site is available for intermolecular excimer formation without appreciable strain during formation and the spectra are similar to that found in bulk polystyrene (Frank & Harrah, 1974).

Solution spectra of these compounds exhibit both monomer and intramolecular excimer fluorescence. The ratio of these two emissions is temperature dependent, indicating that all compounds show a conformational barrier to excimer formation. Barrier-height determinations are now under way.

The authors gratefully acknowledge the assistance of Bruce P. Engler, who prepared these materials, and David T. Sanders, who assisted in the X-ray laboratory. The authors also thank Professor G. A. Jeffery for useful discussions concerning the possible differences in molecular conformations represented by these structures as well as for kindly providing a preprint of their work.

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# The Structures of 1,2,3,4,5,6-*cis*-Cyclohexanehexacarboxylic Acid and Its Hexamethyl Ester

By Sergio Brückner and Luciana Malpezzi Giunchi

*Istituto di Chimica, Politecnico di Milano, via Golgi* 39, 20133 *Milano, Italy*

and Giuseppe Di Silvestro and Maria Grassi

*Istituto di Chimica Industriale, Cattedra di Chimica Macromolecolare, Università di Milano, via Saldini* 50, 20133 *Milano, Italy*

(*Received* 20 *May* 1980; *accepted* 16 *September* 1980)

## Abstract

$C_{12}H_{12}O_{12}.3H_2O$ is orthorhombic, $P2_12_12_1$, with $a$ = 13·44 (1), $b$ = 11·18 (1), $c$ = 10·37 (1) Å, $M_r$ = 402·3, $Z$ = 4, final $R$ = 0·055; $C_{18}H_{24}O_{12}$, is orthorhombic, $Pbca$, with $a$ = 34·79 (3), $b$ = 20·63 (2), $c$ = 11·58 (1) Å, $M_r$ = 432·4, $Z$ = 16 (two independent molecules per asymmetric unit), final $R$ = 0·059. A comparison is drawn between observed geometries and data calculated for a model molecule by use of the molecular-mechanics method.

## Introduction

1,2,3,4,5,6-*cis*-Cyclohexanehexacarboxylic acid (I) and its hexamethyl ester (II) were prepared as part of a study concerning gyrochiral molecules (high-symmetry

0567-7408/81/030586-05$01.00

chiral molecules) (Grassi, Di Silvestro, Brückner & Malpezzi Giunchi, 1980). Their $^1$H and $^{13}$C NMR spectra show that such molecules exist in the chair conformation, with three axial substituents. Interconversion between the two equivalent conformations is slow at room temperature on the time scale of the experiment. These features are quite unusual for structures in this monocyclic series. In order to clarify the origin of this phenomenon, we carried out a conformational study, both experimental and theoretical, on these molecules. In this paper we report the crystallographic analyses of (I) and (II) and a comparison of the observed structures with the conformation of a model molecule, calculated by the molecular-mechanics method.

(I) was obtained from an aqueous solution and crystallized from methanol. Crystals contain three molecules of water per molecule of acid. (II), obtained from (I), was crystallized from methanol, giving rise to a structure which has two independent molecules per asymmetric unit, and shows an enantiotropic phase transition at 439 K. The observed structure of (II) refers to the crystal phase which is stable at room temperature.

Unit-cell parameters and intensity data for both compounds were obtained with a Philips PW 1100 automatic four-circle diffractometer. Systematically absent reflections indicated the space groups to be $P2_12_12_1$ and *Pbca* respectively. Diffraction data for (I) were collected with graphite-monochromated Mo $K\alpha$ radiation to $\theta = 28°$ with the $\theta/2\theta$ scan technique (scan speed 0·05° $s^{-1}$, scan range 1·2°). 2173 reflections were recorded of which 2153 were considered observed, having $I > 3\sigma(I)$. Diffraction data for (II) were collected to $\theta = 65°$ with graphite-monochromated Cu $K\alpha$ radiation with the $\theta/2\theta$ scan technique (scan speed 0·06° $s^{-1}$, scan range 1·0°). 6075 independent reflections were recorded of which 5148 were considered observed, having $I > 3\sigma(I)$. The intensities were corrected by application of Lorentz and polarization factors; no absorption correction was applied. The structures were solved using *MULTAN* 74 (Main, Woolfson, Lessinger, Germain & Declercq, 1974) and refined with a block-diagonal least-squares procedure with anisotropic temperature factors for the non-H atoms.

For (I), successive difference maps were calculated to locate the H atoms; those bonded to water O atoms were not easily located, suggesting some vibrational displacement of the protons relative to their O partners. Geometrically reasonable positions consistent with the difference map were calculated for these H atoms and were included isotropically in the final refinement. The final weighting scheme was $w^{-1} = 20{\cdot}0 + |F_o| + 0{\cdot}015|F_o|^2$; the final $R$ was 0·055 and $R_w = 0{\cdot}059$.

For (II), the selected $E$ map of the *MULTAN* 74 procedure showed 42 independent non-H atoms and a subsequent observed Fourier synthesis showed all 60 atoms belonging to the two independent molecules. The successive block-diagonal least-squares refinement was performed with a fixed contribution of H atoms located on a difference map and with isotropic temperature factors roughly correlated with the heights of the corresponding peaks. The final weighting scheme was $w^{-1} = 30{\cdot}0 + |F_o| + 0{\cdot}011|F_o|^2$, giving $R = 0{\cdot}059$ and $R_w = 0{\cdot}073$ for all observed reflections.

Table 1. *Atomic coordinates* (×10$^4$) *for non-hydrogen atoms of* (I) *with e.s.d.'s in parentheses*

The equivalent temperature factors (Å$^2$), calculated by $B_{eq} = \frac{1}{3}(B_{11} + B_{22} + B_{33})$, are given in the last column (e.s.d.'s *ca* 0·1–0·2 Å$^2$).

| | $x$ | $y$ | $z$ | $B_{eq}$ |
|---|---|---|---|---|
| O(1) | −833 (2) | 1682 (3) | 4121 (4) | 2·2 |
| O(2) | −1540 (2) | −111 (3) | 4035 (4) | 2·5 |
| O(3) | −430 (3) | −1007 (4) | 6422 (4) | 2·7 |
| O(4) | −477 (3) | −2876 (3) | 5792 (4) | 2·4 |
| O(5) | 563 (3) | −3913 (3) | 3936 (4) | 2·5 |
| O(6) | 2189 (2) | −3644 (3) | 3704 (4) | 2·7 |
| O(7) | 1607 (3) | −2599 (4) | 6451 (4) | 2·9 |
| O(8) | 3027 (3) | −1655 (3) | 6707 (4) | 2·4 |
| O(9) | 3641 (3) | 301 (4) | 5600 (5) | 3·2 |
| O(10) | 2768 (3) | 1869 (3) | 4942 (5) | 3·5 |
| O(11) | 1505 (3) | 357 (4) | 7046 (4) | 3·2 |
| O(12) | 200 (3) | 1513 (4) | 6579 (4) | 2·9 |
| C(1) | 220 (3) | −39 (4) | 4076 (4) | 1·3 |
| C(2) | 180 (3) | −1408 (4) | 4304 (4) | 1·3 |
| C(3) | 1232 (3) | −1906 (4) | 3946 (5) | 1·3 |
| C(4) | 2111 (3) | −1343 (4) | 4696 (4) | 1·1 |
| C(5) | 2062 (3) | 36 (4) | 4510 (5) | 1·4 |
| C(6) | 1050 (3) | 598 (4) | 4824 (5) | 1·5 |
| C(7) | −777 (3) | 593 (4) | 4130 (5) | 1·6 |
| C(8) | −233 (3) | −1732 (4) | 5616 (5) | 1·6 |
| C(9) | 1296 (3) | −3251 (4) | 3896 (5) | 1·7 |
| C(10) | 2183 (3) | −1882 (4) | 6028 (5) | 1·9 |
| C(11) | 2904 (3) | 736 (4) | 5090 (6) | 2·0 |
| C(12) | 935 (3) | 772 (5) | 6275 (5) | 1·9 |
| O(*W*1) | 2529 (3) | 4114 (3) | 3464 (4) | 2·8 |
| O(*W*2) | 583 (3) | 3527 (4) | 3985 (6) | 4·0 |
| O(*W*3) | 1705 (3) | 4181 (5) | 6276 (4) | 4·3 |

Atomic scattering factors for O and C were taken from Cromer & Mann (1968), while values for H were those of Stewart, Davidson & Simpson (1965). Atomic fractional coordinates for the non-H atoms of (I) and (II) are reported in Tables 1 and 2 respectively.*

## Discussion

In Tables 3 and 4 we report the bond lengths, valence angles, intra-annular torsion angles and torsional

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35743 (43 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Atomic coordinates* ($\times 10^4$) *for non-hydrogen atoms of the two independent molecules of* (II) *with e.s.d.'s in parentheses*

The equivalent temperature factors (Å$^2$), calculated by $B_{eq} = \frac{1}{3}(B_{11} + B_{22} + B_{33})$, are given in the last column (e.s.d.'s *ca* 0·1–0·2 Å$^2$).

| | $x$ | $y$ | $z$ | $B_{eq}$ |
|---|---|---|---|---|
| O(1) | 2652 (1) | −751 (1) | 5424 (3) | 6·1 |
| O(2) | 2144 (1) | −1087 (1) | 4563 (2) | 4·3 |
| O(3) | 1646 (1) | 897 (1) | 5346 (2) | 3·7 |
| O(4) | 1618 (1) | −168 (1) | 5631 (2) | 4·9 |
| O(5) | 1215 (1) | 702 (1) | 3155 (2) | 4·6 |
| O(6) | 1488 (1) | 1321 (1) | 1809 (2) | 4·2 |
| O(7) | 1743 (1) | 2101 (1) | 3814 (2) | 5·0 |
| O(8) | 2217 (1) | 1832 (1) | 5011 (2) | 3·7 |
| O(9) | 2813 (1) | 2114 (1) | 3269 (2) | 4·4 |
| O(10) | 3240 (1) | 1303 (1) | 3433 (2) | 4·3 |
| O(11) | 2414 (1) | 533 (1) | 6299 (2) | 3·9 |
| O(12) | 2904 (1) | 1152 (1) | 5704 (2) | 3·8 |
| O(13) | 132 (1) | 1554 (1) | 1314 (2) | 4·5 |
| O(14) | −410 (1) | 1358 (1) | 2300 (2) | 4·0 |
| O(15) | −721 (1) | 2459 (1) | 698 (2) | 4·0 |
| O(16) | −640 (1) | 3512 (1) | 1087 (2) | 3·7 |
| O(17) | −1126 (1) | 3522 (2) | 3090 (3) | 5·8 |
| O(18) | −798 (1) | 4225 (1) | 4159 (2) | 4·0 |
| O(19) | 153 (1) | 4187 (1) | 1400 (2) | 3·9 |
| O(20) | −333 (1) | 4688 (1) | 2274 (2) | 3·8 |
| O(21) | 682 (1) | 4258 (1) | 3412 (3) | 4·6 |
| O(22) | 935 (1) | 3264 (1) | 3468 (2) | 3·4 |
| O(23) | 101 (1) | 2888 (1) | 432 (2) | 3·7 |
| O(24) | 699 (1) | 3092 (1) | 1054 (2) | 3·0 |
| C(1) | 2335 (1) | −54 (1) | 4039 (2) | 2·8 |
| C(2) | 1912 (1) | 172 (1) | 3908 (2) | 2·5 |
| C(3) | 1902 (1) | 707 (1) | 2984 (2) | 2·5 |
| C(4) | 2178 (1) | 1285 (1) | 3179 (2) | 2·5 |
| C(5) | 2586 (1) | 1014 (1) | 3363 (2) | 2·6 |
| C(6) | 2627 (1) | 480 (1) | 4309 (2) | 2·7 |
| C(7) | 2391 (1) | −655 (1) | 4782 (3) | 3·6 |
| C(8) | 1717 (1) | 361 (1) | 5035 (3) | 2·8 |
| C(9) | 1495 (1) | 907 (1) | 2686 (2) | 3·1 |
| C(10) | 2019 (1) | 1780 (1) | 4036 (3) | 3·1 |
| C(11) | 2883 (1) | 1553 (2) | 3380 (3) | 3·2 |
| C(12) | 2624 (1) | 722 (1) | 5548 (2) | 2·9 |
| C(13) | 2129 (2) | −1692 (2) | 5191 (4) | 6·8 |
| C(14) | 1438 (2) | −52 (2) | 6730 (4) | 6·6 |
| C(15) | 1119 (1) | 1600 (2) | 1540 (4) | 6·2 |
| C(16) | 2036 (1) | 2242 (2) | 5887 (4) | 5·4 |
| C(17) | 3550 (1) | 1775 (2) | 3496 (5) | 4·9 |
| C(18) | 2937 (1) | 1450 (2) | 6824 (3) | 6·4 |
| C(19) | −112 (1) | 2357 (1) | 2651 (2) | 2·6 |
| C(20) | −484 (1) | 2761 (1) | 2561 (2) | 2·7 |
| C(21) | −451 (1) | 3350 (1) | 3375 (2) | 2·7 |
| C(22) | −85 (1) | 3776 (1) | 3230 (2) | 2·5 |
| C(23) | 265 (1) | 3323 (1) | 3318 (2) | 2·5 |
| C(24) | 260 (1) | 2746 (1) | 2453 (2) | 2·4 |
| C(25) | −114 (1) | 1728 (1) | 1976 (3) | 3·1 |
| C(26) | −622 (1) | 2886 (1) | 1336 (2) | 2·8 |
| C(27) | −830 (1) | 3704 (2) | 3486 (3) | 3·4 |
| C(28) | −72 (1) | 4219 (1) | 2177 (2) | 2·7 |
| C(29) | 644 (1) | 3681 (1) | 3378 (2) | 2·9 |
| C(30) | 335 (1) | 2920 (1) | 1201 (2) | 2·5 |
| C(31) | −433 (1) | 721 (2) | 1786 (4) | 5·1 |
| C(32) | −806 (2) | 3677 (2) | 1 (4) | 6·8 |
| C(33) | −1141 (2) | 4609 (2) | 4307 (4) | 5·4 |
| C(34) | −342 (1) | 5161 (2) | 1339 (4) | 5·1 |
| C(35) | 1322 (1) | 3538 (2) | 3444 (4) | 3·9 |
| C(36) | 808 (1) | 3310 (2) | −86 (3) | 4·6 |

orientations of side groups for (I) and (II) respectively. In Table 5 we report mean values of geometrical features, calculated from equivalent observed data; in the last column of Table 5 we report, for comparison, data calculated on a model molecule of (I) using the molecular-mechanics method. The strain-energy parameters are those of Shieh, McNally & Boyd (1969) with the addition of new ones in connection with the carboxylic group. There are some significant differences between the average geometrical data of the –COOH and –COOCH$_3$ groups which are in good agreement with predicted values obtained from a regression analysis carried out on a large number of experimental crystallographic data (Borthwick, 1980).

Bond angles within the six-membered rings show the effect of non-bonded interactions between axial substituents, reflected in differences of 6–7° between angles at axially and equatorially substituted C atoms. This effect is present, but to a lesser extent, in the model molecule. There is no clear indication of flattening of the rings due to substituents; while the mean bond angles, ±54·8 (20) for (I) and ±54·0 (10)° for (II), are smaller than the values determined for free cyclohexane, ±58° from NMR data (Buys, 1969; Geise, Buys & Mijlhoff, 1971) or ±55·9° from electron diffraction data (Buys & Geise, 1970), the e.s.d.'s of the means are too high for these differences to be meaningful.

Hydrogen bonding plays an important role in the structure of the acid (I). Fig. 1 shows a perspective view of the molecule together with relevant intermolecular contacts. In particular, we have displayed

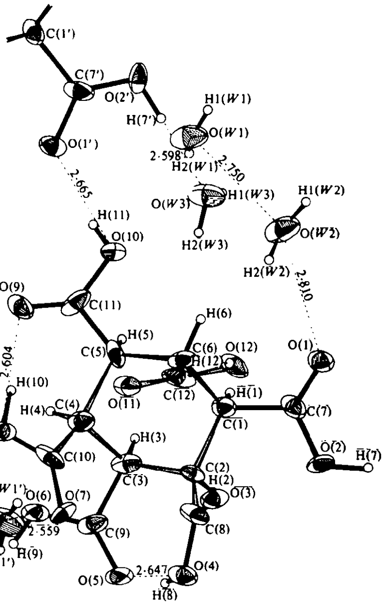

Fig. 1. A perspective view of compound (I) with the atom labels and some intermolecular contacts (Å) (e.s.d.'s are ~0·01 Å). Dashed lines indicate the hydrogen bonds.

Table 3. *Bond distances* (Å), *valence angles* (°), *intra-annular torsion angles* (°) *and torsional orientations of side groups of* (I)

E.s.d.'s in units of the last decimal place are given in parentheses.

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| O(1)–C(7) | 1·220 (6) | O(7)–C(10) | 1·197 (6) | C(1)–C(2) | 1·550 (6) | C(3)–C(9) | 1·507 (7) |
| O(2)–C(7) | 1·297 (6) | O(8)–C(10) | 1·358 (6) | C(1)–C(2) | 1·534 (6) | C(4)–C(5) | 1·555 (6) |
| O(3)–C(8) | 1·195 (6) | O(9)–C(11) | 1·223 (6) | C(1)–C(7) | 1·517 (6) | C(4)–C(10) | 1·511 (7) |
| O(4)–C(8) | 1·333 (6) | O(10)–C(11) | 1·290 (6) | C(2)–C(3) | 1·564 (6) | C(5)–C(6) | 1·533 (6) |
| O(5)–C(9) | 1·233 (6) | O(11)–C(12) | 1·200 (7) | C(2)–C(8) | 1·512 (7) | C(5)–C(11) | 1·501 (7) |
| O(6)–C(9) | 1·294 (6) | O(12)–C(12) | 1·327 (6) | C(3)–C(4) | 1·548 (6) | C(6)–C(12) | 1·526 (7) |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| O(1)–C(7)–O(2) | 123·9 (3) | O(7)–C(10)–O(8) | 118·4 (4) | C(1)–C(2)–C(3) | 106·5 (3) | C(3)–C(2)–C(8) | 117·4 (3) |
| O(1)–C(7)–C(1) | 121·3 (3) | O(7)–C(10)–C(4) | 124·1 (3) | C(1)–C(6)–C(5) | 110·4 (3) | C(3)–C(4)–C(10) | 110·3 (3) |
| O(2)–C(7)–C(1) | 114·4 (3) | O(8)–C(10)–C(4) | 116·9 (3) | C(1)–C(2)–C(8) | 112·7 (3) | C(4)–C(5)–C(6) | 114·7 (3) |
| O(3)–C(8)–O(4) | 120·1 (4) | O(9)–C(11)–O(10) | 123·9 (3) | C(1)–C(6)–C(12) | 118·9 (3) | C(4)–C(3)–C(9) | 112·3 (3) |
| O(3)–C(8)–C(2) | 123·2 (3) | O(9)–C(11)–C(5) | 125·2 (3) | C(2)–C(3)–C(4) | 115·2 (3) | C(4)–C(5)–C(11) | 115·8 (3) |
| O(4)–C(8)–C(2) | 116·3 (3) | O(10)–C(11)–C(5) | 110·9 (4) | C(2)–C(1)–C(6) | 114·0 (3) | C(5)–C(4)–C(10) | 120·8 (3) |
| O(5)–C(9)–O(6) | 122·8 (3) | O(11)–C(12)–O(12) | 123·9 (3) | C(2)–C(1)–C(7) | 115·1 (3) | C(5)–C(6)–C(12) | 110·6 (3) |
| O(5)–C(9)–C(3) | 123·6 (3) | O(11)–C(12)–C(6) | 122·9 (3) | C(2)–C(3)–C(9) | 114·5 (3) | C(6)–C(1)–C(7) | 114·1 (3) |
| O(6)–C(9)–C(3) | 113·4 (3) | O(12)–C(12)–C(6) | 112·9 (4) | C(3)–C(4)–C(5) | 108·0 (3) | C(6)–C(5)–C(11) | 111·7 (3) |

| | | | | | |
|---|---|---|---|---|---|
| C(1)–C(2)–C(3)–C(4) | 57·1 (6) | C(5)–C(6)–C(1)–C(2) | 55·7 (6) | C(3)–C(4)–C(10)–O(8) | 167·4 (7) |
| C(2)–C(3)–C(4)–C(5) | −55·1 (6) | C(6)–C(1)–C(2)–C(3) | −56·2 (6) | C(4)–C(5)–C(11)–O(10) | −176·6 (6) |
| C(3)–C(4)–C(5)–C(6) | 52·0 (6) | C(1)–C(2)–C(8)–O(4) | 167·1 (6) | C(5)–C(6)–C(12)–O(12) | 164·2 (7) |
| C(4)–C(5)–C(6)–C(7) | −53·0 (7) | C(2)–C(3)–C(9)–O(6) | −174·6 (6) | C(6)–C(1)–C(7)–O(2) | −151·0 (6) |

Table 4. *Bond distances* (Å), *valence angles* (°), *intra-annular torsion angles* (°) *and torsional orientations of side groups of* (II)

E.s.d.'s in units of the last decimal place are given in parentheses.

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| O(1)–C(7) | 1·192 (5) | O(11)–C(12) | 1·200 (4) | O(21)–C(29) | 1·199 (4) | C(5)–C(6) | 1·559 (4) |
| O(2)–C(7) | 1·335 (4) | O(12)–C(12) | 1·332 (4) | O(22)–C(29) | 1·332 (4) | C(5)–C(11) | 1·518 (4) |
| O(2)–C(13) | 1·445 (5) | O(12)–C(18) | 1·440 (4) | O(22)–C(35) | 1·458 (4) | C(6)–C(12) | 1·519 (4) |
| O(3)–C(8) | 1·190 (4) | O(13)–C(25) | 1·204 (4) | O(23)–C(30) | 1·208 (3) | C(19)–C(20) | 1·543 (4) |
| O(4)–C(8) | 1·335 (4) | O(14)–C(25) | 1·335 (4) | O(24)–C(30) | 1·328 (3) | C(19)–C(24) | 1·541 (4) |
| O(4)–C(14) | 1·438 (5) | O(14)–C(31) | 1·444 (4) | O(25)–C(36) | 1·446 (4) | C(19)–C(25) | 1·515 (4) |
| O(5)–C(9) | 1·193 (4) | O(15)–C(26) | 1·200 (4) | C(1)–C(2) | 1·551 (4) | C(20)–C(21) | 1·542 (4) |
| O(6)–C(9) | 1·326 (4) | O(16)–C(26) | 1·325 (4) | C(1)–C(6) | 1·530 (4) | C(20)–C(26) | 1·519 (4) |
| O(6)–C(15) | 1·443 (5) | O(16)–C(32) | 1·426 (5) | C(1)–C(7) | 1·522 (4) | C(21)–C(22) | 1·555 (4) |
| O(7)–C(10) | 1·198 (4) | O(17)–C(27) | 1·186 (4) | C(2)–C(3) | 1·538 (4) | C(21)–C(27) | 1·514 (4) |
| O(8)–C(10) | 1·325 (4) | O(18)–C(27) | 1·334 (4) | C(2)–C(8) | 1·522 (4) | C(22)–C(23) | 1·540 (4) |
| O(8)–C(16) | 1·462 (5) | O(18)–C(33) | 1·442 (5) | C(3)–C(4) | 1·549 (4) | C(22)–C(28) | 1·525 (4) |
| O(9)–C(11) | 1·188 (4) | O(19)–C(28) | 1·195 (4) | C(3)–C(9) | 1·517 (4) | C(23)–C(24) | 1·556 (4) |
| O(10)–C(11) | 1·347 (4) | O(20)–C(28) | 1·329 (4) | C(4)–C(5) | 1·539 (4) | C(23)–C(29) | 1·513 (4) |
| O(10)–C(17) | 1·456 (5) | O(20)–C(34) | 1·458 (5) | C(4)–C(10) | 1·527 (4) | C(24)–C(30) | 1·516 (4) |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| O(1)–C(7)–O(2) | 123·9 (2) | O(15)–C(26)–O(16) | 124·6 (2) | C(2)–C(3)–C(9) | 112·1 (2) | C(20)–C(21)–C(22) | 116·1 (2) |
| O(1)–C(7)–C(1) | 125·8 (2) | O(15)–C(26)–C(20) | 122·8 (2) | C(3)–C(4)–C(5) | 108·1 (2) | C(20)–C(19)–C(24) | 114·4 (2) |
| O(2)–C(7)–C(1) | 110·2 (2) | O(16)–C(26)–C(20) | 112·5 (2) | C(3)–C(2)–C(8) | 113·8 (2) | C(20)–C(19)–C(25) | 115·1 (2) |
| O(3)–C(8)–O(4) | 123·3 (2) | O(17)–C(27)–O(18) | 123·6 (2) | C(3)–C(4)–C(10) | 112·7 (2) | C(20)–C(21)–C(27) | 111·5 (3) |
| O(3)–C(8)–C(2) | 126·2 (2) | O(17)–C(27)–C(21) | 124·9 (2) | C(4)–C(5)–C(6) | 116·0 (2) | C(21)–C(22)–C(23) | 107·3 (2) |
| O(4)–C(8)–C(2) | 110·5 (2) | O(18)–C(27)–C(21) | 111·4 (2) | C(4)–C(3)–C(9) | 113·7 (2) | C(21)–C(20)–C(26) | 117·5 (2) |
| O(5)–C(9)–O(6) | 124·2 (2) | O(19)–C(28)–O(20) | 123·5 (2) | C(4)–C(5)–C(11) | 111·2 (2) | C(21)–C(22)–C(28) | 116·7 (2) |
| O(5)–C(9)–C(3) | 124·3 (2) | O(19)–C(28)–C(22) | 126·0 (2) | C(5)–C(4)–C(10) | 119·1 (2) | C(22)–C(23)–C(24) | 114·4 (2) |
| O(6)–C(9)–C(3) | 111·5 (2) | O(20)–C(28)–C(22) | 110·3 (2) | C(5)–C(6)–C(12) | 115·6 (2) | C(22)–C(21)–C(27) | 116·7 (2) |
| O(7)–C(10)–O(8) | 123·6 (2) | O(21)–C(29)–O(22) | 123·7 (2) | C(6)–C(1)–C(7) | 112·8 (2) | C(22)–C(23)–C(29) | 113·4 (2) |
| O(7)–C(10)–C(4) | 121·4 (2) | O(21)–C(29)–C(23) | 125·6 (2) | C(6)–C(5)–C(11) | 116·5 (2) | C(23)–C(22)–C(28) | 113·1 (2) |
| O(8)–C(10)–C(4) | 114·9 (2) | O(22)–C(29)–C(23) | 110·6 (2) | C(7)–O(2)–C(13) | 117·1 (2) | C(23)–C(24)–C(30) | 115·7 (2) |
| O(9)–C(11)–O(10) | 124·4 (2) | O(23)–C(30)–O(24) | 124·3 (2) | C(8)–O(4)–C(14) | 115·8 (2) | C(24)–C(19)–C(25) | 111·9 (2) |
| O(9)–C(11)–C(5) | 125·1 (2) | O(23)–C(30)–C(24) | 125·3 (2) | C(9)–O(6)–C(15) | 115·9 (2) | C(24)–C(23)–C(29) | 114·3 (2) |
| O(10)–C(11)–C(5) | 110·3 (2) | O(24)–C(30)–C(24) | 110·4 (2) | C(10)–O(8)–C(16) | 114·6 (2) | C(25)–O(14)–C(31) | 116·6 (2) |
| O(11)–C(12)–O(12) | 124·3 (2) | C(1)–C(2)–C(3) | 107·8 (2) | C(11)–O(10)–C(17) | 115·5 (2) | C(26)–O(16)–C(32) | 116·4 (2) |
| O(11)–C(12)–C(6) | 125·6 (2) | C(1)–C(6)–C(5) | 107·7 (2) | C(12)–O(12)–C(18) | 117·7 (2) | C(27)–O(18)–C(33) | 116·2 (2) |
| O(12)–C(12)–C(6) | 110·0 (2) | C(1)–C(2)–C(8) | 114·6 (2) | C(19)–C(20)–C(21) | 108·8 (2) | C(28)–O(20)–C(34) | 116·0 (2) |
| O(13)–C(25)–O(14) | 123·8 (2) | C(1)–C(6)–C(12) | 115·1 (2) | C(19)–C(24)–C(23) | 108·2 (2) | C(29)–O(22)–C(35) | 116·7 (2) |
| O(13)–C(25)–C(19) | 125·5 (2) | C(2)–C(3)–C(4) | 115·9 (2) | C(19)–C(20)–C(26) | 114·8 (2) | C(30)–O(24)–C(36) | 116·8 (2) |
| O(14)–C(25)–C(19) | 110·4 (2) | C(2)–C(1)–C(6) | 115·6 (2) | C(19)–C(24)–C(30) | 114·2 (2) | | |
| | | C(2)–C(1)–C(7) | 114·9 (2) | | | | |

Table 4 (*cont.*)

| | | | | | |
|---|---|---|---|---|---|
| O(2)–C(7)–C(1)–C(6) | 176·0 (5) | C(3)–C(4)–C(5)–C(6) | −52·4 (5) | O(22)–C(29)–C(23)–C(22) | 179·2 (5) |
| O(4)–C(8)–C(2)–C(1) | −76·7 (5) | C(4)–C(5)–C(6)–C(1) | 53·4 (5) | O(24)–C(30)–C(24)–C(23) | 70·4 (5) |
| O(6)–C(9)–C(3)–C(2) | −173·8 (5) | C(5)–C(6)–C(1)–C(2) | −54·4 (6) | C(19)–C(20)–C(21)–C(22) | 52·8 (5) |
| O(8)–C(10)–C(4)–C(3) | 114·5 (5) | C(6)–C(1)–C(2)–C(3) | 55·0 (5) | C(20)–C(21)–C(22)–C(23) | −53·5 (5) |
| O(10)–C(11)–C(5)–C(6) | −174·3 (5) | O(14)–C(25)–C(19)–C(24) | 170·5 (5) | C(21)–C(22)–C(23)–C(24) | 55·3 (6) |
| O(12)–C(12)–C(6)–C(5) | −57·5 (5) | O(16)–C(26)–C(20)–C(19) | −120·1 (5) | C(22)–C(23)–C(24)–C(19) | −57·2 (5) |
| C(1)–C(2)–C(3)–C(4) | −53·8 (5) | O(18)–C(27)–C(21)–C(20) | −177·9 (5) | C(23)–C(24)–C(19)–C(20) | 55·5 (5) |
| C(2)–C(3)–C(4)–C(5) | 53·0 (5) | O(20)–C(28)–C(22)–C(21) | 68·2 (5) | C(24)–C(19)–C(20)–C(21) | −53·3 (6) |

Table 5. *Comparison between the observed geometries of the two compounds and the calculated values for a model molecule*

Observed bond lengths (Å), valence angles (°) and intra-annular torsion angles (°) are reported as means for the determined structures with the e.s.d. of the mean in parentheses. The observed orientations of carboxyl groups with respect to the cyclohexane moiety are given with the individual e.s.d.'s.

| | (I) | (II) | | Model (I) |
|---|---|---|---|---|
| (*a*) Bond lengths (Å) | | | | |
| Ring distances (C–C) | 1·547 (12) | 1·545 (9) | | 1·552 |
| C($sp^3$)–C($sp^2$) | 1·513 (9) | 1·519 (4) | | 1·513 |
| C=O | 1·211 (16) | 1·196 (6) | | 1·207 |
| C–O | 1·316 (27) | 1·332 (6) | | 1·333 |
| O–CH$_3$ | | 1·446 (10) | | |
| (*b*) Bond angles | | | | |
| Ring bond angles C–C*–C | 114·6 (6) | 115·4 (8) | | 113·2 |
| Ring bond angles C–C†–C | 108·3 (20) | 108·0 (5) | | 109·2 |
| Carboxyl group bond angles C–C=O | 122·8 (19) | 124·9 (14) | | 122·5 |
| Carboxyl group bond angles C–C–O | 114·1 (22) | 111·1 (14) | | 115·7 |
| Carboxyl group bond angles O–C=O | 122·0 (20) | 123·9 (4) | | 121·9 |
| (*c*) Torsional angles | | | | |
| Cyclohexane ring | ±54·8 (20) | ±54·0 (10) | | ±55·4 |
| Orientations of carboxyl groups with respect to the cyclohexane ring | 167·1 (6) | 176·0 (5) | 179·2 (5) | 170·1 |
| | −174·0 (6) | −76·7 (5) | 70·4 (5) | −176·5 |
| | 167·4 (7) | −173·8 (5) | 170·5 (5) | 170·1 |
| | −176·6 (6) | 114·5 (5) | −129·1 (5) | −176·5 |
| | 164·2 (7) | −174·3 (5) | −177·9 (5) | 170·1 |
| | −151·0 (6) | −57·4 (5) | 68·2 (5) | −176·5 |

* Equatorially substituted ring carbons.
† Axially substituted ring carbons.

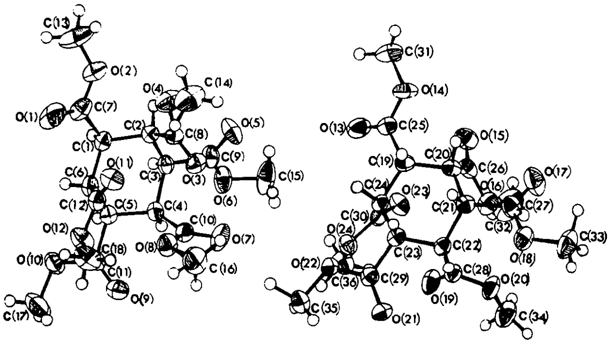

Fig. 2. A perspective view of the two independent molecules of compound (II) with the atom labels.

the O···O inter- and intramolecular distances, which range from 2·54 (1) to 2·81 (1) Å and therefore may be attributed to hydrogen bonding (Speakman, 1974, 1975; Cameron, 1974). Such interactions involve all three water molecules to a different extent; $W(1)$ and $W(3)$ are rather tightly bonded to O(6) and O(2) respectively, while $W(2)$ is weakly bonded to both O($W$1) and O(1).

The two independent molecules of (II) have almost identical bond lengths and angles (see Table 4), but they show some differences in the orientations of the methoxycarbonyl groups with respect to the cyclohexane moiety, as may be seen from Table 5 and Fig. 2. The two molecules have their two mean ring planes almost parallel, and have no intermolecular contact shorter than the sum of the van der Waals radii, the shortest contact (3·05 Å) being between O(15) and C(17) $(x-\frac{1}{2}, y, \frac{1}{2}-z)$.

The presence of a solid–solid phase transition at 439 K might be interpreted as a transition to a more symmetric structure with only one molecule per asymmetric unit.

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