ, as determined by the earlier MW studies[10,11] on one side, and as determined by the recent *ab initio* study[12] and the present investigation on the other side, is considerable. However, the most striking discrepancy is clearly the existence of axial and equatorial conformers of MCCB. As indicated in Table 8, the axial conformer could not be detected by the former MW studies.

Conclusions

In summary, the following conclusion may be derived from the above presented structural analysis of MCCB: (1) MCCB exists in two conformers with the equatorial form predominant (77%). This is in excellent agreement with both *ab initio* and MW results published recently. (2) The cyano group appears to be linear, although slight bending of the $C-X\equiv N$ chain cannot be definitely excluded. (3) There is no agreement with the JB-R except for the puckering angle. According to the results and arguments presented thus far it is most likely that substituent effects based on the interaction between substituents displaying both σ and π charge transfer and the strained cyclobutane ring obey their own systematic rules. Nevertheless, it should be stressed that the conclusions reached here are qualitative. From the present point of view we find ourselves at a loss to assess whether σ or π effects are dominant in addition to "through-space" effects exerted by the cyano group. (4) The changes in the ring geometry of MCCB are substantial in comparison with the parent molecule and with a variety of previously studied monosubstituted cyclobutanes. In contrast, these changes are fairly small in comparison with the geminally substituted homologues DCCB. (5) The cyano group, providing both inductive and mesomeric effects simultaneously, engenders substantial changes in the ring geometry and the population of conformers when attached to cyclobutane. The specific mutual $C\equiv N$/ring interaction is manifested in the positive value of Δ_{CC}, the puckering angle θ, the lengthening of the $C\equiv N$ bond distance, and in the shortening of the C_1-C_5 bond. Finally, by combining spectroscopic, electron diffraction and

Table 8. Percentage of the equatorial conformer, $\Delta E = E(ax) - E(eq)$, and puckering angle (degrees) of MCCB as determined by different methods ($T = 323$ K).

Equatorial/%	ΔE/kJ mol^{-1}	θ_{eq}	θ_{ax}	Method
100	–	–	−20.0	MW[a]
100	–	–	−21.4	MW[b]
76	3.09			MW[c]
75	2.93	27.4	−24.4	*ab initio*[c]
77	3.09	27.0	−19.1	ED[d]

[a]Ref. 10. [b]Ref. 11. [c]Ref. 12. [d]This work.

ab initio results the conformational analysis can readily be performed.

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