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THE CRYSTAL AND MOLECULAR STRUCTURE AND SOLID STATE CONFORMATION OF 2,2,4,4,6,6,-HEXAMETHYLCYCLOHEXANETRIONE

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Abstract—The crystal and molecular structure of the title compound have been determined by X-ray methods. Crystals are monoclinic, space group $P2_1/n$ with $a = 6.076(2)$, $b = 14.927(3)$, $c = 13.200(3)$ Å, $\beta = 96.71(5)°$. The structure was solved by direct methods and refined by least-squares to a final R value of 0.05 using 1358 significant ($I > 1.5\sigma(I)$) reflections out of a total 2095 measured. The molecule adopts a slightly distorted unsymmetric boat conformation, in between two (of three) degenerate perfect C_s boat structures which it is proposed are interconvertible by a conformational ripple of low energy.

We have shown recently that octamethyl-1,4-cyclohexanedione, unlike 1,4-cyclohexanedione itself, exists as a flattened chair, i.e. with a C_{2v} conformation, in the solid state. Minimization of severe non-bonded Me–Me repulsion in the octamethyl derivative was proposed to explain the deviation from the well-established twist-boat conformation of simple 1,4-cyclohexanedione(s).[1]

In the further search for unusual conformations of 6-membered rings,[2] the structure of 2,2,4,4,6,6-hexamethylcyclohexanetrione (1) which has previously been discussed by Dale[3a] and Le Fèvre,[3b] is of interest. We have now determined the crystal structure of this compound by X-ray methods and report that the molecule exists in an almost perfect boat conformation in the solid.

RESULTS AND DISCUSSION

The molecular structure found is shown in Fig. 1; bond lengths and angles are given in Table 1, some of the more important torsion angles in Table 2 and the results of some least squares planes calculations in Table 3.

The molecule is strongly flattened, as can be seen from the sum of the six ring torsion angles 36° + 5° + 47° + 56° + 20° + 28° = 192°. By comparison, the corresponding torsion angle sum in cyclohexane, which itself is slightly flattened, is 336° (compared with the "ideal" 360°), and in octamethyl-1,4-cyclohexanedione is 272.4°.[1]

The distribution of torsion angles around the ring is irregular and clearly corresponds to an unsymmetrical conformation, unlike any of those considered by Dale.[3a] However, despite the irregular torsion angles closer examination of our data shows that the actual conformation deviates only little from a perfect boat. The nature of the conformation and the way in which it might arise are very interesting. The ideal boat form of this permethylated trione has C_s symmetry and the ring comprises two planar halves, as can be seen in Fig. 2 which is based on Dale's representation of the ideal C_s boat structure. Two points relating to this diagram are to be noted—that one of the Me...Me contacts is extremely close and that one of the CO groups, lying on the mirror plane is different from the other two.

The molecular structure of 1 as found in the crystal has retained the basic arrangement of the three CO's shown for the perfect boat (i.e. one on one side of the ring, two on the other), only the potentially short Me...Me contact (C(21)...C(61) in this case) has become 3.40 Å, essentially equal to the C(62)...C(42) distance which has been reduced from an estimated[3a] 3.75 Å (Fig. 2) to 3.38 Å. Examination of Fig. 3(a), a view of 1 in the direction C(4)→C(1), shows that deviation from the ideal boat form (shown in equivalent view in Fig. 3b) has occurred by a slight movement of atoms on one side of the molecule only (C(5), C(6), etc.) leaving the other side, the C(1)–C(2)–C(3)–C(4) fragment, in its

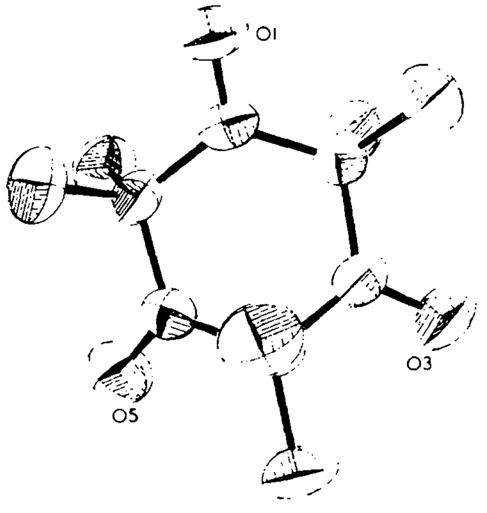


Fig. 1. The molecular structure of 1.

Table 1. Interatomic distances and angles for 1 including some non-bonded intramolecular contacts

Bond lengths (Å)

C(2)-C(1)	1.515(5)	C(5)-C(4)	1.528(6)
C(6)-C(1)	1.514(6)	C(41)-C(4)	1.526(6)
O(1)-C(1)	1.223(4)	C(42)-C(4)	1.531(6)
C(3)-C(2)	1.527(5)	C(6)-C(5)	1.531(5)
C(21)-C(2)	1.534(6)	O(5)-C(5)	1.205(4)
C(22)-C(2)	1.531(6)	C(61)-C(6)	1.561(6)
C(4)-C(3)	1.511(6)	C(62)-C(6)	1.528(6)
O(3)-C(3)	1.211(4)		
H(21A)-C(21)	1.048(54)	H(42A)-C(42)	0.965(42)
H(21B)-C(21)	1.047(36)	H(42B)-C(42)	1.014(38)
H(21C)-C(21)	0.952(31)	H(42C)-C(42)	1.26[illegible](36)
H(22A)-C(22)	1.020(37)	H(61A)-C(61)	0.946(29)
H(22B)-C(22)	1.026(41)	H(61B)-C(61)	0.989(42)
H(22C)-C(22)	1.018(48)	H(61C)-C(61)	0.937(56)
H(41A)-C(41)	0.9[illegible](42)	H(62A)-C(62)	0.849(51)
H(41B)-C(41)	0.974(55)	H(62B)-C(62)	0.980(46)
H(41C)-C(41)	1.044(65)	H(62C)-C(62)	1.086(49)

Bond angles (deg.)

C(6)-C(1)-C(2)	120.7(3)	C(42)-C(4)-C(3)	107.5(3)
O(1)-C(1)-C(2)	119.5(3)	C(41)-C(4)-C(5)	111.4(4)
O(1)-C(1)-C(6)	119.7(3)	C(42)-C(4)-C(5)	109.6(4)
C(3)-C(2)-C(1)	112.4(3)	C(42)-C(4)-C(41)	109.8(4)
C(21)-C(2)-C(1)	10[illegible](3)	C(6)-C(5)-C(4)	117.8(3)
C(22)-C(2)-C(1)	111.6(3)	O(5)-C(5)-C(4)	121.5(3)
C(21)-C(2)-C(3)	107.5(3)	O(5)-C(5)-C(6)	120.7(3)
C(22)-C(2)-C(3)	108.1(3)	C(5)-C(6)-C(1)	111.6(3)
C(22)-C(2)-C(21)	109.1(4)	C(61)-C(6)-C(1)	108.6(3)
C(4)-C(3)-C(2)	119.1(3)	C(62)-C(6)-C(1)	110.8(4)
O(3)-C(3)-C(2)	119.8(4)	C(61)-C(6)-C(5)	108.3(3)
O(3)-C(3)-C(4)	121.1(3)	C(62)-C(6)-C(5)	108.3(4)
C(5)-C(4)-C(3)	107.2(3)	C(62)-C(6)-C(61)	109.1(4)
C(41)-C(4)-C(3)	111.2(4)		

Non-Bonded Contacts (Å)

C(21)....C(61)	3.40		
C(42)....C(22)	3.69		
C(42)....C(62)	3.38		
O(1).....C(21)	3.19	O(3).....C(41)	2.73
O(1).....C(22)	2.79	O(3).....C(21)	2.88
O(1).....C(62)	2.76	O(3).....C(22)	2.92
O(5).....C(41)	2.74		
O(5).....C(61)	2.81		
O(5).....C(62)	3.07		

Table 2. Selected torsion angles for 1

C(6) - C(1) - C(2) - C(3)	-36.0
C(1) - C(2) - C(3) - C(4)	-4.6
C(2) - C(3) - C(4) - C(5)	46.9
C(3) - C(4) - C(5) - C(6)	-55.7
C(4) - C(5) - C(6) - C(1)	20.2
C(5) - C(6) - C(1) - C(2)	-27.9
O(1) - C(1) - C(2) - C(3)	147.9
O(1) - C(1) - C(6) - C(5)	-155.9
O(3) - C(3) - C(2) - C(1)	175.7
O(3) - C(3) - C(4) - C(5)	-133.4
O(5) - C(5) - C(4) - C(3)	125.1
O(5) - C(5) - C(6) - C(1)	-160.6

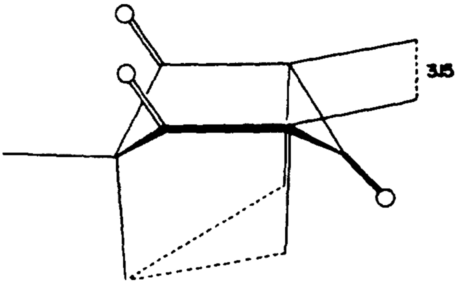


Fig. 2. The C_s ideal boat form of 1 (after Dale[3a]).

original planar form. Examination of a Dreiding model of 1 suggests that the boat conformation is quite flexible and conformationally mobile and that given a conformational ripple of low energy, one ideal boat structure (e.g. as here, with O(3), O(5) related by the mirror plane) can be converted into one of two more conformational equivalents (e.g. with O(5), O(1) *or* O(1), O(3) related by the

Table 3. Least squares planes calculations

Equations of planes are given in the form Ax + By + Cz = D where x, y, z correspond to fractional coordinates. Atomic deviations (Å) from the plane are given in square brackets

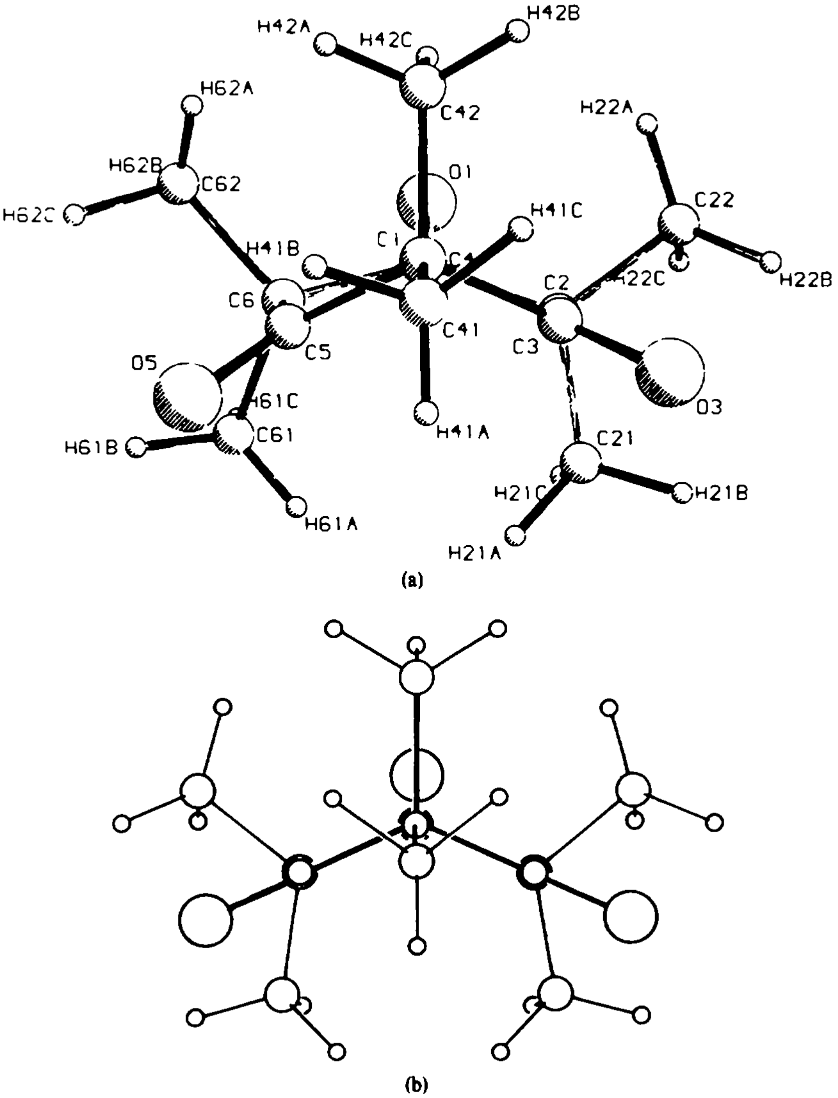
Plane 1 C(1) [-0.012], C(2) [0.022], C(3) [-0.023] C(4) [0.013]
$5.424x - 0.039y + 4.529z = 0.665$

Plane 2 C(1) [-0.053], C(4) [0.055], C(5) [-0.103], C(6) [0.100]
$4.4103x + 9.7912y + 1.5938z = 0.8063$

Plane 3 C(1) [0.015], C(4) [0.004], O(1) [-0.015], C(41) [-0.008], C(42) [0.004]
$-1.3664x + 13.3825y - 4.6554z = 0.0175$

Angles between Normals to Planes

Plane 1	Plane 2	42.31
Plane 1	Plane 3	112.03
Plane 2	Plane 3	69.77



(a)

(b)

Fig. 3. (a) The molecular structure of 1 viewed in the direction of the C(1)→C(4) trans-annular vector. (b) The idealized boat form of 1 in the same direction.

Table 4. Final atomic positional (fractional × 10^4) and thermal parameters (U_{ij} × 10^3)

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C(1)	-101(4)	560(2)	1568(2)	45(1)	52(2)	36(1)	-7(1)	9(1)	-9(1)
C(2)	-593(4)	-229(2)	2226(2)	55(1)	49(1)	47(1)	0(1)	8(1)	4(1)
C(3)	-1494(4)	62(2)	3207(2)	55(2)	65(2)	42(1)	8(1)	9(1)	0(1)
C(4)	-1621(4)	1049(2)	3447(2)	56(2)	68(2)	41(1)	-9(1)	9(1)	5(1)
C(5)	-2665(4)	1516(2)	2477(2)	55(1)	46(1)	50(1)	-5(1)	8(1)	2(1)
C(6)	-1561(4)	1384(2)	1503(2)	60(2)	51(2)	45(1)	7(1)	11(1)	-4(1)
O(1)	1424(3)	510(1)	1041(2)	69(1)	81(1)	69(1)	-2(1)	33(1)	-1(1)
O(3)	-2085(5)	-499(2)	3781(2)	143(2)	83(2)	64(1)	18(1)	36(1)	-9(1)
O(5)	-4286(4)	1980(2)	2476(2)	80(1)	81(2)	88(2)	3(1)	17(1)	34(1)
C(21)	-2380(7)	-802(3)	1617(3)	93(3)	64(2)	62(2)	-3(2)	8(2)	-25(2)
C(22)	1471(7)	-804(3)	2515(3)	75(2)	78(2)	85(3)	9(2)	15(2)	24(2)
C(41)	-2965(8)	1213(4)	4336(3)	93(3)	125(4)	51(2)	-10(2)	27(2)	22(3)
C(42)	753(6)	1368(3)	3722(3)	72(2)	91(3)	62(2)	-14(2)	-5(2)	-15(2)
C(61)	-3418(7)	1268(3)	591(3)	78(2)	93(3)	52(2)	6(2)	-2(2)	11(2)
C(62)	-217(8)	2225(3)	1331(4)	102(3)	61(2)	92(3)	15(2)	29(3)	-15(2)
H(21A)	-3932(91)	-488(32)	1566(36)	140(18)					
H(21B)	-2545(51)	-1377(24)	2055(24)	83(10)					
H(21C)	-2241(46)	-915(21)	917(25)	66(8)					
H(22A)	2729(60)	-365(24)	2727(25)	34(11)					
H(22B)	1032(62)	-1308(27)	2979(29)	104(12)					
H(22C)	1510(69)	-1103(32)	1825(36)	128(15)					
H(41A)	-4334(72)	994(30)	4154(32)	108(15)					
H(41B)	-3094(67)	1862(38)	4356(43)	144(21)					
H(41C)	-1928(*)	949(44)	4951(47)	190(22)					
H(42A)	709(59)	2032(29)	3777(32)	111(15)					
H(42B)	1578(56)	1074(25)	4334(28)	37(10)					
H(42C)	1957(57)	1242(23)	3024(27)	108(12)					
H(61A)	-4279(59)	761(26)	719(27)	85(12)					
H(61B)	-4178(63)	1855(26)	536(28)	96(12)					
H(61C)	-2753(*)	1153(44)	-1(50)	205(24)					
H(62A)	733(80)	2368(33)	1828(39)	126(20)					
H(62B)	340(71)	2138(28)	671(36)	118(14)					
H(62C)	-1343(72)	2792(33)	1257(33)	125(14)					

The temperature factor exponent takes the form: $-2\pi^2(U_{11} \cdot h^2 \cdot a^{*2} + \ldots + 2U_{12} \cdot h \cdot k \cdot a^* \cdot b^*)$

mirror). In conclusion, although the structure of 1 minimizes nonbonded repulsion of Me groups, it remains close to that of a C_s boat.

EXPERIMENTAL

2,2,4,4,6,6-Hexamethylcyclohexanetrione was prepared as described.[3a]

Crystallography. Crystals, obtained from pentane, are monoclinic, space group $P2_1/n$. The unit cell parameters, determined by least-squares refinement of setting angles for 15 reflections with, $12 < \theta < 15°$, automatically centred on a Nonius CAD4 diffractometer are: $a = 6.076(2)$, $b = 14.027(3)$, $c = 13.200(3)$ Å, $\beta = 96.71(5)°$ $U = 1188.9$ Å.[3] The measured density (flotation in aqueous KBr) is 1.16 g cm^{-3}; the calculated value is 1.174 g cm^{-3} for $Z = 4$.

Intensity data were recorded on the CAD4 using an $\omega/2\theta$ scan mode and Mo K_α radiation ($\lambda = 0.71069$ Å) in a manner described previously.[4] Of the 2095 unique reflections measured, 1358 satisfied the condition $I = 1.5\sigma(I)$ and were considered observed. The structure was solved using the automatic direct-methods routine in SHELX[5] and refined by least squares. Hydrogen atom positions were located on difference electron-density maps and refined with isotropic temperature factors; the heavier atoms were assigned anisotropic temperature factors. Convergence was reached at $R = 0.053$, $R_w = 0.059$ with the weighting scheme $w = 1/(\sigma^2(F) + 0.0013F_0^2)$ giving flat agreement analyses. The final atomic parameters are given in Table 4. Lists of F_0 and F_c are available as supplementary material. Computers, programs and scattering factor data used are those quoted in Ref. 4.

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