7684 J. Am. Chem. Soc. **1992**, *114*, 7684-7687

Crystal Structure of Cyclobutane at 117 K

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Abstract: The crystal structure of cyclobutane was determined from X-ray diffraction data at 117 K. The crystal used was grown by sublimation. Since a rotationally-disordered high-temperature phase is present over a temperature range of 38 deg, no crystals could be obtained from the melt. The cell dimensions at 117 K are $a = 6.742$ (4) Å, $b = 4.204$ (4) Å, $c = 6.917$ (4) Å, $\beta = 90.17$ (4)°, space group $I2/m$, $Z = 2$. The space group symmetry requires the space- or time-averaged molecules to have $C_{2h}(2/m)$ symmetry. The carbon atoms show initially large anisotropic displacement parameters perpendicular to the mirror plane. Two explanations are discussed. The first is based on earlier investigations and assumes the time-averaged molecules to undergo puckering motions, which is established for the gas phase and the solid state. The other explanation which is more compatible with the experimental data is a statistical disorder of bent molecules. The latter results in a dihedral angle of 31 (2)°, which agrees with most other investigations.

Introduction

The molecular structure of cyclobutane[1] has been studied in the past by many experimental[2-10] and theoretical investigations.[11-14] The gas-phase equilibrium conformation, as derived from electron diffraction[9,10] and spectroscopic experiments,[2-6,8] is nonplanar with a dihedral angle of about 35° and an inversion barrier of only 6 kJ mol^{-1}.[3-5] The puckering of the molecule is observed in Raman-spectra, and the corresponding absorption band is still present in the solid at 113 K.[6] Theoretical calculations[11-14] using ab initio methods also result in a bent conformation as the energetic minimum.

The structure and molecular conformation of cyclobutane in the crystal has not been previously determined. Early X-ray investigations[15] did not yield structural information. The solid substance undergoes a phase transition at 145 K (melting point 182 K),[16] having a high-temperature plastic cubic phase with rotationally disordered molecules. The low-temperature phase was obtained only as powder; the pattern was identified as belonging to a crystal lattice with lower than cubic symmetry.[15]

Therefore crystallographic molecular structure information has been obtained only for substituted cyclobutanes. As one would expect from the shallow potential of the ring inversion[2-5,17] there are various planar and bent derivatives,[18] and it does not seem possible to predict the ring conformation from the substitution pattern. Therefore derivatives with eight equal substituents are of particular interest for comparison with parent cyclobutane. Of this type there are only two crystal structures known, octachlorocyclobutane[19,20] and octahydroxycyclobutane.[21] The latter is planar due to strong hydrogen bonding, while the chlorinated derivative has a dihedral angle of 26°.

In this paper we report the single crystal structure determination of the low-temperature phase of unsubstituted cyclobutane.

Table I. Crystal Data and Experimental Details

cell constants a, b, c, β	6.742 (4) Å, 4.204 (4) Å, 6.917 (4) Å, 90.17 (4)°
vol, molecules per unit cell	196.0 Å^3, $Z = 2$, $F(000) = 112$
space group	monoclinic, $I2/m$
density, ρ_x	0.948 g cm^{-3}
crystal size	2 mm column of liquid in a capillary of 0.5 mm diameter
radiation	Nb-filtered Mo Kα ($\lambda = 0.71069$ Å)
absorption coeff μ	0.56 cm^{-1}
instrument	Siemens four-circle diffractometer equipped with a liquid nitrogen gas stream cooling system
no. of orienting reflcns	23 with $2\theta_{\min} = 8.38°$, $2\theta_{\max} = 31.84°$
scan method	ω–2θ scan
scan width	49 steps + 0.26°(tan $\omega/\Delta\omega$) with $\Delta\omega = 0.02°$, $\Delta 2\theta = 0.04°$
time per step	0.3–1.8 s to reach $I/\sigma(I) > 25$ within the time limit
interval in 2θ	8.43–60° ($\sin\theta/\lambda = (0.10–0.70)$ Å^{-1})
no. of measured reflcns	729 (129 with $I < 2\sigma(I) = 18\%$)
no. of unique reflcns	329 (43 with $I < 2\sigma(I) = 13\%$)
structure solution	SHELXS-86[a] (direct method option)
structure refinement	XTAL2.2[b,c]
function minimized	$\sum w(F_o - F_c)^2$
weighting scheme	$1/\sigma^2(F_o)$
absorption, extinction corr	none
max residual peak/hole	0.357 e Å^{-3}/–0.418 e Å^{-3}
no. of refined parameters	21 (model I), 25 (model II)
max Δ/σ	0.024 (model I), 0.016 (model II)
R/wR value	7.8%/6.7% (model I), 6.2%/4.7% (model II)
goodness of fit	4.5 (2) (model I), 3.2 (1) (model II)

[a] See ref 29. [b] See ref 30, least-squares refinement of positional and anisotropic displacement parameters for C, positional and isotropic displacement parameters for H. [c] Scattering factors, see refs 31 and 32.

Experimental Section

Cyclobutane was synthesized by Wolff-Kishner reduction of cyclobutanone.[22] It was found that this method gave a very pure compound in high yield.[23] Most other reported syntheses[24-26] showed considerable

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Table II. Final Atomic Parameters (esd's in Parentheses) for the Puckering Model (I) and the Disordered Model (II), U_{ij} and U_{iso} in ×100 Å^2

atom/model		x	y	z	U_{11}/U_{iso}	U_{22}	U_{33}	U_{13}[a]
C(1)	I	0.1549 (4)	0.000 (–)	0.0331 (4)	2.8 (1)	3.9 (2)	3.1 (2)	–0.1 (1)
	II	0.1551 (3)	–0.023 (1)	0.0332 (2)	3.03 (6)			
C(2)	I	0.0331 (4)	0.000 (–)	–0.1520 (4)	3.3 (2)	8.9 (3)	2.6 (1)	–0.2 (1)
	II	0.0333 (3)	0.0499 (6)	–0.1525 (3)	3.15 (6)			
H(1)	I	0.239 (3)	0.175 (7)	0.047 (4)	9 (1)			
H(11)	II	0.201 (4)	–0.23 (1)	0.035 (4)	5 (1)			
H(12)	II	0.275 (6)	0.124 (7)	0.057 (4)	6 (1)			
H(2)	I	0.060 (4)	0.130 (6)	–0.235 (3)	9 (1)			
H(21)	II	0.031 (4)	0.279 (7)	–0.191 (4)	4.0 (7)			
H(22)	II	0.071 (3)	–0.080 (6)	–0.264 (3)	4.4 (8)			

[a] U_{12} and U_{23} are 0. due to $2/m$ site symmetry. Displacement parameters are given as: $T_{iso} = e^{-2U(2\pi\sin\theta/\lambda)^2}$; $T = e^{-2\pi^2[U_{11}(ha^*)^2+U_{22}(kb^*)^2+U_{33}(lc^*)^2+2U_{12}hka^*b^*\cos\gamma^*+2U_{13}hla^*c^*\cos\beta^*+2U_{23}klb^*c^*\cos\alpha^*]}$.

Table III. Bond Lengths (Å) of Cyclobutane (esd's in Parentheses)

atom 1	atom 2	model I[a]	model II
C(1)	C(2)	1.519 (4)	1.553 (3)
C(1)	C(2)′	1.513 (4)	1.548 (3)
C(1)	H(1)	0.94 (3)	0.92 (4)/1.03 (4)[b]
C(2)	H(2)	0.81 (2)	1.00 (3)/0.98 (2)[b]

[a] Model I: parameters obtained using the puckering model. Model II: parameters obtained using the disordered model. [b] In the disordered model there are two independent hydrogen atoms per carbon atom.

contamination by n-butane and were thus unsuitable for the crystallization.

Growing crystals of cyclobutane is complicated due to the presence of the high-temperature phase, which extends over a range of 38 deg. On annealing the melt crystals are formed in this phase, which on cooling down into the phase II region crack into powder grains. Crystals of phase II can then be grown by sublimation[27] at 130 K. Therefore a sample was sealed into a capillary (0.5-mm diameter) and solidified as polycrystalline material in the nitrogen cold gas stream of the diffractometer, leaving a small empty compartment at one end of the capillary. The coldest part of the gas stream was then moved directly over the empty tip of the capillary. Within 24 h a few single crystals grew inside the compartment.

It was possible to identify a sufficient number of reflections of an individual crystal so that the determination of lattice constants and orientation matrix was possible. A monoclinic unit cell was found and a body centered setting[28] (hkl absent for $h + k + l = 2n + 1$) was chosen. This nonstandard monoclinic body-centered cell was used to give a monoclinic angle close to 90°.

No further systematic extinctions were detected, and thus the space group could be chosen from $I2$, Im, or $I2/m$. For details of the data collection and data analysis see Table I.

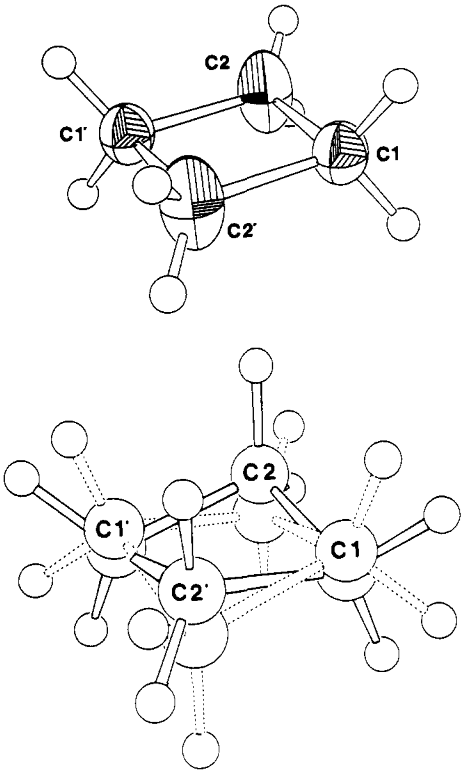

Figure 1. (a, top) ORTEP[33] plot of cyclobutane in the planar conformation. The displacement ellipsoids are plotted at a 50% probability level. (b, bottom) ORTEP[33] plot of cyclobutane as disordered model II. The isotropic displacement spheres are plotted at a 50% probability level.

Table IV. Bond Angles (deg) of Cyclobutane (esd's in Parentheses)

atom 1	atom 2	atom 3	model I[a]	model II[b]
C(2)	C(1)	C(2)′	90.4 (2)	88.2 (2)
C(2)	C(1)	H(1)	115 (2)	112 (2)/115 (2)
C(2)′	C(1)	H(1)	117 (2)	116 (2)/117 (2)
H(1)	C(1)	H(1)	104 (2)	108 (3)
C(1)	C(2)	C(1)′	89.6 (2)	87.3 (2)
C(1)	C(2)	H(2)	118 (2)	115 (2)/114 (1)
C(1)′	C(2)	H(2)	125 (2)	109 (2)/121 (1)
H(2)	C(2)	H(2)	85 (2)	109 (2)

[a] See footnote a in Table III. [b] In the disordered model there are two independent hydrogen atoms per carbon atom.

Results and Discussion

Refinement was carried out in all three possible space groups. The E-value statistics indicated the presence of an inversion center, so that $I2/m$ was considered first. This space group implies an electron distribution with point group symmetry C_{2h}. The simplest interpretation positions a planar molecule on the crystallographic mirror plane with the 2-fold axis passing through the ring center.

However, careful investigation of the anisotropic displacement parameters for the carbon atoms indicates significantly larger U_{22} components, which are perpendicular to the a,c plane.

A first explanation was derived from earlier, especially Raman, experiments. As already mentioned, the Raman spectra of cy-

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(23) In a 100-mL flask which was attached to a vigreux column and a condenser, connected to a methanol/dry ice cooled trap, 2.5 g of cyclobutanone (35.7 mmol) was dissolved in 6 mL of Carbitol. After addition of 5 g of potassium hydroxide (89.1 mmol) in 30 mL of Carbitol and 3.6 mL of 85% hydrazine hydrate the dark solution was heated until no further condensation in the trap was observed. NMR, IR, and mass spectra were used to establish the purity of the obtained cyclobutane.

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Table V. Comparison of the Results Obtained from Different Investigations on Cyclobutane

		length, Å		angle, deg		puck. angle,	inv barrier,	
method		C–C	C–H	H–C–H	C–C–C	deg	kJ mol^{-1}	lit
electron-diffraction		1.548 (3)	1.09 (1)	110		35		9, 10
IR/Raman						35	6.19 (6)	5
IR						35	6.02	4
						34	5.35	3
					77	37		7
NMR				108.1		27		8
X-ray-diffraction	I	1.516 (4)	0.88 (3)	95 (2)	90.0 (2)	16 (2)		this work
	II	1.551 (3)	0.98 (5)	109 (3)	87.8 (2)	31 (2)		
4-21		1.567	1.08	109.4	88.7	24.1		13
6-31G*	D_{2d}	1.547	1.084	108.3		24	3.7	12
	D_{4h}	1.549	1.084	107.9				
4-31G	D_{2d}	1.554	1.081	108.5		21	1.67	12
	D_{4h}	1.556	1.081	108.2				
STO-3G	D_{2d}	1.553	1.086	108.3		13	0.042	12
	D_{4d}	1.554	1.088	108.8				
FSGO	D_{2d}	1.524	1.116	110		32	14.63	11
	D_{4h}	1.535	1.116	110				

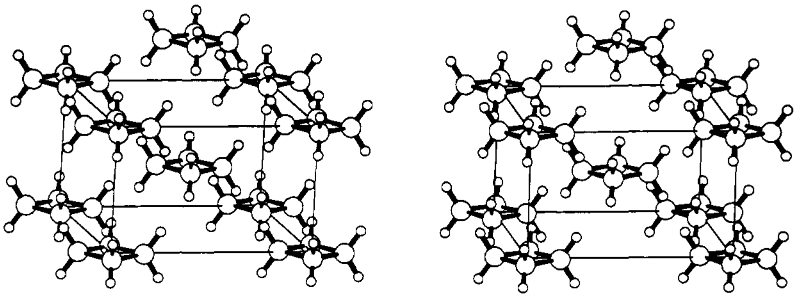

Figure 2. Stereoview of the crystal packing.[40] Molecules are time/space averaged and hence planar. The axes directions are the following: $\vec{c}$ across the page, $\vec{b}$ upwards, and $\vec{a}$ into the page.

clobutane show some absorption bands which represent the ring puckering in the gas phase as well as in the solid.[6] The large U_{22} component of the anisotropic displacement parameter for C(2) and to some extent that of C(1) could be the result of a puckering of the ring in the crystal (model I). Assuming isotropic motion of the carbon atoms ($\bar{U}_{eq}$ = 0.030 (3) Å^2, excluding the U_{22} components), a maximum bending angle of 16 (2)° is deduced (Figure 1a and Table II). The height of the inversion barrier and moreover the form of the potential well cannot be determined by means of this experiment. Nevertheless, this bending angle is smaller than those reported in previous studies (Table V), and in particular it deviates considerably from the angle of 37 (6)° found in the intensity comparison of IR bands from the solid at 21 K in an Argon matrix.[7]

The C–C bond lengths obtained from the refinement of this model (Table III) are somewhat shorter than those from electron diffraction[9,10] and theoretical calculations.[11-14] Although the crystallographic site symmetry of the molecule is C_{2h}, the higher point group symmetry D_{2h} is observed within four times the standard deviation. However, the large anisotropic displacement parameters make it difficult to obtain very precise results. The C–H bond lengths are even less precisely determined. The applied rigid body correction[34] did not improve the bond lengths. All corrections were within the estimated standard deviations. However, a comparison with the average C–C bond lengths of cyclopropane (1.499 Å, 94 K)[35-37] and cyclohexane (1.52 Å, 115 K)[38] in the crystal shows that the average bond length in this model (1.516 Å, 117 K) is in accordance.

Another explanation for the larger U_{22} components was sought in a statistically disordered model (model II). This was examined by shifting the *y* coordinates of C(2) and C(1) by 0.04 Å to opposite sites of the mirror plane. The site occupancy factor was fixed at 0.5. The initial displacement parameters were those of the isotropic refinement. After refinement of the positional and isotropic displacement parameters for the carbon atoms the hydrogen atom positions (H(11), H(12), H(21), H(22)) were calculated by using standard values. Subsequent refinements included atomic positions and isotropic displacement parameters for all atoms. The final distance between C(1) and the mirror plane was 0.097 (6) and 0.210 (3) Å for C(2), respectively (Figure 1b). According to the significance test of Hamilton[39] this model is a significantly better description of the experimental data, even at a 99.5% probability level.

The bond parameters of this disordered model are in better agreement with other experimental and theoretical results than those of model I. Particular good agreement occurs between the average C–C bond lengths (1.551 (3) Å) of this experiment and the electron diffraction and theoretical calculations (Table V). The C–H mean bond distance (0.98 (5) Å) and the H–C–H mean angle (109 (3)°) are consistent with standard X-ray data (Table IV).

Theoretical studies by Wright and Salem[14,17] show that the double minimum potential is reproduced only if rocking of the methylene groups is permitted. That means, the H–C–H angle is no longer bisected by the local C–C–C plane. The tilt angle τ determined from the X-ray data is 3.4° for C(1) and 5.5° for C(2), averaging to 4.5°. This is in very good agreement with the value 4.4° obtained at the 6-31G* level by Cremer.[12]

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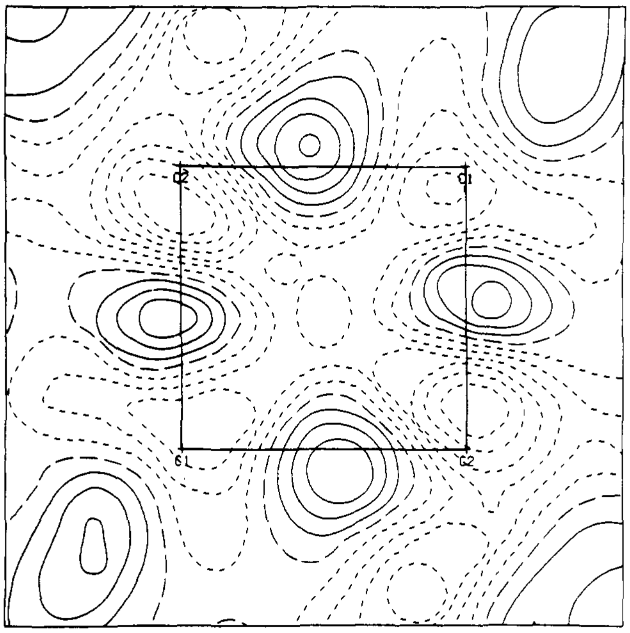

Figure 3. Difference map derived from difference Fourier synthesis. The maximum of the electron density is observed outside the direct C–C bond vectors.

Due to the better agreement of model II to the experimental data and to the results of all the previous investigations on this molecule as well (electron diffraction, spectroscopy, theoretical calculations, as discussed above), we believe model II to be the more reliable one and model I to be a less likely alternative.

Model II was also tested in the other two possible space groups, *I*2 and *Im*. The refinement converged if hydrogen atoms were kept at those positions obtained in *I*2/*m*, but became unstable when hydrogen atoms were allowed to refine.

The time- and space-averaged crystal packing is given in Figure 2. The general arrangement is the same in both models and in all tested space groups. The molecules form stacks parallel to the monoclinic *b* axis. In the *a*,*c* plane the molecules are slightly rotated around the *b* axis. The angle between the *a* axis and C(1)–C(1)′ is 13°. No particular close H–H contacts are observed.

The residual electron density (Figure 3) shows significant maxima in positions between the carbon atoms. These maxima are displaced tangentially by 0.10 (3) Å to the outside of the C–C bond vectors of the time- and space-averaged molecule, indicating a "banana bond" type electronic arrangement which is frequently found in highly strained small ring systems. In cyclopropane the covalent bonding maxima are displaced by 0.2 Å from the C–C vectors of the carbon triangle. Since in cyclobutane there is reduced ring strain our observation is in good agreement with the cyclopropane findings.

Acknowledgment. We thank the Graduiertenkolleg "Struktur und Synthese niedermolekularer Verbindungen" (A.S.) and the Fonds der Chemie for the granted studentships (C.W.L.) and for further financial support. We thank one of the referees for suggesting some improvements in the handling of refinement for model II.

Supplementary Material Available: List of observed and calculated structure factors (8 pages). Ordering information is given on any current masthead page.

Atropisomerism in Natural Products. Absolute Stereochemistry of Biflavone, (−)-4′,4‴,7,7″-Tetra-*O*-methylcupressuflavone, As Determined by the Theoretical Calculation of CD Spectra

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Abstract: The molecular asymmetry due to the atropisomerism of biflavone, (−)-4′,4‴,7,7″-tetra-*O*-methylcupressuflavone (**1**), has been studied by CD spectroscopy, and its absolute stereochemistry has been theoretically determined by the π-electron SCF-CI-DV MO calculation of CD spectra. The molecular geometry of compound (*aR*)-**1** was calculated by molecular mechanics to give a stable conformation with a counterclockwise screw sense, in which the dihedral angle of the biphenyl part was 91°. The calculated CD and UV curves of (*aR*)-**1** were in very good agreement, including sign, position, and amplitude, with those of observed spectra of the natural product: calcd UV, λ_{max} 322.6 nm (ϵ 66 200), and 226.8 (78 300); calcd CD, λ_{ext} 359.7 nm ($\Delta\epsilon$ +28.6), 317.5 (−45.0), and 263.2 (+21.7); obsd UV, λ_{max} 324.2 nm (ϵ 40 900), 273.0 (41 400), and 225.8 (51 800); obsd CD, λ_{ext} 362.0 nm ($\Delta\epsilon$ +25.6), 326.2 (−54.4), and 267.5 (+21.3). The absolute stereochemistry of biflavone (−)-**1** has thus been theoretically determined to be *aR* (or *M* helicity).

Introduction

Optically active biflavones are unique natural products in the sense that they are chiral molecules with molecular dissymmetry. Although monomeric flavones have no chiral center and hence are optically inactive, some biflavones can exist as chiral molecules due to the atropisomerism of the biflavone moiety.[2,3] Such optically active biflavones have been isolated as natural products from various plants and their plane structures have been reported.[2-6] However, the absolute stereochemistry of these natural

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