

(Ia) = 2,880 (9) Å, N—H...O = 153 (1)°; (II): N(1)...O(3) = 2,947 (6) Å, N—H...O = 177 (1)°; (III): N(1)...O(3) = 2,846 (7) Å, N—H...O = 166 (1)°. Les valeurs des masses volumiques calculées et des points de fusion mesurés indiquent que les cohésions cristallines décroissent dans l'ordre (II), (III) puis (I).

Les auteurs remercient M N. Busch, Directeur scientifique de Riom Laboratoires – CERM, qui leur a proposé le travail et fourni les échantillons.

*Acta Cryst.* (1985), **C41**, 630–632

## Structure of 5,5-Dimethyltricyclo[6.2.2.0<sup>2,7</sup>]dodecane-3,9-dione, C<sub>14</sub>H<sub>20</sub>O<sub>2</sub>

BY ZBIGNIEW DAUTER\*

*Departments of Chemistry and Physics, University of York, Heslington, York YO1 5DD, England*

JOHN V. GREENHILL

*School of Pharmacy, University of Bradford, Bradford BD7 1DP, England*

AND ALEXANDER KARAULOV AND COLIN D. REYNOLDS

*Departments of Chemistry and Physics, University of York, Heslington, York YO1 5DD, England*

(Received 20 July 1984; accepted 14 December 1984)

**Abstract.**  $M_r = 220.3$ , monoclinic,  $P2/c$ ,  $a = 10.731$  (3),  $b = 6.411$  (2),  $c = 17.719$  (3) Å,  $\beta = 94.40$  (2)°,  $V = 1215.4$  Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.204$  Mg m<sup>-3</sup>,  $\lambda(\text{Cu } K\alpha) = 1.5418$  Å,  $\mu(\text{Cu } K\alpha) = 0.543$  mm<sup>-1</sup>,  $F(000) = 480$ ,  $T = 290$  (1) K,  $R = 0.077$  for 1000 observed reflections. The bridged rings of the tricyclododecane system are in the usual boat conformation; the unbridged ring adopts a half-boat conformation. Bond lengths and angles are normal.

**Introduction.** 1,3-Cyclohexanedione (Ia) and dimedone (Ib) react with 2-cyclohexen-1-one (II) under acid catalysis to give stable products which are not furans (Greenhill, Moten & Hanke, 1984). The molecular formulae of the products were established by elemental analysis and mass spectrometry to be C<sub>12</sub>H<sub>14</sub>O<sub>2</sub> (IIIa) and C<sub>14</sub>H<sub>18</sub>O<sub>2</sub> (IIIb). The IR spectrum of (IIIb) showed  $\nu(\text{C}=\text{O})$  (saturated) at 1720,  $\nu(\text{C}=\text{O})$  (conjugated) at 1650 and  $\nu(\text{C}=\text{C})$  at 1620 cm<sup>-1</sup>. The last two bands were similar in appearance to those of the dibenzofuranones and unusually low for an enone system. Hydrogenations of the C=C double bonds of (IIIa) and (IIIb) were complete in a few minutes. The saturated diketones (IVa)  $\nu(\text{C}=\text{O})$  1718, 1700 cm<sup>-1</sup> and (IVb)  $\nu(\text{C}=\text{O})$  1715, 1690 cm<sup>-1</sup> both showed carbonyl

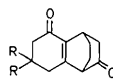
doublets. In order to confirm the formation of the tricyclododecane ring system and to establish the positions of the ketone groups an X-ray structure determination of (IVb) was undertaken.



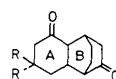
(Ia) R = H  
(Ib) R = Me



(II)



(IIIa) R = H  
(IIIb) R = Me



(IVa) R = H  
(IVb) R = Me

**Experimental.** Colourless needles from ethanol. Crystal 0.60 × 0.25 × 0.15 mm. Hilger & Watts Y290 four-circle diffractometer controlled by a LSI-11 micro-computer. Unit cell from setting angles of 20 reflections, least-squares refinement. No absorption correction. Intensity measurements by  $\omega$  scans, 30 steps of 0.02°, count time per step 1 s;  $\theta_{\text{max}} = 51^\circ$ ,  $h = -10$  to 10,  $k = 0$  to 6,  $l = 0$  to 17; 1958 reflections recorded including some Friedel pairs, 1272 unique, 270 with  $I < 2\sigma(I)$  classified as unobserved,  $R_{\text{int}} = 0.0182$ . Intensity variation of

### Références

- MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1980). *MULTAN80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univ. de York, Angleterre, et Louvain, Belgique.  
NORTH, A. C. T., PHILLIPS, D. C. & MATHEWS, F. S. (1968). *Acta Cryst.* **A24**, 351–359.  
SHELDRIK, G. M. (1976). *SHELX76*. Programme pour la détermination des structures cristallines. Univ. de Cambridge, Angleterre.

\* Permanent address: Department of Biochemistry, Technical University of Gdansk, Gdansk, Poland.

three standard reflections ( $334, \bar{3}\bar{3}4, \bar{5}16$ )  $< 1\%$ . Structure solved by direct methods using *SAYTAN*, a program using a powerful new tangent formula which optimizes a set of Sayre equations (Debaerdemaeker, Tate & Woolfson, 1984). Earlier attempts to solve the structure with *MULTAN80* (Main *et al.*, 1980) failed. None of the phase sets with good figures of merit yielded the correct structure. Structure refined on  $F$  by full-matrix least squares with *SHELX76* (Sheldrick, 1976). Final refinement cycles included anisotropic thermal parameters for the non-hydrogen atoms. Fourteen H atoms out of 20 located from a difference map. All H atoms included at calculated positions but not refined; methyl groups treated as rigid groups. Final  $R = 0.077$ ,  $wR = 0.079$  for 1000 observed reflections,  $w = 1.0/|\sigma^2(F_o) + 0.0005|F_o|^2|$ . Two reflections (020; 220) with large  $\Delta/\sigma$  omitted from refinement. Atomic scattering factors,  $f'$  and  $f''$  from *International Tables for X-ray Crystallography* (1974). Max. least-squares  $\Delta/\sigma = 1.4$  for methyl-group rotation, others  $< 0.35$ . Max. and min. heights in final difference Fourier map  $0.220$  and  $-0.353 \text{ e } \text{\AA}^{-3}$ . No secondary-extinction correction applied. All crystallographic calculations performed on the University of York DEC 10 computer. The least-squares planes and torsion angles were calculated with *XANADU* (Roberts & Sheldrick, 1975). The figures were drawn with *PLUTO* (Motherwell, 1972).

**Discussion.** The final atomic coordinates for the non-hydrogen atoms are listed in Table 1\* and bond lengths and angles in Table 2. The molecular structure (IVb) is shown in Fig. 1 with the atom-numbering scheme used in the structure analysis. Ring *A* exists in a half-boat conformation relative to the best plane through atoms C(2), C(3), C(5) and C(6) [r.m.s. deviation  $0.13$  (1)  $\text{\AA}$ ], with C(1), C(4) and O(4) lying  $0.65$  (1),  $0.14$  (1) and  $0.35$  (1)  $\text{\AA}$  respectively from this plane. The endocyclic torsion angles for ring *A* are C(1)–C(2)–C(3)–C(4)  $41.5$ , C(2)–C(3)–C(4)–C(5)  $1.2$ , C(3)–C(4)–C(5)–C(6)  $-21.9$ , C(4)–C(5)–C(6)–C(1)  $-2.1$ , C(5)–C(6)–C(1)–C(2)  $47.0$  and C(6)–C(1)–C(2)–C(3)  $-66.6^\circ$  (mean e.s.d.  $0.8^\circ$ ). The bicyclic bridged rings have the expected boat conformation. The torsion angles involving the ketone groups C(2)–C(3)–C(4)–O(4), C(6)–C(5)–C(4)–O(4), C(6)–C(10)–C(11)–O(11), C(7)–C(12)–C(11)–O(11) are  $180.0$ ,  $159.0$ ,  $121.8$  and  $178.4^\circ$  (e.s.d.  $0.8^\circ$ ). All bond lengths are in good agreement with accepted values (Sutton, 1965).

\* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and details of the preparation and characterization of the diones (IIIa), (IIIb), (IVa) and (IVb) have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39975 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Fractional atomic coordinates ( $\times 10^4$ ) and equivalent isotropic temperature factors ( $\text{\AA}^2 \times 10^4$ ) (e.s.d.'s in parentheses)

	x	y	z	$U_{\text{eq}}^*$
C(1)	1529 (4)	3113 (7)	4797 (3)	699
C(2)	2134 (4)	2025 (7)	4163 (3)	676
C(21)	1671 (5)	2998 (9)	3393 (3)	963
C(22)	1832 (5)	-319 (7)	4130 (3)	900
C(3)	3544 (5)	2390 (7)	4293 (3)	787
C(4)	4106 (5)	2230 (6)	5085 (3)	683
O(4)	5228 (3)	2516 (5)	5222 (2)	856
C(5)	3296 (4)	1678 (7)	5733 (3)	664
C(6)	1869 (4)	2116 (7)	5577 (2)	607
C(7)	3788 (5)	2719 (8)	6476 (3)	727
C(8)	3078 (5)	1819 (9)	7121 (3)	934
C(9)	1666 (4)	2211 (7)	6975 (3)	758
C(10)	1410 (4)	3414 (7)	6227 (2)	635
C(11)	2135 (5)	5430 (9)	6295 (3)	730
O(11)	1675 (3)	7170 (6)	6249 (2)	946
C(12)	3523 (4)	5054 (8)	6423 (3)	830

$$* U_{\text{eq}} = \frac{1}{3}(U_{11} + U_{22} + U_{33} + 2U_{13}\cos\beta).$$

Table 2. Bond lengths ( $\text{\AA}$ ) and angles ( $^\circ$ )

C(1)–C(2)	1.512 (6)	C(5)–C(7)	1.534 (6)
C(1)–C(6)	1.540 (6)	C(6)–C(10)	1.532 (6)
C(2)–C(3)	1.531 (6)	C(7)–C(8)	1.534 (6)
C(2)–C(21)	1.547 (6)	C(7)–C(12)	1.525 (6)
C(2)–C(22)	1.538 (6)	C(8)–C(9)	1.538 (6)
C(3)–C(4)	1.488 (7)	C(9)–C(10)	1.540 (6)
C(4)–O(4)	1.224 (5)	C(10)–C(11)	1.509 (6)
C(4)–C(5)	1.533 (6)	C(11)–O(11)	1.220 (5)
C(5)–C(6)	1.561 (6)	C(11)–C(12)	1.509 (6)
C(2)–C(1)–C(6)	112.9 (4)	C(1)–C(6)–C(10)	112.4 (4)
C(1)–C(2)–C(21)	110.0 (4)	C(5)–C(6)–C(10)	109.4 (4)
C(1)–C(2)–C(22)	112.2 (4)	C(5)–C(7)–C(8)	108.6 (4)
C(21)–C(2)–C(22)	108.0 (4)	C(5)–C(7)–C(12)	108.9 (4)
C(1)–C(2)–C(3)	107.0 (4)	C(8)–C(7)–C(12)	108.3 (4)
C(3)–C(2)–C(21)	108.5 (4)	C(7)–C(8)–C(9)	110.6 (4)
C(3)–C(2)–C(22)	111.0 (4)	C(8)–C(9)–C(10)	109.6 (4)
C(2)–C(3)–C(4)	117.1 (4)	C(6)–C(10)–C(9)	109.2 (4)
C(3)–C(4)–O(4)	119.8 (5)	C(6)–C(10)–C(11)	109.4 (4)
C(3)–C(4)–C(5)	120.7 (4)	C(9)–C(10)–C(11)	107.6 (4)
C(5)–C(4)–O(4)	119.5 (5)	C(10)–C(11)–O(11)	125.1 (5)
C(4)–C(5)–C(6)	115.5 (4)	C(10)–C(11)–C(12)	111.8 (5)
C(4)–C(5)–C(7)	111.4 (4)	O(11)–C(11)–C(12)	123.1 (5)
C(6)–C(5)–C(7)	110.0 (4)	C(7)–C(12)–C(11)	110.1 (4)
C(1)–C(6)–C(5)	113.3 (4)		

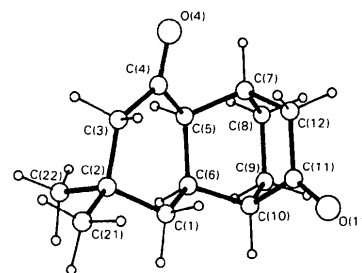


Fig. 1. Perspective view of the molecule with atomic nomenclature.

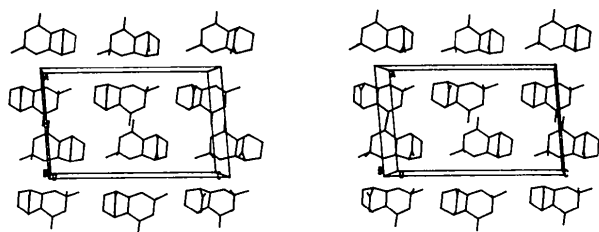


Fig. 2. Packing diagram.

The packing of the molecules is illustrated in Fig. 2. The only intermolecular close contacts less than 3.5 Å involving non-hydrogen atoms are across centres of symmetry [symmetry key: (i)  $1-x, -y, 1-z$ ; (ii)  $1-x, 1-y, 1-z$ ]: C(4)···C(4<sup>ii</sup>) 3.47 (1), C(4<sup>i</sup>)···O(4<sup>i</sup>) 3.18 (1) and O(4)···O(4<sup>ii</sup>) 3.31 (1) Å.

We thank Dr C. Tate for helpful discussions on the use of his program.

#### References

- DEBAERDEMAEKER, T. D. J., TATE, C. & WOOLFSON, M. M. (1984). *SAYTAN*. A program for determining crystal structures by direct methods using a new tangent formula. Univ. of York, England.
- GREENHILL, J. V., MOTEN, M. A. & HANKE, R. (1984). *J. Chem. Soc. Perkin Trans. 1*, pp. 1213–1217.
- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)
- MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1980). *MULTAN80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.
- MOTHERWELL, W. (1972). *PLUTO*. A program for drawing crystal structures. Univ. of Cambridge, England.
- ROBERTS, P. & SHELDRIK, G. M. (1975). *XANADU*. A program for crystallographic calculations. Univ. of Cambridge, England.
- SHELDRIK, G. M. (1976). *SHELX76*. Program system for crystal structure determination. Univ. of Cambridge, England.
- SUTTON, L. E. (1965). Editor. *Tables of Interatomic Distances and Configuration in Molecules and Ions*. London: The Chemical Society.

## International Union of Crystallography

*Acta Cryst.* (1985). C41, 632

### *Acta Crystallographica* Indexes

The indexes to Volume 39 (1983) of *Acta Crystallographica* have just been distributed to subscribers. The International Union of Crystallography regrets the delay in publishing these indexes, which is due to the introduction of a computerized index-production system. The system will be

used to produce the next five-year index to Volumes 39–43. The indexes to Volume 40 (1984) are expected to be distributed on time.

A ten-year compilation of the indexes for Volumes 29–38 (1973–1982) was distributed to subscribers in mid-1984. Further copies are available at a price of Dkr 150 (Dkr 75 for scientists who give an undertaking that the index is for their own personal use).