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The Crystal Structure of Bicyclopropyl

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The crystal structure of bicyclopropyl, C_6H_{10}, m.p. $-83°C$, has been determined by a three-dimensional X-ray diffraction analysis. The crystals are orthorhombic, space group *Cmca*; the unit cell, containing four molecules, has the dimensions

$a = 8.904$ Å, $b = 5.137$ Å, $c = 11.807$ Å

A trial structure was obtained by Patterson methods. Refinement was carried out by least-squares methods yielding a final R-factor of 0.066.

The molecules were found to have the *trans* conformation with $2/m$ symmetry. In contrast to what is the case in the gas phase, the molecules in the crystals show no large amplitudes of torsional vibration about the central carbon-carbon bond. The average cyclopropyl carbon-carbon bond length was found to be 1.506 Å and the central bond to be 1.487 Å with estimated standard deviations of 0.004 Å.

As part of their investigation of the conformations of bicycloalkyl homologues Lüttke *et al.*[1] examined bicyclopropyl by infrared and Raman spectroscopic methods. They were able to conclude that whereas the molecules exist in the centrocymmetrical *trans* conformation in the crystals, there is another conformation present in equilibrium with the *trans* conformation in the liquid state.

Bastiansen and de Meijere[2,3] employed electron diffraction methods in order to analyse the conformations of bicyclopropyl present in the vapour phase and also to determine bond lengths and angles in the molecule. The presence of both the *trans* and the *gauche* conformations was established and an estimate of the relative amounts of the two was given, the amplitudes of torsional vibration about the central bond were shown to be large. The carbon-carbon bonds were of too similar length to be resolved, however, and only the average bond length of 1.517 Å could be determined.

In order to obtain supplementary data a three dimensional X-ray crystallographic analysis of bicyclopropyl was undertaken.

EXPERIMENTAL

Since the melting point of bicyclopropyl is −83°C, the compound was kept at temperatures of −100 to −110° during the X-ray exposures, sealed off in thin-walled pyrex capillary tubes with diameters of 0.1−0.2 mm.

The dimensions of the crystallographic unit cell were determined from Debye-Scherrer diagrams. Cu$K\alpha$ (λ=1.5418 Å) was employed and powdered KCl ($a_{-100°C}$ = 6.265 Å) was used as a standard. 13 strong lines from bicyclopropyl were measured; the axes of the (orthorhombic) unit cell were determined by the least-squares method.

The intensity data were obtained using the multi-film, integrating equi-inclination Weissenberg technique. Several attempts to freeze out single crystals were made; the crystals formed appeared to have no preferred orientation relative to the capillary tube axis. It was thus possible to obtain a nearly full, three-dimensional set of reflections from intersecting reciprocal layers. These were obtained from crystals rotating about the [100], [010], [110] and [310] directions. The intensities were measured photometrically except for the weakest reflections which were estimated visually with use of a calibrated scale. Cu$K\alpha$-radiation was used for the intensity experiments. Out of the 323 independent reflections obtainable with this wave length, 261 were actually observed whereas 45 were too weak to be measured, and 17 the ($15l$) and ($26l$) reflections were not obtained.

The intensities were corrected with the Lp^{-1}-factor and put on a common, arbitrary scale. No absorption corrections were applied, the μR value of the cylindrical specimen being only about 0.04. Prior to the last stage of the refinement procedure the intensities were corrected for secondary extinction effects by the method given by Zachariassen.[4]

The full-matrix least-squares program used in the refinement procedure was written by Gantzel, Sparks and Trueblood (IUCr World List No. 384), modified to include a weight analysis and adapted for UNIVAC 1107 by Chr. Rømming. The program minimizes the function $\Sigma w(F_o - G \cdot F_c)^2$; the weight ($w^{\frac{1}{2}}$) applied to the structure factors was constant for $|F_o| \leq 3$ and proportional to $|F_o|^{-\frac{1}{2}}$ for larger values of $|F_o|$. Non-observed reflections were included with a structure factor corresponding to the most probable value [5] and assigned a weight of one third of the weight given to the observed reflections. These weight assignments turned out to give satisfactory results in the weight analysis.

The program for three-dimensional Fourier calculations was written by Gantzel and Hope, the program for secondary extinction corrections was written by A. Christensen.

The atomic form factors used in the calculations were those given by Hanson *et al.*[6] for hydrogen and by Hoerni and Ibers [7] for carbon atoms.

CRYSTAL DATA

Bicyclopropyl, C_6H_{10}, m.p. −83°C
Orthorhombic, unit cell constants at −100°C:
a = 8.904 (0.007) Å; b = 5.137 (0.004) Å; c = 11.807 (0.005) Å.
Figures in parenthesis are estimated standard deviations.
V = 540.05 Å^3, M = 84.16, F(000) = 184, Z = 4.
Calculated density: 1.035 g cm^{-3} at −100°C.
Absent reflections: hkl when $h + k = 2n + 1$
$hk0$ when $h = 2n + 1$ (and $k = 2n + 1$)
$h0l$ when $l = 2n + 1$ (and $h = 2n + 1$)
Space group: *C2cb* or *Cmca*. (*Cmca* is indicated by the present analysis).

STRUCTURE DETERMINATION

There are two space groups, *C2cb* and *Cmca*, both compatible with the systematic absent reflections. The spectroscopic evidence, however, showed that the molecular symmetry is C_{2h}, indicating that *Cmca* probably is the

correct one; during the structure analysis nothing was found to contradict this conclusion.

In the space group *Cmca* there are 16 equivalent general positions, it follows that with *four* molecules in the unit cell the molecular symmetry is $2/m$.There were only 13 positional parameters to be determined, approximate values of which were found by standard methods in the *a* and *b* projections. The resulting model was then refined by least-squares methods using the three-dimensional data set. In these calculations thermal vibrations were assumed to be anisotropic for carbon atoms and isotropic for hydrogen atoms. Successive cycles of refinement reduced the conventional *R*-factor to 0.08; correction for secondary extinction effects and further least-squares calculations resulted in a final *R*-factor of 0.066.

Table 1. Final atomic coordinates with estimated standard deviations.

	x	*y*	*z*
C(1)	0	−0.0022 (0.0005)	0.0630 (0.0002)
C(2)	0.0848 (0.0002)	0.2017 (0.0004)	0.1278 (0.0002)
H(1)	0	−0.180 (0.008)	0.094 (0.003)
H(2)	0.143 (0.003)	0.327 (0.006)	0.081 (0.002)
H(3)	0.139 (0.003)	0.149 (0.006)	0.202 (0.002)

Table 2. Anisotropic thermal parameters, $B_{ij} \times 10^4$, for carbon atoms according to the expression $\exp-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{12}hk + B_{13}hl + B_{23}kl)$, and isotropic thermal parameters for the hydrogen atoms.

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
C(1)	92 (3)	268 (11)	47 (2)	0	0	4(7)
C(2)	95 (3)	379 (10)	59 (2)	−8 (7)	−20 (3)	−55 (5)

	B
H(1)	2.0 (0.7)
H(2)	2.3 (0.5)
H(3)	2.4 (0.5)

The calculations were based on 306 reflections. The scale factor, 13 positional and 13 thermal parameters were varied in the least-squares procedure. The final parameters are listed in Tables 2 and 3, a comparison of observed and calculated structure factors is given in Table 3.

A three-dimensional Fourier synthesis and a partial difference synthesis, with the carbon atoms subtracted, were finally calculated. A composite electron density map as viewed down the *b*-axis is shown in Fig. 1. Sections through hydrogen atoms are taken from the partial difference synthesis.

The bond distances and interbond angles calculated on the basis of the parameters of Table 1 are listed in Table 4 together with their estimated standard deviations. They are also shown in Fig. 2.

Table 3. Observed and calculated structure factors. The columns are h, h, l, $10 \times |F_o|$ and $10 \times F_c$. Non-observed reflections are denoted by an asterisk.

0	0	2	256	246	
0	0	4	585	-619	
0	0	6	164	-157	
0	0	8	91	79	
0	0	10	63	-74	
0	0	12	107	-107	
0	0	14	60	58	
0	2	0	687	754	
0	2	2	239	242	
0	2	4	255	-260	
0	2	6	125	-112	
0	2	8	20	-10	*
0	2	10	71	-78	
0	2	12	48	-47	
0	2	14	50	47	
0	4	0	108	-91	
0	4	2	174	174	
0	4	4	172	164	
0	4	6	91	-93	
0	4	8	172	-182	
0	4	10	56	-54	
0	4	12	60	54	
0	4	14	26	26	
0	6	0	96	-87	
0	6	2	104	99	
0	6	4	213	203	
0	6	6	94	-98	
0	6	8	228	-216	
0	6	10	16	-16	
0	6	12	70	76	
0	8	0	36	31	
0	8	2	66	62	
0	8	4	62	56	
0	8	6	67	-66	
0	8	8	97	-96	
0	8	10	10	-9	*
0	10	0	105	105	
0	10	2	47	38	
0	10	4	48	-53	
0	10	6	36	-32	
1	1	1	453	468	
1	1	2	531	-575	
1	1	3	38	-35	
1	1	4	55	53	
1	1	5	121	-120	
1	1	6	239	244	
1	1	7	83	-80	
1	1	8	24	-19	
1	1	9	64	-70	
1	1	10	131	-125	
1	1	11	56	-58	
1	1	12	19	19	
1	1	13	20	15	
1	1	14	58	59	
1	3	1	251	259	
1	3	2	112	110	
1	3	3	112	103	
1	3	4	29	28	
1	3	5	105	-99	
1	3	6	10	8	*
1	3	7	119	-116	
1	3	8	35	-32	
1	3	9	84	-89	
1	3	10	11	-2	*
1	3	11	21	-21	
1	3	12	9	8	*
1	3	13	31	26	
1	3	14	4	-2	*
1	5	1	98	94	
1	5	2	262	270	
1	5	3	118	111	
1	5	4	7	-2	*
1	5	5	15	-21	
1	5	6	155	-164	
1	5	7	125	-128	
1	5	8	10	4	*
1	5	9	87	-85	
1	5	10	94	93	
1	5	11	7	5	*
1	5	12	8	-8	*
1	5	13	25	26	
1	7	1	57	57	
1	7	2	132	136	
1	7	3	64	62	
1	7	4	9	-9	*
1	7	5	9	-5	*
1	7	6	111	-115	
1	7	7	91	-91	
1	7	8	21	22	
1	7	9	60	-58	
1	7	10	67	67	
1	9	1	59	62	
1	9	2	8	-5	*
1	9	3	21	20	
1	9	4	7	-4	*
1	9	5	27	-26	
1	9	6	7	8	*
1	9	7	41	-43	
1	9	8	5	8	*
1	9	9	24	-31	
1	11	1	46	51	
1	11	2	54	-59	
2	0	0	235	-235	
2	0	1	218	-222	
2	0	2	169	165	
2	0	3	45	-45	
2	0	4	314	310	
2	0	5	162	164	
2	0	6	98	-95	
2	0	7	42	44	
2	0	8	252	254	
2	0	9	87	-86	
2	0	10	51	-50	
2	0	11	38	-36	
2	0	12	80	79	
2	0	13	44	47	
2	0	14	23	24	
2	2	0	57	45	
2	2	1	69	-67	
2	2	2	152	150	
2	2	3	52	-52	
2	2	4	143	133	
2	2	5	67	68	
2	2	6	106	-100	
2	2	7	28	26	
2	2	8	173	-172	
2	2	9	47	-42	
2	2	10	45	-45	
2	2	11	11	-10	*
2	2	12	44	38	
2	2	13	20	20	
2	2	14	20	25	
2	4	0	286	302	
2	4	1	94	90	
2	4	2	110	103	
2	4	3	34	33	
2	4	4	103	-103	
2	4	5	63	-54	
2	4	6	84	-79	
2	4	7	25	-25	
2	4	8	28	-24	
2	4	9	34	30	
2	4	10	42	-43	
2	4	11	18	20	
2	4	12	31	-33	
2	4	13	20	-21	
2	6	0	237	253	
2	6	1	87	83	
2	6	2	66	64	
2	6	3	82	83	
2	6	4	133	-136	
2	6	5	69	-68	
2	6	6	47	-43	
2	6	7	47	-42	
2	6	8	33	30	
2	6	9	54	49	
2	6	10	49	-45	
2	6	11	15	14	
2	6	12	38	-51	
2	8	0	107	110	
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2	8	2	43	43	
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2	8	6	29	-28	
2	8	7	12	-9	
2	8	8	18	-17	
2	8	9	15	17	
2	10	0	6	7	*
2	10	1	20	-18	
2	10	2	26	29	
2	10	3	16	-19	
2	10	4	30	35	
2	10	5	17	18	
3	1	1	7	11	*
3	1	2	144	141	
3	1	3	205	200	
3	1	4	8	10	*
3	1	5	32	24	
3	1	6	106	-97	
3	1	7	182	-179	
3	1	8	9	2	*
3	1	9	116	-113	
3	1	10	57	56	
3	1	11	45	36	
3	1	12	6	-2	*
3	1	13	34	36	
3	3	1	101	102	
3	3	2	10	0	*
3	3	3	41	31	
3	3	4	10	-6	*
3	3	5	10	-17	*
3	3	6	11	9	*
3	3	7	76	-74	
3	3	8	11	5	*
3	3	9	64	-55	
3	3	10	10	-2	*
3	3	11	23	-22	
3	3	12	7	-5	*
3	5	1	164	167	
3	5	2	86	-90	
3	5	3	59	-55	
3	5	4	9	-2	*
3	5	5	87	-84	
3	5	6	77	74	
3	5	7	9	5	*
3	5	8	8	5	*
3	5	9	20	-17	
3	5	10	47	-45	
3	5	11	57	-59	
3	7	1	130	119	
3	7	2	64	-62	
3	7	3	36	-30	
3	7	4	7	6	*
3	7	5	73	-66	
3	7	6	57	50	
3	7	7	6	3	*
3	7	8	5	-1	*
3	7	9	20	-22	
3	9	1	38	36	
3	9	2	6	4	*
3	9	3	20	20	
3	9	4	10	5	
3	9	5	11	-7	
4	0	0	144	147	
4	0	1	114	117	
4	0	2	76	83	
4	0	3	79	80	
4	0	4	60	-56	
4	0	5	110	-105	
4	0	6	62	-66	
4	0	7	51	-51	
4	0	8	27	-23	
4	0	9	76	75	
4	0	10	30	-28	
4	0	11	28	31	
4	0	12	15	-21	
4	2	0	131	129	
4	2	1	58	52	
4	2	2	71	67	
4	2	3	44	45	
4	2	4	31	-26	
4	2	5	50	-44	
4	2	6	58	-58	
4	2	7	24	-22	
4	2	8	48	-45	
4	2	9	42	35	
4	2	10	40	-30	
4	2	11	5	9	*
4	4	0	72	68	
4	4	1	71	-51	
4	4	2	57	49	
4	4	3	38	-35	
4	4	4	26	22	
4	4	5	55	48	
4	4	6	41	-40	
4	4	7	36	31	
4	4	8	74	-71	
4	4	9	30	-30	
4	4	10	40	-34	
4	6	0	28	23	
4	6	1	74	-71	
4	6	2	44	41	
4	6	3	62	-63	
4	6	4	36	32	
4	6	5	72	66	
4	6	6	31	-29	
4	6	7	45	43	
4	6	8	64	-66	
4	6	9	34	-46	
4	8	0	30	30	
4	8	1	23	-22	
4	8	2	32	32	
4	8	3	16	-17	
4	8	4	11	11	
4	8	5	24	24	
4	8	6	12	-26	
5	3	1	64	61	
5	3	2	8	-5	*
5	3	3	25	23	
5	3	4	8	4	*
5	3	5	19	-22	
5	3	6	7	2	*
5	3	7	47	-46	
5	3	9	28	-38	
5	5	1	9	1	*
5	5	2	9	3	*
5	5	3	72	67	
5	5	4	8	10	*
5	5	5	22	19	
5	5	6	6	-1	*
5	5	7	66	-76	
6	0	0	70	71	
6	0	1	42	-40	
6	0	2	29	29	
6	0	3	35	-37	
6	0	4	9	-16	
6	0	5	35	43	
6	0	6	13	-20	
6	4	0	31	30	
6	4	1	14	19	
6	4	2	30	30	
6	4	3	17	22	

Table 4. Bond lengths and interbond angles with estimated standard deviations.

Bonds (Å)

C(1)−C(3)	1.487 (0.004)	C(1)−H(1)	0.99 (0.04)
C(1)−C(2)	1.501 (0.003)	C(2)−H(2)	1.04 (0.03)
C(2)−C(2′)	1.510 (0.004)	C(2)−H(3)	0.99 (0.03)

Angles not involving hydrogen atoms (°)

C(3)−C(1)−C(2)	120.0 (0.2)
C(2′)−C(1)−C(2)	60.4 (0.2)
C(1)−C(2)−C(2′)	59.8 (0.1)

Angles involving hydrogen atoms (°)

C(3)−C(1)−H(1)	113	C(2′)−C(2)−H(2)	119
C(2)−C(1)−H(1)	117	C(1)−C(2)−H(2)	113
H(2)−C(2)−H(3)	113	C(1) −C(2)−H(3)	123
C(2′)−C(2)−H(3)	122		

Standard deviations approximately 2°.

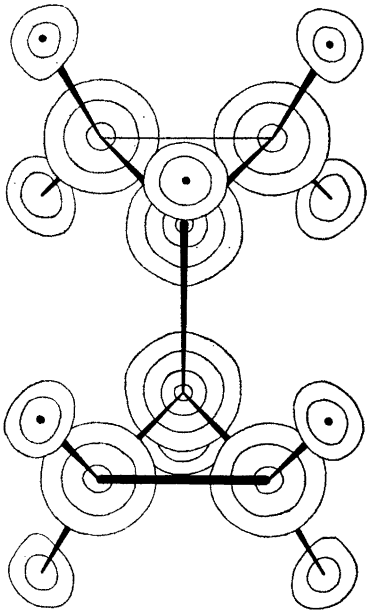

Fig. 1. Composite electron density map as viewed down the *b*-axis. Contour intervals are 2 eÅ^{-3} for carbon and 0.5 eÅ^{-3} for hydrogen atoms.

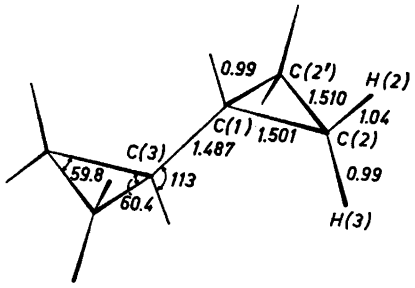

Fig. 2. Bond lengths and inter-bond angles.

Intermolecular distances were calculated and found to be of magnitudes normal for the packing of this type of molecules.

DISCUSSION

The conformation of bicyclopropyl molecules in the crystals is found to be *trans* about the central carbon-carbon bond which was to be expected from the spectroscopic evidence. The thermal vibrations of the molecule do not appear to be unusually large. The principal axes of the ellipsoids of vibration were calculated for the two independent carbon atoms. The C(1) atom was found to vibrate almost isotropically with a root mean square amplitude of 0.19 Å. For the C(2) atom the root mean square amplitudes were found to be 0.18, 0.21, and 0.24 Å along the principal axes, respectively, the axis of largest amplitude being approximately normal to the *a* axis. The number of independent atoms is too small to allow a closer analysis of the molecular oscillations, but certainly no large amplitude of twist motion about the central bond is indicated.

The carbon-hydrogen bond distances were all found to be close to the value normally obtained by X-ray methods.

The two independent C—C bonds in the cyclopropane ring were found to be 1.501 Å and 1.510 Å, respectively. With respect to these bond lengths

the value of $t = |l_1 - l_2|/(\sigma_1^2 + \sigma_2^2)^{\frac{1}{2}}$ is 1.8, corresponding [8] to a probability of 4 % that the bonds actually are of equal lengths. The values of t when comparing the ring carbon-carbon bonds with the exocyclic carbon-carbon bond of 1.487 Å, are 2.8 and 4.0, respectively, with corresponding probability values of 0.3 % and 0.003 %. Using the usual significance levels we must conclude that the carbon-carbon bond joining the cyclopropane rings is shorter than the ring bonds by a highly significant amount, whereas the difference observed between C(1)—C(2) and C(2)—C(2′) bond lengths is possibly significant.

The central carbon-carbon bond is shorter than the aliphatic C—C single bond. This observation is in accordance with the fact that the cyclopropane ring chemically behaves much like a double bond, the central bond in bicyclopropyl is thus to be compared with a single bond in a conjugated system, and the bond is indeed found to be only about 0.01 Å longer than such a bond.

The weighted average carbon-carbon bond length is 1.502 Å. This is the value to compare to the one of 1.517 Å found by electron-diffraction methods for bicyclopropyl in the vapor phase. The authors consider the difference too small to justify a discussion of the possible reasons for this discrepancy.

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