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MOLECULAR GEOMETRY – I
STRUCTURE OF *TRANS*-9.10-PENTACYCLO-[4.4.0.$0^{2,5}$.$0^{3,8}$.$0^{4,7}$]-DECANDIOIC ACID
CONFORMATION OF CYCLOBUTANES

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Abstract—Determination of the crystal structure of *trans*-9.10-pentacyclo-[4.4.0.$0^{2,5}$.$0^{3,8}$.$0^{4,7}$]-decandioic acid has shown that two types of cyclobutane rings are present in this bridged polycyclic system: one is planar while the other is puckered with dihedral angle of 160·7 . The compound crystallizes in the monoclinic space group C2/c with a = 6·070 (1) Å. b = 14·774 (3) Å. C = 11·344 (1) Å and cos β = −0·0923 (3): Z = 4. The structure was refined to R = 0·048 and all H atoms were located.

RECENT synthetic efforts have led to the preparation of a large number of novel highly strained ring systems. Molecules of this class frequently exhibit unusual chemical reactivity but in the absence of definitive structural information. the source of the driving force for reactions is a matter of conjecture. In an effort to clarify some of the ambiguities that exist. we have begun a program that is directed toward accurately defining structural parameters in organic molecules of special interest. We now report our results from an investigation of the crystal structure of *trans*-9.10-pentacyclo-[4.4.0.$0^{2,5}$0.^{3,8}.$0^{4,7}$]-decandioic acid (1). Fig 1 shows a stereoview of the molecule.

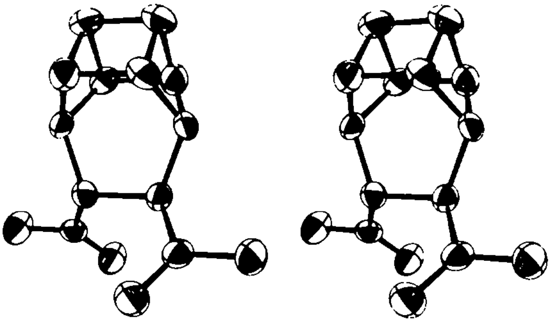


FIG. 1. Stereoview of the $C_{10}H_{10}(CO_2)_2$ molecule.

EXPERIMENTAL

Crystals[2] of 1 were grown as thin plantes from EtOAc. Weissenberg and precession photographs recorded from a suitable specimen showed that the crystal was monoclinic. From the conditions required for a reflection to be observed (h0l. l = 2n: hkl. h + k = 2n) the space group was determined to be either C2/c or Cc.

Unit cell parameters were determined by the least squares refinement of the setting angles from ten reflections that had been centered on a Picker FACS-I diffractometer and are as follows:

a = 6·070 (1) Å; b = 14·774 (3) Å; c = 11·344 (1) Å; cos β = −0·0923 (3)

The crystal density, determined as 1·44 g.cm^{-3} by flotation in a chlorobenzene-bromobenzene mixture, is in excellent agreement with the value of 1·444 g.cm^{-3} calculated on the basis of four molecules in the unit cell.

An intensity data set was collected using CuKα radiation (λ = 1·5418 Å) on a Picker FACS-I computer controlled four-circle diffractometer equipped with a graphite monochromator. A take off angle of 2·5° was used. Data were collected by the θ–2θ scan technique at a scan rate of 2°/min and a basic 2° scan width that was modified to correct for radiation dispersion. Background counts of 10 sec were taken at both ends of the scan. During the data collection three reflections were monitored as standards and checked every fifty reflections. No significant changes in the intensities of the standards occurred during the time required to collect the data set. A total of 749 unique data with $2\theta \leq 120°$ were collected; standard Lorentz-polarization factors were applied, but no absorption corrections were made (μ = 9·2 cm^{-1}).

A set of |E| values were calculated. The reflection statistics are summarized in Table 1. On the basis of these calculations 1 was assumed to crystallize in the centric space group C2/c. Because the molecule lacks a center of symmetry, the two-fold axis of the molecule must be coincident with the crystallographic two-fold axis to account for the number of molecules in the unit cell.

TABLE 1. REFLECTION STATISTICS

	Calculated	Theoretical (centric)	Theoretical (acentric)
$\langle\lvert E\rvert\rangle$	0·794	0·798	0·886
$\langle E^2\rangle$	1·000	1·000	1·000
$\langle\lvert E^2-1\rvert\rangle$	0·984	0·968	0·736
% > 1	29·54	32·00	37·00
% > 2	4·37	5·00	1·50
% > 3	0·93	0·30	0·01

The structure was solved by direct methods using Sayre's equation[4] as applied by Long's computer program.[5] An E-map calculated from 100 signed reflections from Long's program revealed seven of the eight non-hydrogen atoms in the asymmetric unit. A difference electron-density map located the position of the remaining heavy atom.

This model was refined using isotropic thermal parameters to an unweighted residual (R) of 0·143 for the 659 data with $F_0 \geq 3\sigma(F_0)$. Further refinement in an anisotropic mode reduced the value of R to 0·086. At this point a difference electron-density map was calculated. The positions of all six hydrogen atoms were easily located from this map. Least-squares refinement was continued until convergence was obtained. The final R for the 659 data with $F_0 \geq 3\sigma(F_0)$ was 0·042 and the final R for all 749 data was 0·048. In this refinement all hydrogen atoms were assigned an arbitrary temperature factor of 3·0 Å^2.

RESULTS AND DISCUSSION

Each molecule of 1 is H-bonded to two other molecules to give infinite chains running parallel to the a axis. The hydrogen bonding is shown in Fig 2. The distance between 01 and 02′ that are involved in hydrogen bonding is 2·652 Å. The numbering scheme and a perspective view of the molecule is shown in Fig 3. The final positional and anisotropic thermal parameters are listed in Table 2. The bond lengths and angles are given in Tables 3 and 4, respectively.

Compound 1 contains one unique cyclohexane ring and two unique cyclobutane rings (The other rings are related by symmetry). The cyclohexane ring (C1—C2—C5—C6—C9—C10) is in a skew boat conformation. The two unique cyclobutane rings are in different conformations, one of which is planar (C3—C4—C7—C8) and the other is puckered (C1—C2—C3—C8) with a dihedral angle of 160·7°. It is

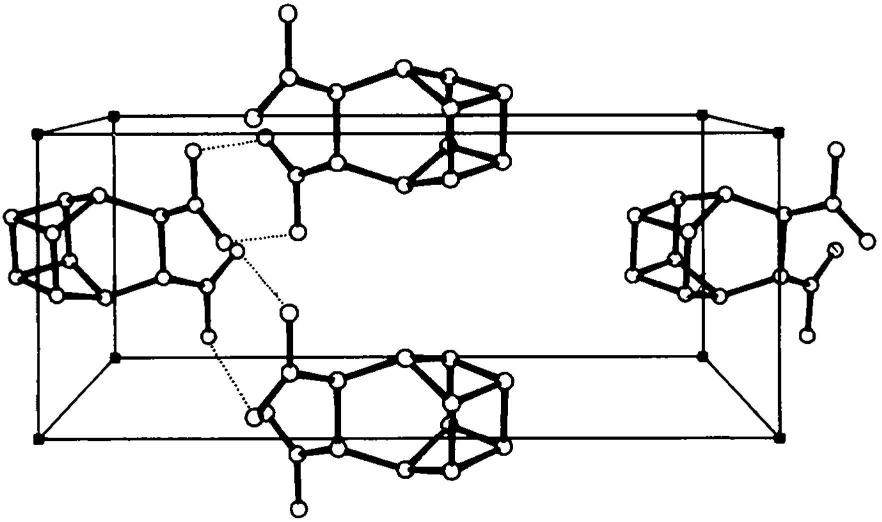


FIG 2. Hydrogen bonding in the unit cell is shown looking down the c axis. The vertical axis is a and the horizontal axis is b. For clarity only half of the molecules in the unit cell are shown. The other molecules are related to the ones shown by $\bar{1}$

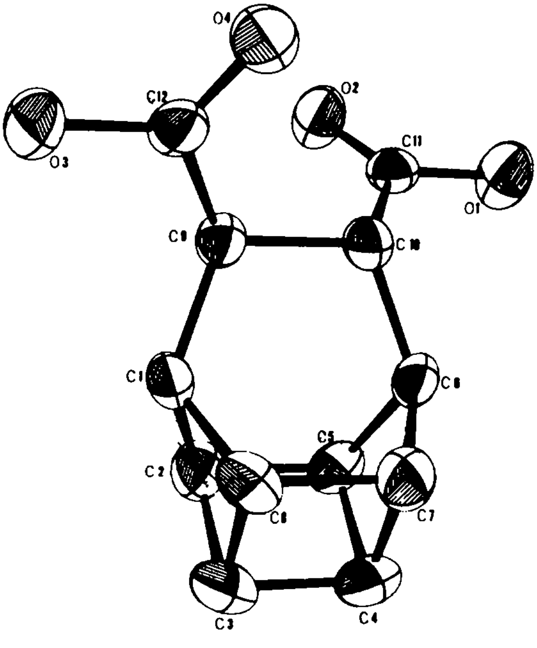


FIG 3. Perspective view of the $C_{10}H_{10}(CO_2H)_2$ molecule. The puckered and the planar rings can be clearly seen

interesting to note that the two bonds (C1—C8. C1—C2) that are unique to the puckered cyclobutane are normal in length. but that three of the four bonds in the planar are considerably longer than the expected value for a simple carbon–carbon bond.

TABLE 2. ATOMIC PARAMETERS[a]

Atom	X[b]	Y	Z
C1	0·7075 (5)	−0·0062 (2)	0·2933 (3)
C2	0·6751 (5)	0·0597 (2)	0·1884 (3)
C3	0·6214 (5)	0·1368 (2)	0·2758 (3)
C8	0·5727 (5)	0·0595 (2)	0·3643 (3)
C9	0·6241 (4)	0·8970 (2)	0·2702 (3)
C12	0·6797 (4)	0·8341 (2)	0·3730 (2)
O3	0·8905 (3)	0·8347 (2)	0·4120 (2)
O4	0·5446 (3)	0·7865 (1)	0·4158 (2)
H1	0·396 (4)	0·061 (2)	0·041 (3)
H2	0·778 (4)	0·062 (2)	0·122 (2)
H3	0·714 (5)	0·191 (2)	0·303 (2)
H4	0·863 (5)	−0·007 (2)	0·332 (2)
H5	0·695 (5)	0·975 (2)	0·205 (3)
H6	0·907 (5)	0·796 (2)	0·473 (3)

	$10^4\beta_{11}$[c]	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{12}$	$10^4\beta_{13}$	$10^4\beta_{23}$
C1	158 (8)	34 (1)	79 (3)	−11 (3)	−9 (4)	8 (3)
C2	213 (9)	43 (2)	92 (3)	−1 (3)	20 (4)	2 (2)
C3	292 (10)	32 (1)	128 (4)	−19 (3)	−15 (5)	3 (2)
C8	247 (9)	38 (2)	79 (3)	−19 (3)	−5 (4)	−7 (2)
C9	173 (8)	34 (1)	56 (2)	5 (3)	−5 (3)	0 (1)
C12	211 (9)	28 (1)	64 (3)	3 (3)	−16 (4)	−6 (1)
O3	219 (6)	53 (1)	104 (2)	−7 (2)	−44 (3)	30 (1)
O4	240 (6)	48 (1)	99 (2)	−16 (2)	−23 (3)	26 (1)
H[d]						

[a] Standard deviation of least significant figure is given in parentheses

[b] X. Y. and Z are in fractional monoclinic coordinates

[c] Anisotropic thermal parameters are in the form
$\exp -(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23}$

[d] All H atoms had an isotropic temperature factor set to 3·0 Å^2

Other known cyclobutanes also show an apparent lengthening of the carbon–carbon bonds. The average bond distance for the eight reported planar cyclobutane rings listed in Table 5 is $1{\cdot}56_2$ (12) Å. The corresponding distance for the thirteen cyclobutane derivatives that are not polyhalogenated is $1{\cdot}54_6$ (10) Å. Although the difference in bond lengths between planar and puckered rings are too small to say conclusively that the planar rings have longer bonds, further studies on cyclobutanes may show that this difference is significant. As previously mentioned. the structure reported in this paper, which contains planar and puckered rings in the same molecule, shows that the two bonds that are unique to the puckered rings are shorter than the average of the bonds in the planar rings.

Table 3. Bond lengths in Å

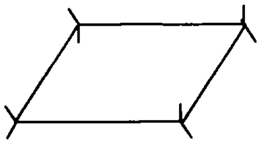
C1—C2	1·536 (4)	C1—H4	1·00 (3)
C2—C3	1·564 (5)	C2—H2	1·03 (3)
C3—C8	1·567 (4)	C3—H3	1·01 (3)
C1—C8	1·543 (4)	C8—H1	1·08 (3)
C2—C5	1·567 (4)	C9—H5	0·95 (3)
C3—C4	1·535 (6)	O3—H6	0·89 (3)
C1—C9	1·531 (4)		
C9—C10	1·534 (5)		
C9—C12	1·505 (4)		
C12—O3	1·315 (3)		
C12—O4	1·214 (3)		

A possible explanation for the bond lengthening can be found by considering the possible molecular conformations. There are three ways in which spatial relationships between atoms can be altered to minimize unfavorable steric and electronic interactions. These are (1) rotation of bonds, (2) distortion of bond angles, and (3) distortion of bond distances. Although examples of the first two are common, the third is rarely encountered. We suggest that it is an important factor in determining the structural parameters of cyclobutanes.

Table 4. Bond angles in degrees

C3—C8—C7	89·14 (24)	C1—C9—C10	110·54 (14)
C8—C7—C4	89·70 (23)	C2—C1—C9	116·31 (24)
C7—C4—C3	90·40 (25)	C8—C1—C9	119·58 (23)
C4—C3—C8	90·77 (25)	C1—C9—C12	113·40 (22)
C1—C2—C3	89·39 (24)	C12—C9—C10	112·02 (24)
C2—C3—C8	86·48 (22)	O3—C12—C9	113·47 (24)
C3—C8—C1	89·03 (23)	O4—C12—C9	123·77 (24)
C8—C1—C2	88·29 (22)	O3—C12—O4	122·76 (26)
C1—C2—C5	110·09 (23)		
C2—C5—C6	109·81 (24)		

The cyclobutane framework can exist in either a planar (2) or a puckered (3) conformer. The energy barrier between these forms appears to be very low (*ca* 1 kcal mole^{-1}).[9] In the planar conformer every atom attached to a member of the ring will be perfectly eclipsed by two of its neighbors on the adjacent ring C atoms.



2

3

The repulsions that arise due to eclipsing can be minimized either by puckering the framework or stretching C—C bonds.

By puckering the 4-membered ring the bond angles are compressed to values less than 90°. Consequently. the relief of strain due to an easing of the eclipsing interactions is offset by an increase in angle strain. The magnitude of unfavorable 1.3-eclipsing interactions. caused by puckering. increases directly as a function of the dihedral angle. In view of the low energy barrier between **2** and **3**. it follows that the increased angle strain and 1.3-interactions in puckered forms of cyclobutanes are of the same order of magnitude as the eclipsing interactions that occur in the planar form. Consequently. bond stretching becomes a reasonable alternative for absorbing the strain energy inherent in the cyclobutane framework. The bond lengthening that is predicted for planar forms by this theory is observed in the present structural investigation and the other structures given in Table 5.

TABLE 5. STRUCTURAL PARAMETERS OF CYCLOBUTANES

Compound	Dihedral angle	Bond lengths	Method	Refs
Octahydroxycyclobutane	180	⟨1·562⟩	X-ray	[a]
Cubane	180°	⟨1·551 ± 0·003⟩	X-ray	[b]
cis.trans.cis-1.2.3.4-Tetraphenylcyclobutane	180°	1·573 ± 0·015. 1·566 ± 0·015	X-ray	[c, d]
Cyclopentenone photodimer	180°	1·59 ± 0·015. 1·54 ± 0·015	X-ray	[e]
Bicyclo[3.1.1]heptane	137°	1·553 ± 0·009	E.D.	[f]
Bicyclo[2.1.1]hexane	129·5°	1·547	E.D.	[g]
Bicyclo[1.1.1]pentane	120°	1·545 ± 0·006	E.D.	[h]
Methylcyclobutane	~155° ± 5	⟨1·56 ± 0·03⟩	E.D.	[i]
Octafluorocyclobutane	160° ± 4	⟨1·60 ± 0·04⟩	E.D.	[i]
Octachlorocyclobutane	161°	1·57 ± 0·03. 1·58 ± 0·03	X-ray	[j, d]
Cyclobutane		1·548 ± 0·003	E.D.	[k, l]
Anemonin	152°	1·537 ± 0·008	X-ray	[m]
Cyclobutyl chloride	160°	⟨1·537⟩	M.W.	[n]
Cyclobutyl bromide	151°	1·544 ± 0·003	M.W.	[o]
Biscyclobutyl	147°	1·548 ± 0·004	E.D.	[p]
trans-1.3-Dibromocyclobutane	148°	1·562 ± 0·006	E.D.	[q]
trans-1.3-Dichlorocyclobutane	147°	1·551 ± 0·003	E.D.	[q]
cis-1.3-Dibromocyclobutane	147°	1·556 ± 0·007	E.D.	[q]
cis-1.3-Dichlorocyclobutane	147°	1·549 ± 0·002	E.D.	[q]
sodium *trans*-1.3-cyclobutanedicarboxylate	180°	⟨1·563⟩	X-ray	[r]
trans-1.3-Cyclobutanedicarboxylic acid	155°	⟨1·552⟩	X-ray	[r]
trans-1.3-Cyclobutanedicarboxylic acid	180°	1·552 ± 0·006 1·567 ± 0·006	X-ray	[s]
cis-1.3-Cyclobutanedicarboxylic acid	149°	1·554	X-ray	[t]
trans-1.2-Dibromo-1.2-dicarbomethoxycyclobutane	153	⟨1·55 ± 0·027⟩	X-ray	[u]
cis-1.2-Dibromo-1.2-dicarbomethoxycyclobutane	150°	⟨1·56 ± 0·027⟩	X-ray	[u]
trans-1.2-Cyclobutanedicarboxylic acid	150°	1·553. 1·517	X-ray	[v]
trans-Bicyclo[4.2.0]octyl 1-3.5-dinitrobenzoate	147°	⟨1·544⟩ ± 0·004	X-ray	[w]
3.4:7.8-Dibenzotricyclo[4.2.0.0^{2,5}]octa-3.7-diene	180°	1·559 ± 0·007 1·593 ± 0·007	X-ray	[x]
1.4-Epoxy-1.4-dihydronaphthalene photodimer	180°	⟨1·54⟩ ± 0·005	X-ray	[y]

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TABLE 5 – *continued*

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