

étude de deux dipeptides aromatiques (1,365 et 1,361 Å).

Les groupements carboxyliques, qui s'associent en formant des dimères, C(1)O(2)O(3) et C(1')O(2')O(3') ne sont pas rigoureusement coplanaires. Ils sont situés dans des plans parallèles distants de 0,24 Å. Il est intéressant de remarquer que ce résultat recoupe les observations de Jeffrey & Sax (1963), qui ont noté des écarts analogues variant entre 0,011 et 0,549 Å suivant les cas.

Si nous considérons le plan moyen relatif à ces deux groupements COO, l'oxygène de la fonction carbonyle en est distant de 0,015 Å, alors que les écarts-type sont inférieurs à 0,002 Å (Tableau 5). Donohue (1968) indique pour cet oxygène de la fonction carbonyle des écarts allant de 0,011 à 0,039 Å, invoquant des considérations d'ordre géométrique pour expliquer une planéité imparfaite.

Les deux cycles benzéniques *A* et *B* sont plans, dans la limite des erreurs expérimentales. Ces deux cycles font entre eux un angle dièdre de 64°.

Le cycle *B* est le moins incliné sur l'ensemble de la chaîne carbonée C(1)C(2)C(3) et du groupement carboxylique, l'angle dièdre correspondant est voisin de 15°.

Une forte cohésion cristalline s'établit entre deux molécules d'acide dibenzylpyruvique par liaisons hydrogène entre les groupements carboxyliques. En effet, la distance entre les atomes d'oxygène liés par l'hydrogène est 2,649 Å.

Le groupement O—H se place en position *syn*. L'angle C(2)—C(1)—O(2) (114°) est plus petit que l'angle C(2)—C(1)—O(3) (120°). Ce résultat est en accord avec les remarques de Donohue (1968) qui permettent de distinguer les groupements hydroxyle et carbonyle.

L'acide dibenzylpyruvique cristallise, comme l'acide pyruvique, en formant des dimères par liaisons hydro-

gène au niveau des groupements carboxyliques. La chaîne C_β—C_α—C=O adopte la conformation *syn*.

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Hexamethyl-2,3;5,6-diepoxybicyclo[2.2.0]hexane

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Abstract. C₁₂H₁₈O₂, monoclinic, *P2₁/c*, *a* = 7.464 (5), *b* = 13.853 (8), *c* = 12.317 (9) Å, β = 114.58 (5)°, *Z* = 4, *D_m* = 1.097, *D_x* = 1.118 Mg m⁻³. Final *R* = 0.06. Both epoxy groups are in *exo* positions and the

bicyclo[2.2.0]hexane nucleus is characterized by a lengthening of the central C—C bond to 1.632 (8) Å.

Introduction. Prismatic crystals were kindly provided by Dr U. Burger (Department of Organic Chemistry, University of Geneva). A crystal 0.16 × 0.16 × 0.20

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Table 1. Final positional and isotropic thermal parameters ($\times 10^4$ for non-hydrogen atoms and $\times 10^3$ for hydrogen atoms)

	x	y	z	$U(\text{\AA}^2)$
C(1)	2850 (7)	3195 (4)	2044 (5)	441 (35)
C(2)	3814 (8)	3719 (4)	3243 (5)	450 (39)
C(3)	1896 (7)	4021 (4)	3208 (5)	410 (34)
C(4)	730 (7)	3527 (3)	2011 (4)	342 (32)
C(5)	378 (7)	2461 (4)	2194 (5)	408 (36)
C(6)	2292 (7)	2155 (4)	2200 (5)	411 (36)
C(7)	3525 (9)	3413 (5)	1073 (5)	745 (45)
C(8)	5755 (8)	3524 (5)	4263 (5)	621 (43)
C(9)	1274 (9)	4284 (4)	4171 (5)	619 (42)
C(10)	-819 (8)	4086 (4)	1013 (5)	546 (39)
C(11)	-920 (8)	2025 (4)	2708 (5)	571 (39)
C(12)	3582 (9)	1311 (4)	2737 (6)	662 (45)
O(1)	3176 (5)	4718 (3)	2984 (3)	533 (28)
O(2)	449 (5)	1969 (3)	1160 (3)	531 (25)
H(1)	271 (10)	303 (5)	29 (6)	145 (26)
H(2)	349 (8)	414 (4)	84 (5)	97 (19)
H(3)	478 (8)	325 (4)	122 (5)	90 (18)
H(4)	578 (6)	386 (3)	502 (4)	65 (15)
H(5)	610 (10)	283 (7)	463 (9)	231 (40)
H(6)	674 (8)	374 (4)	397 (5)	88 (18)
H(7)	51 (6)	371 (3)	434 (4)	52 (13)
H(8)	243 (8)	437 (4)	500 (5)	91 (19)
H(9)	58 (7)	483 (4)	401 (4)	73 (16)
H(10)	-21 (8)	476 (4)	91 (5)	102 (19)
H(11)	-126 (7)	369 (4)	17 (5)	84 (17)
H(12)	-201 (6)	417 (3)	118 (4)	61 (14)
H(13)	-80 (6)	136 (3)	279 (4)	52 (13)
H(14)	-57 (8)	230 (4)	359 (5)	97 (19)
H(15)	-233 (7)	221 (4)	225 (4)	79 (17)
H(16)	465 (8)	144 (4)	362 (5)	100 (19)
H(17)	295 (8)	76 (4)	279 (5)	90 (19)
H(18)	435 (8)	119 (4)	226 (5)	109 (21)

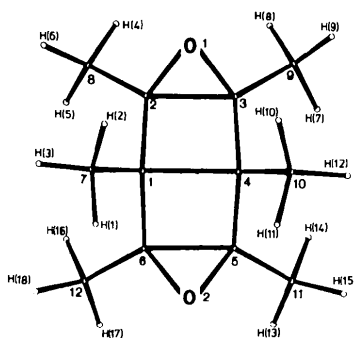


Fig. 1. The atom numbering.

mm was sealed in a Lindemann capillary. The cell parameters and intensities were obtained at room temperature on an automatic four-circle Philips PW 1100 diffractometer (graphite monochromator, Mo $K\alpha$ radiation, θ - 2θ scan). Of the 1369 reflections measured in the range $3 < \theta < 21^\circ$, 810 had $|F| \geq 3\sigma_F$ and $|F| > 4.0$ and were used in the analysis. No significant decrease in the intensities of two monitor reflections was observed. The phase problem was solved with

SINGEN and *TANGEN* of the XRAY system (1976). The *E* map revealed the positions of all the non-hydrogen atoms. Positional and anisotropic thermal parameters were refined by full-matrix least squares. The calculated positions of the H atoms were included in the model and isotropically refined. After application of the weighting scheme $\omega = (0.5 + \sigma_F^2)^{-1}$, convergence was achieved at $R = 0.061$. Final positional parameters are given in Table 1.* The atom-numbering scheme is given in Fig. 1.

Discussion. In recent years hexamethyl-Dewar-benzene has been of interest since it can undergo numerous electrophilic additions and rearrangements (Delay-Soutter, 1976). The mono- and diepoxide of hexamethyl-Dewar-benzene were first prepared by Junker, Schäfer & Niedenbrück (1967). Hydrolysis of the mono derivative to the corresponding alcohol proceeds readily whereas the diepoxide demonstrates extraordinary sluggishness even in forcing conditions (Burger & Delay-Soutter, 1976). In view of these unexpected results, the present structure determination was carried out to support the postulated *exo* position of both epoxy groups and to provide steric information about the strained bicyclo[2.2.0]hexane nucleus.

Within limits of error, the observed conformation has the expected C_{2v} symmetry, with both epoxy groups in *exo* positions. The largest deviations between chemically equivalent parameters for non-hydrogen atoms are $< 2\sigma$. The average geometry of a methyl group is: C-H = 1.01 (6) Å; H-C-H and C-C-H = 107 (5) and 112 (4)°, respectively. Bond distances and angles are given in Table 2.

There is evidence that substitution at the bridgehead atoms of the bicyclo[2.2.0]hexadiene nucleus brings about a lengthening of the central C-C bond from 1.574 Å in Dewar-benzene to 1.629 Å in hexamethyl-Dewar-benzene, with an intermediate distance 1.597 Å in the perfluoro analogue (McNeill & Scholer, 1976). It is likely that a similar lengthening effect occurs in the title compound where the bridgehead methyls are in loose van der Waals contacts through H(1)···H(11) and H(2)···H(10) at 3.04 and 2.92 Å respectively. Additional electronic effects such as σ delocalization and rehybridization probably also occur. For instance, the dimensions of the three-membered rings are in good agreement with those found for ethylene oxide (Turner & Howe, 1956); therefore the external angular strain placed on the C atoms by the shortening of C(2)-C(3) and C(5)-C(6) will be minimized by the increased length of the central C(1)-C(4) bond. The

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34794 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Bond distances (Å) with e.s.d.'s and angles (°)

The mean e.s.d. in the bond angles is 0.5°.

C(1)—C(2)	1.531 (7)	C(3)—O(1)	1.462 (7)
C(1)—C(4)	1.632 (8)	C(4)—C(5)	1.533 (7)
C(1)—C(6)	1.534 (8)	C(4)—C(10)	1.505 (7)
C(1)—C(7)	1.509 (10)	C(5)—C(6)	1.486 (8)
C(2)—C(3)	1.474 (9)	C(5)—C(11)	1.489 (9)
C(2)—C(8)	1.495 (7)	C(5)—O(2)	1.463 (8)
C(2)—O(1)	1.455 (6)	C(6)—C(12)	1.483 (8)
C(3)—C(4)	1.527 (7)	C(6)—O(2)	1.461 (5)
C(3)—C(9)	1.489 (10)		
C(2)—C(1)—C(4)	87.3	C(1)—C(4)—C(5)	87.0
C(2)—C(1)—C(6)	111.5	C(1)—C(4)—C(10)	125.0
C(2)—C(1)—C(7)	119.5	C(3)—C(4)—C(5)	110.7
C(4)—C(1)—C(6)	87.5	C(3)—C(4)—C(10)	119.6
C(4)—C(1)—C(7)	124.3	C(5)—C(4)—C(10)	119.7
C(6)—C(1)—C(7)	119.0	C(4)—C(5)—C(6)	93.0
C(1)—C(2)—C(3)	92.6	C(4)—C(5)—C(11)	129.4
C(1)—C(2)—C(8)	128.9	C(4)—C(5)—O(2)	104.5
C(1)—C(2)—O(1)	105.0	C(6)—C(5)—C(11)	132.5
C(3)—C(2)—C(8)	131.7	C(6)—C(5)—O(2)	59.3
C(3)—C(2)—O(1)	59.9	C(11)—C(5)—O(2)	116.5
C(8)—C(2)—O(1)	118.1	C(1)—C(6)—C(5)	92.4
C(2)—C(3)—C(4)	93.3	C(1)—C(6)—C(12)	129.5
C(2)—C(3)—C(9)	131.8	C(1)—C(6)—O(2)	105.2
C(2)—C(3)—O(1)	59.4	C(5)—C(6)—C(12)	132.2
C(4)—C(3)—C(9)	129.6	C(5)—C(6)—O(2)	59.6
C(4)—C(3)—O(1)	105.6	C(12)—C(6)—O(2)	116.8
C(9)—C(3)—O(1)	115.7	C(2)—O(1)—C(3)	60.7
C(1)—C(4)—C(3)	86.8	C(5)—O(2)—C(6)	61.1

four-membered rings are planar within experimental error, and the three-membered rings are inclined to these planes at an average angle of 105.8°. Owing to the nearly perfect C_{2v} symmetry of the molecule, additional mean planes are defined by pairs of equivalent C—CH₃ bonds. The magnitudes of characteristic dihedral angles between intramolecular mean planes are reported in Fig. 2. The repulsion between the O atoms and the bridgehead methyl C atoms at 3.06–3.08 Å is reflected in the increased folding of the bicyclo[2.2.0]hexane moiety to 111.3° compared with the value of 124.5° in hexamethyl-Dewar-benzene (Cardillo & Bauer, 1970). A marked distinction can be made in the *endo* methyl interactions across and along the bisector plane passing through the O atoms. In the former case there is little interaction because the methyl groups are splayed apart by the intervening O atom; in the latter case a strong repulsion ensues owing to the increased folding across C(1)—C(4) as discussed above. The H(7)···H(14) and H(5)···H(16) distances are 2.15 and 2.30 Å respectively. This steric repulsion is also apparent in the considerable angular distortion at the ring C atoms adjacent to O [e.g. C(1)—C(2)—C(8) = 129°] and in the dihedral angles of 153.6 and 155° as defined in Fig. 2. The rotational orientation of the *endo* methyl groups is severely controlled by clamping of two of their H atoms on the O atom, from which they are equally separated by 2.7–2.8 Å.

A stereoscopic view of the content of one unit cell is shown in Fig. 3. Most of the intermolecular inter-

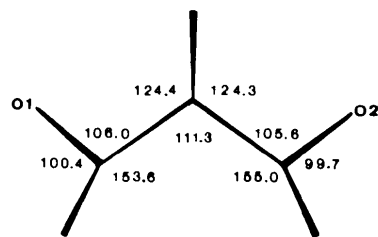


Fig. 2. Idealized molecular projection on the symmetry plane passing through the O atoms. The magnitudes (°) of characteristic dihedral angles are indicated. The mean e.s.d. is 0.57° for dihedral angles involving the methyl groups, and 0.40° for the others.

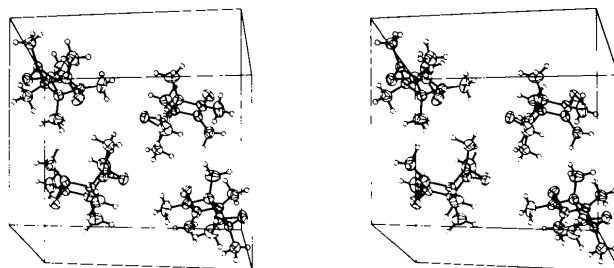


Fig. 3. Stereoscopic view of the contents of one unit cell. The origin and the basic molecule are in the rear, upper right corner, with the positive direction of *y* pointing to the left.

actions are van der Waals contacts, with only a short separation [H(7)···O(2)' = 2.45 Å] between vicinal molecules related by a glide plane.

All the observed C—CH₃ lengths are too short and it is likely that these systematic errors arise from the rather large thermal motion. As appears from the preceding discussion the molecule is highly strained and little motional freedom is available for the substituents; therefore the rigid-body approximation may hold well in this case. Inspection of the thermal ellipsoids reveals that their mutual orientation roughly obeys the molecular symmetry, and also suggests that librational motions of large amplitude (some r.m.s. displacements >0.3 Å) occur about axes perpendicular to the symmetry planes.

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