

Acta Cryst. (1975). B31, 585**1,8-Dicarboxymethyltricyclo[4,3,1,1^{3,8}]undecane**

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Abstract. C₁₅H₂₂O₄, triclinic, P $\bar{1}$ (from structure analysis), $a=6.81$ (1), $b=8.80$ (1), $c=12.10$ (2) Å, $\alpha=104.3$ (3), $\beta=93.5$ (3), $\gamma=98.1$ (3)° from precession photography and diffractometer measurements. $Z=2$, $M=266.34$, $U=694.7$ Å³, D_m (floatation)=1.27, $D_c=1.273$ g cm⁻³. The structure, refined to $R=0.069$, consists of discrete molecules of nearly C_{2v} symmetry and

the ethylene bridge is eclipsed with a torsional angle of 2.0 (6)°.

Introduction. The crystals were irregular prisms and data were collected for layers $0kl$ to $6kl$ with a Hilger-Watts linear diffractometer (Mo $K\alpha$ radiation). 2947 reflexions were collected of which 1271 had intensities greater than 3σ . Lorentz and polarization corrections were applied (but none for absorption) and the layer scales were obtained from a Wilson plot. These were

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Table 1. *Atomic positions and anisotropic temperature factors* ($\times 10^4$)The expression used for the anisotropic temperature factor was $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

	x/a	y/b	z/c	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
O(1)	999 (6)	6909 (5)	-962 (3)	387 (40)	347 (10)	73 (3)	68 (8)	-41 (5)	36 (4)
O(2)	4062 (5)	7070 (5)	-164 (3)	309 (39)	270 (8)	63 (3)	81 (6)	8 (4)	17 (4)
O(3)	3706 (8)	5657 (6)	3526 (3)	696 (41)	438 (9)	94 (4)	405 (7)	80 (6)	106 (4)
O(4)	1923 (5)	6835 (4)	4812 (3)	363 (39)	200 (6)	70 (3)	121 (5)	36 (4)	64 (3)
C(1)	1685 (7)	7961 (5)	1093 (4)	242 (41)	120 (7)	56 (4)	1 (7)	-17 (5)	25 (4)
C(2)	-583 (7)	7898 (6)	1089 (4)	206 (41)	165 (8)	80 (4)	18 (8)	-19 (6)	42 (4)
C(3)	-1291 (7)	8402 (6)	2281 (4)	184 (39)	188 (9)	98 (4)	25 (8)	-12 (6)	62 (4)
C(4)	-1145 (8)	10204 (6)	2754 (5)	284 (41)	145 (9)	133 (6)	49 (8)	6 (7)	40 (5)
C(5)	918 (8)	11233 (6)	3031 (5)	347 (43)	135 (8)	108 (5)	45 (8)	7 (7)	27 (5)
C(6)	2774 (7)	10440 (6)	2792 (4)	273 (40)	121 (8)	74 (4)	-5 (8)	1 (6)	19 (4)
C(7)	3124 (7)	9304 (6)	3538 (4)	226 (40)	174 (9)	63 (4)	3 (8)	-19 (5)	22 (4)
C(8)	1891 (7)	7621 (5)	3082 (4)	199 (41)	136 (7)	58 (3)	30 (7)	0 (5)	33 (4)
C(9)	2379 (6)	6942 (5)	1844 (4)	218 (40)	136 (7)	61 (3)	16 (7)	-7 (5)	36 (4)
C(10)	2890 (7)	9652 (5)	1517 (4)	261 (41)	127 (7)	71 (4)	-15 (7)	1 (5)	39 (4)
C(11)	-348 (7)	7579 (6)	3120 (4)	206 (41)	182 (8)	91 (4)	45 (8)	23 (5)	62 (4)
C(12)	2161 (8)	7276 (5)	-109 (4)	303 (41)	120 (8)	60 (4)	13 (8)	-14 (6)	24 (4)
C(13)	4691 (9)	6401 (7)	-1260 (4)	394 (42)	214 (11)	67 (4)	42 (10)	31 (7)	21 (5)
C(14)	2645 (8)	6610 (6)	3814 (4)	280 (41)	192 (9)	80 (4)	117 (8)	12 (6)	47 (4)
C(15)	2590 (9)	5956 (7)	5590 (5)	401 (43)	195 (9)	90 (4)	68 (10)	-17 (7)	75 (4)
H(2a)*	-1112 (70)	6760 (67)	731 (48)	131	253	112	25	-18	55
H(2b)	-928 (72)	8643 (66)	577 (48)	131	253	112	25	-18	55
H(3)	-2779 (75)	7790 (69)	2060 (50)	204	257	128	47	-10	84
H(4a)	-1881 (81)	10394 (66)	3561 (58)	266	188	196	51	9	50
H(4b)	-1891 (81)	10591 (67)	2137 (59)	266	188	196	51	9	50
H(5a)	1307 (84)	11704 (68)	3856 (55)	320	205	157	74	18	33
H(5b)	1106 (83)	12121 (68)	2667 (55)	320	205	157	74	18	33
H(6)	4210 (79)	11372 (63)	3007 (47)	305	168	102	9	-5	23
H(7a)	2667 (77)	9826 (65)	4379 (47)	234	226	90	-5	-25	36
H(7b)	4486 (76)	9217 (66)	3575 (47)	234	226	90	-5	-25	36
H(9a)	3938 (74)	6977 (60)	1821 (43)	224	181	81	46	-18	40
H(9b)	1449 (73)	5628 (65)	1477 (47)	224	181	81	46	-18	40
H(10a)	4336 (79)	9525 (62)	1337 (47)	272	174	96	-32	2	45
H(10b)	2479 (77)	10209 (61)	1003 (46)	272	174	96	-32	2	45
H(11a)	-685 (69)	8100 (66)	3885 (49)	146	262	124	43	23	93
H(11b)	-635 (71)	6345 (68)	2813 (49)	146	262	124	43	23	93
H(13a)	4434 (83)	7016 (69)	-1836 (53)	250	200	150	20	20	20
H(13b)	4082 (82)	5250 (69)	-1641 (54)	250	200	150	20	20	20
H(13c)	6073 (87)	6546 (68)	-1202 (54)	250	200	150	20	20	20
H(15a)	3912 (83)	6451 (67)	5831 (53)	250	200	150	20	20	20
H(15b)	2395 (82)	5030 (68)	5275 (54)	250	200	150	20	20	20
H(15c)	1877 (84)	6367 (70)	6273 (59)	250	200	150	20	20	20

* The anisotropic temperature factors of the hydrogen atoms were estimated from the temperature factors of the carbon atoms to which they were attached and were not refined.

later refined as parameters in the least-squares analysis. The statistics of the E values suggested the centrosymmetric space group, and the LSAM set of direct method programs (Main, 1971) were used to solve the structure. Apart from the trivial solution there were two sets with the same figure of merit, one of which was totally uninterpretable. The other revealed 15 peaks consistent with the assumed geometry of the molecule and two more were found from a difference synthesis based on this structure. However the model would not refine below $R=0.55$ and it was found necessary to shift the origin of the unit cell relative to the molecule by 0.74 \AA , when all the remaining atoms could be found and the structure refined by standard least-squares techniques (8 cycles with a full matrix) to $R=0.176$. At this stage all the hydrogen atoms were found by difference synthesis and anisotropic temperature factors were introduced for the heavier atoms. Layer scales and the positions of the hydrogen atoms were also refined and the final R was 0.069 ($R = \sum |F_o| - |F_c| / \sum |F_o|$).^{*} Unit weights were used and scattering factors were taken from *International Tables for X-ray Crystallography* (1968). The programs used were our adaptation of the CRYSTAL 69 system of Powell & Griffiths (1969). Atomic parameters are given in Table 1, the numbering of the non-hydrogen atoms in Fig. 1,

Table 2. Bond lengths (\AA) ($e.s.d. = 0.008 \text{ \AA}$)

C(1)–C(2)	1.54	C(4)–C(5)	1.53	C(8)–C(14)	1.52
C(1)–C(9)	1.53	C(5)–C(6)	1.54	C(12)–O(1)	1.21
C(1)–C(10)	1.54	C(6)–C(7)	1.54	C(12)–O(2)	1.34
C(1)–C(12)	1.51	C(6)–C(10)	1.54	C(13)–O(2)	1.43
C(2)–C(3)	1.53	C(7)–C(8)	1.55	C(14)–O(3)	1.19
C(3)–C(4)	1.54	C(8)–C(9)	1.55	C(14)–O(4)	1.32
C(3)–C(11)	1.55	C(8)–C(11)	1.52	C(15)–O(4)	1.45

^{*} A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30715 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

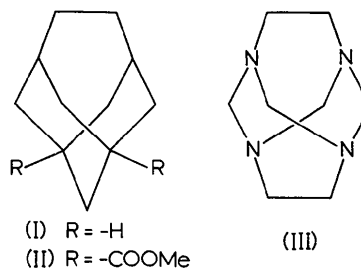
Table 4. Torsional angles in the hydrocarbon nucleus ($^\circ$) ($e.s.d. = 0.5^\circ$)

C(12)–C(1)–C(2)–C(3)	174.0	C(11)–C(8)–C(9)–C(1)	61.0	
C(9)	C(3)	C(7)	C(1)	–64.0
C(10)	C(3)	C(14)	C(1)	–178.6
C(1)–C(2)–C(3)–C(11)	–47.7	C(12)–C(1)–C(9)–C(8)	–179.7	
C(1)	C(4)	C(2)	C(8)	–61.3
C(2)–C(3)–C(4)–C(5)	–66.3	C(10)	C(8)	63.7
C(11)	C(5)	C(12)–C(1)–C(10)–C(6)	–172.7	
C(3)–C(4)–C(5)–C(6)	2.0	C(3)	C(6)	66.5
C(4)–C(5)–C(6)–C(10)	63.3	C(9)	C(6)	–55.7
C(4)	C(7)	C(9)–C(8)–C(11)–C(3)	–53.8	
C(5)–C(6)–C(7)–C(8)	82.9	C(7)	C(3)	67.9
C(10)	C(8)	C(14)	C(3)	–172.7
C(6)–C(7)–C(8)–C(9)	56.4	C(8)–C(11)–C(3)–C(2)	46.5	
C(6)	C(11)	C(8)	C(4)	–84.7
C(6)	C(14)	C(1)–C(10)–C(6)–C(7)	47.3	
		C(1)	C(5)	–83.4

Table 3. Bond angles ($^\circ$) ($e.s.d. = 0.4^\circ$)

C(2)–C(1)–C(9)	109.4	C(7)–C(8)–C(9)	108.0
C(2)–C(1)–C(10)	114.0	C(7)–C(8)–C(11)	113.7
C(2)–C(1)–C(12)	108.8	C(7)–C(8)–C(14)	106.4
C(9)–C(1)–C(10)	108.7	C(9)–C(8)–C(11)	110.6
C(9)–C(1)–C(12)	108.2	C(9)–C(8)–C(14)	107.7
C(10)–C(1)–C(12)	107.7	C(11)–C(8)–C(14)	110.2
C(1)–C(2)–C(3)	114.1	C(1)–C(9)–C(8)	109.0
C(2)–C(3)–C(4)	114.3	C(1)–C(10)–C(6)	114.1
C(2)–C(3)–C(11)	111.6	C(3)–C(11)–C(8)	113.7
C(4)–C(3)–C(11)	113.9	C(1)–C(12)–O(1)	126.1
C(3)–C(4)–C(5)	118.8	C(1)–C(12)–O(2)	113.0
C(4)–C(5)–C(6)	119.1	O(1)–C(12)–O(2)	120.9
C(5)–C(6)–C(7)	113.9	C(8)–C(14)–O(3)	125.2
C(5)–C(6)–C(10)	114.2	C(8)–C(14)–O(4)	113.1
C(7)–C(6)–C(10)	111.3	O(3)–C(14)–O(4)	121.7
C(6)–C(7)–C(8)	113.8	C(12)–O(2)–C(13)	118.3
		C(14)–O(4)–C(15)	117.5

bond lengths in Table 2, bond angles in Table 3 and torsional angles in Table 4.



Discussion. The conformation of homoadamantane (I) is of considerable interest, for whilst a Dreiding model takes up a twisted (C_2) configuration, calculations suggest that the molecule has C_{2v} symmetry with the 4,5 bridge in an eclipsed arrangement (Gleicher & Schleyer, 1967). N.m.r. data on the hydrocarbon (Ligero, Schleyer & Ramey, 1969) and infrared data on the 4,5-diol support the latter structure (Schleyer, Funke & Ligero, 1969), and the crystal structure of the 4,5-dione the former (Braun, Hornstra & Leenhouts,

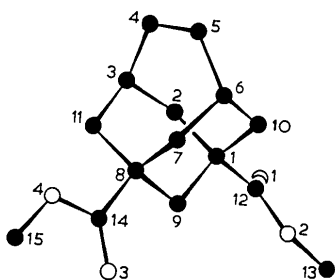


Fig. 1. The shape and numbering of the molecule. Solid circles represent carbon atoms, circles oxygen atoms. The numbers correspond to those used in Table 1.

1970), but there are no structural data for the hydrocarbon. We have shown that an analogous molecule (III) adopts a shape with planar ethylene bridges but with very pronounced vibration of C(4) and C(5) perpendicular to the plane of the bridge, suggesting that the energies of the planar and twisted bridge systems in (I) may be very similar (Murray-Rust, 1974). The crystal structure of the 1,8-disubstituted derivative (II) was undertaken to investigate this [and also to confirm it as the product of synthesis (Henry, Moodie, Parker & Watt, 1975)].

The structure consists of discrete molecules with no unusually short intermolecular contact distances (Table 5), and it is reasonable to assume that the configuration observed is close to that of minimum energy. The homoadamantane nucleus has almost C_{2v} symmetry and the torsional angle in the ethylene bridge is only $2.0 (6)^\circ$. The thermal ellipsoids of the two atoms in this bridge, C(4) and C(5), do not show any unusual anisotropic motion perpendicular to the bridge (the vibration of the ester groups is more pronounced by comparison) and the C_{2v} conformation would thus appear considerably more stable than C_2 arrangements with a torsional angle of about 60° (as predicted from

models). The bond lengths are normal, but although the angles in the nucleus are considerably larger than tetrahedral they are not unusual in this type of system (Murray-Rust, 1974; Murray-Rust & Murray-Rust, 1975; Murray-Rust & Smith, 1975).

Table 5. Intermolecular contact distances (\AA) less than 3.60\AA (*e.s.d.* = 0.008\AA)

C(13)···O(3)	\bar{x} ,	\bar{y} ,	$1-z$	3.24
O(3)···C(1)	\bar{x} ,	\bar{y} ,	\bar{z}	3.31
C(4)···O(4)	$\bar{x}-1$,	$1-y$,	\bar{z}	3.55
O(4)···C(15)	$\bar{x}-1$,	\bar{y} ,	\bar{z}	3.58
O(4)···C(5)	$\bar{x}-1$,	$1-y$,	\bar{z}	3.58
O(1)···C(5)	$\bar{x}-1$,	$1-y$,	$\bar{z}-1$	3.59

References

- BRAUN, P. B. & HORNSTRA, J. & LEENHOUTS, J. I. (1970). *Acta Cryst.* **B26**, 1802–1806.
- GLEICHER, G. J. & SCHLEYER, P. VON R. (1967). *J. Amer. Chem. Soc.* **89**, 582–593.
- HENRY, R. S., MOODIE, W. T., PARKER, W. & WATT, C. I. F. (1975). *J. Chem. Soc. Perkin I*. In the press.
- International Tables for X-ray Crystallography* (1968). Vol. III. Birmingham: Kynoch Press.
- LIGGERO, S. H., SCHLEYER, P. VON R. & RAMEY, K. C. (1969). *Spectrosc. Lett.* **2**, 197–199.
- MAIN, P. (1971). LSAM system of crystallographic programs, Univ. of York.
- MURRAY-RUST, J. & MURRAY-RUST, P. (1975). *Acta Cryst.* **B31**, 310–311.
- MURRAY-RUST, P. (1974). *J. Chem. Soc. Perkin II*, pp. 1136–1141.
- MURRAY-RUST, P. & SMITH, I. (1975). *Acta Cryst.* **B31**, 587–589.
- POWELL, M. T. G. & GRIFFITHS, A. (1969). CRYSTAL 69 programs, Portsmouth Polytechnic.
- SCHLEYER, P. VON R., FUNKE, E. & LIGGERO, S. H. (1969). *J. Amer. Chem. Soc.* **91**, 3965–3967.

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1,4-Dimethanodibenzo[*d,i*]-1,3,6,8-tetrazeine

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Abstract. $C_{16}H_{16}N_4$, $M=264.33$, orthorhombic, $Pbcn$, $a=10.57 (1)$, $b=7.46 (1)$, $c=16.93 (2) \text{\AA}$ from precession photographs, refined by diffractometer. $Z=4$, $D_m=1.33$ (floatation), $D_c=1.316 \text{ g cm}^{-3}$. The compound was crystallized from petrol as needle prisms. The structure, refined to $R=0.056$, shows discrete molecules of almost D_{2d} symmetry with some angle strain in the heterocyclic rings.

Introduction. Systematic absences $hk0$ $h+k=2n+1$, $h0l$ $l=2n+1$, $0kl$ $k=2n+1$ gave the space group as $Pbcn$. Data were collected for layers $0kl$ to $4kl$ and $h0l$ to $h7l$ with a Hilger-Watts linear diffractometer (Mo $K\alpha$ radiation). 792 unique reflexions were recorded for which the intensity was greater than 3σ and the agreement between the two sets of data is shown in a merging R of 0.043 [$R = \sum |(F_1 - F_2)| / \frac{1}{2} \sum (F_1 + F_2)$].