formed into one another by changing the temperature. By lowering or increasing the temperature one should cause differences in the energy state of the nitrato groups or of the water molecules in a way similar to that operated by changing the central metal atom.

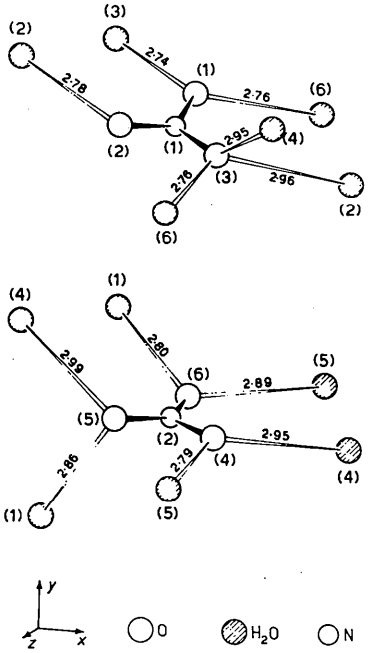


Fig. 5. Hydrogen bonds pointing towards oxygen atoms of nitrato anions.

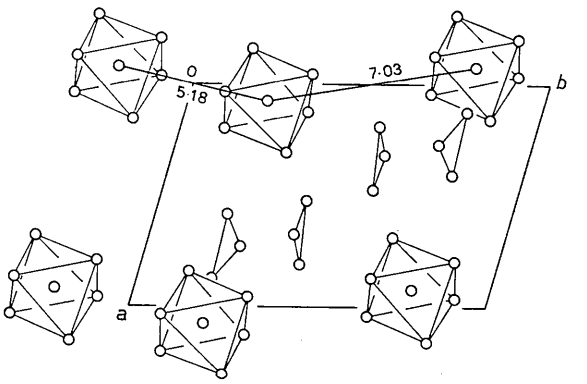


Fig. 6. Packing of cations and anions, viewed down [001].

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# The Structure of Phragmalin : An X-ray Analysis of Phragmalin Iodoacetate

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The molecular structure of phragmalin, the methyl ester of a $C_{28}H_{34}O_{11}$ terpenoid constituent of the tree *Entandrophragma caudatum* (a member of the Meliaceae family), has been determined by means of an X-ray study of phragmalin iodoacetate. The crystals of phragmalin iodoacetate are orthorhombic with space group $P2_12_12_1$ and 4 molecules in the unit cell of dimensions $a = 15{\cdot}70$, $b = 19{\cdot}59$ and $c = 11{\cdot}25$ Å. An orthoester linkage spanning a cyclohexane ring results in an atomic arrangement which is unique for this class of natural product.

## Introduction

The major alkaloid isolated from the tree *Entandrophragma caudatum* of the plant family Meliaceae was found to be an ester of nicotinic acid (Baarschers, 1967). On alkaline hydrolysis of the *Entandrophragma* alkaloid, the products isobutyric acid and nicotinic acid were readily identified. A larger fragment, the acid $C_{28}H_{34}O_{11}$, was converted into its methyl ester which was subsequently named 'phragmalin' (Baarschers, 1967).

Several compounds showing a marked resemblance to limonin (II) (Arnott, Davie, Robertson, Sim & Watson, 1961) have in recent years been found to occur

in many species of the Meliaceae family. The name 'meliacins' was later proposed to characterize these compounds (Bevan, Ekong & Taylor, 1965).

Chemical and spectroscopic data (Baarschers, 1967) showed the presence of the following functional groups in phragmalin: (i) three hydroxyl groups (vicinal), (ii) a $\beta$-substituted furan ring, (iii) a $\delta$-lactone, (iv) a methyl ester, (v) four tertiary methyl groups.

This evidence, together with the botanical origin of phragmalin, is suggestive of a possible relationship with the meliacins.

## Experimental

Samples of phragmalin iodoacetate were supplied by Dr R. R. Arndt of the National Chemical Laboratories. Colourless, well defined, needles of the material were obtained by recrystallization from methylene chloride. The crystals thus obtained, however, rapidly decayed to a white powder. When sealed in a Lindemann capillary tube this decomposition was retarded to such an extent that the intensity of a reference reflexion dropped by only 5% over a period of two weeks.

With the aid of oscillation, Weissenberg and precession photographs, the crystals were determined to be orthorhombic with space group $P2_12_12_1$ ($hkl$, no conditions; $h00$, $h=2n$; $0k0$, $k=2n$; $00l$, $l=2n$). Using a least-squares method, the unit-cell dimensions were calculated from the spot positions measured on a Hilger and Watts four-circle automatic diffractometer.

*Crystal data*:

$a = 15{\cdot}70 \pm 0{\cdot}01$
$b = 19{\cdot}59 \pm 0{\cdot}02$
$c = 11{\cdot}25 \pm 0{\cdot}01$ Å

Table 1. *Final atomic parameters (fractional coordinates and isotropic temperature factors)*

Standard deviations are given in parentheses.

| | $x$ | $y$ | $z$ | $B$(Å$^2$) |
|---|---|---|---|---|
| I | 0·4373 (3) | −0·1631 (2) | 0·6243 (5) | 9·87 (15) |
| Cl(1) | 0·2857 (9) | 0·2338 (8) | 0·2657 (14) | 8·17 (39) |
| Cl(2) | 0·2958 (10) | 0·2349 (9) | 0·0113 (15) | 8·68 (43) |
| O(1) | 0·5251 (20) | −0·1718 (18) | 0·3746 (35) | 8·55 (87) |
| O(2) | 0·4743 (17) | −0·0711 (15) | 0·3046 (26) | 5·01 (65) |
| O(3) | 0·6872 (14) | −0·0610 (12) | 0·3044 (21) | 3·14 (52) |
| O(4) | 0·6048 (14) | −0·0142 (12) | 0·4924 (20) | 2·97 (51) |
| O(5) | 0·6353 (18) | 0·0490 (16) | 0·7806 (28) | 5·67 (70) |
| O(6) | 0·5248 (16) | 0·0908 (13) | 0·6962 (24) | 4·27 (60) |
| O(7) | 0·2850 (31) | 0·1827 (26) | 0·7108 (47) | 6·80 (123) |
| O(8) | 0·3172 (17) | 0·0467 (14) | 0·2215 (25) | 4·75 (61) |
| O(9) | 0·2788 (22) | 0·0449 (18) | 0·0347 (32) | 7·94 (88) |
| O(10) | 0·7267 (15) | 0·0497 (13) | 0·1657 (22) | 4·13 (58) |
| O(11) | 0·7212 (14) | 0·0777 (11) | 0·3611 (22) | 3·44 (51) |
| O(12) | 0·6872 (13) | 0·1594 (12) | 0·2347 (19) | 2·92 (47) |
| C(1) | 0·4002 (29) | −0·1183 (23) | 0·4545 (43) | 5·97 (113) |
| C(2) | 0·4675 (23) | −0·1270 (20) | 0·3681 (38) | 4·42 (87) |
| C(3) | 0·5461 (24) | −0·0655 (19) | 0·2268 (35) | 4·03 (88) |
| C(4) | 0·6194 (26) | −0·0198 (22) | 0·2730 (38) | 4·41 (97) |
| C(5) | 0·5915 (17) | 0·0246 (15) | 0·3753 (30) | 2·09 (64) |
| C(6) | 0·6281 (18) | 0·0945 (16) | 0·3791 (32) | 2·27 (65) |
| C(7) | 0·6209 (22) | 0·1392 (19) | 0·4866 (33) | 3·21 (82) |
| C(8) | 0·6685 (19) | 0·1120 (16) | 0·6050 (30) | 2·23 (67) |
| C(9) | 0·6113 (28) | 0·0854 (23) | 0·6966 (43) | 4·99 (109) |
| C(10) | 0·4808 (22) | 0·1085 (18) | 0·5780 (31) | 3·03 (81) |
| C(11) | 0·5334 (21) | 0·1626 (20) | 0·5107 (32) | 3·43 (79) |
| C(12) | 0·4842 (20) | 0·1785 (17) | 0·3901 (34) | 2·73 (75) |
| C(13) | 0·5528 (24) | 0·1948 (18) | 0·2844 (34) | 3·97 (86) |
| C(14) | 0·6087 (25) | 0·1302 (20) | 0·2635 (36) | 3·64 (91) |
| C(15) | 0·5773 (22) | 0·0846 (17) | 0·1527 (31) | 2·96 (76) |
| C(16) | 0·4893 (20) | 0·0452 (17) | 0·1543 (32) | 7·82 (85) |
| C(17) | 0·5171 (22) | −0·0272 (18) | 0·1030 (35) | 3·32 (84) |
| C(18) | 0·6098 (25) | −0·0194 (22) | 0·0589 (37) | 4·13 (94) |
| C(19) | 0·6377 (22) | 0·0257 (18) | 0·1663 (32) | 2·91 (78) |
| C(20) | 0·7410 (25) | 0·1042 (20) | 0·2394 (36) | 3·83 (90) |
| C(21) | 0·8320 (24) | 0·1209 (20) | 0·2463 (37) | 4·16 (90) |
| C(22) | 0·4537 (27) | −0·0667 (23) | 0·0364 (38) | 5·54 (107) |
| C(23) | 0·4184 (34) | 0·0867 (19) | 0·0774 (33) | 3·84 (89) |
| C(24) | 0·3348 (26) | 0·0574 (22) | 0·1070 (41) | 4·82 (96) |
| C(25) | 0·2342 (30) | 0·0209 (23) | 0·2551 (43) | 6·05 (116) |
| C(26) | 0·5940 (27) | 0·1284 (22) | 0·0357 (38) | 4·93 (102) |
| C(27) | 0·5420 (23) | 0·2308 (19) | 0·5829 (33) | 4·08 (90) |
| C(28) | 0·4005 (22) | 0·1374 (19) | 0·6237 (40) | 4·05 (85) |
| C(29) | 0·3676 (27) | 0·1699 (23) | 0·7190 (41) | 5·39 (99) |
| C(30) | 0·2553 (21) | 0·1584 (18) | 0·6095 (33) | 7·88 (82) |
| C(31) | 0·3226 (27) | 0·1263 (23) | 0·5595 (40) | 4·87 (100) |

$\varrho$ (experimental) = 1·57 (flotation)
$\varrho$ (calculated) = 1·56
Molecular weight = 813·44
$Z = 4$

The single crystal selected for the intensity measurements was cylindrical in shape with a diameter of 0·2 mm and a length of 0·4 mm. Using Mo $K\alpha$ (Zr, $\beta$-filtered) radiation, the intensities of 1322 independent reflexions were recorded on the diffractometer using the $\omega$-scan technique. A reference standard, the strong 102 reflexion, was measured after each set of 10 reflexions. Two readings of the background were taken at points 4° apart in $\omega$ on opposite sides of each reflexion maximum. Each measured intensity was corrected for background by subtraction of the mean of the background readings on each side of the spot. The standard Lp corrections were applied but the low value of $\mu R \sim 0{\cdot}10$ obviated absorption corrections.

## Structure refinement

Three-dimensional Patterson and Fourier techniques were used to establish the trial structure. With the aid of the *ORFLS* full-matrix, least-squares program (Busing, Martin & Levy, 1962), which minimizes the function $\sum w(|F_o| - |kF_c|)^2$, the trial structure was refined to $R = 14{\cdot}2\%$, $(R = (\sum||F_o| - |F_c||)/\sum|F_o|)$, with individual isotropic thermal parameters for all atoms. Refinement with individual anisotropic thermal parameters for the three heavy atoms, *viz*, I, Cl(1) and Cl(2), reduced the $R$-value to 11·4%. The form factors of Hanson, Herman, Lea & Skillman (1964) were employed in the calculations.

The refinement was carried out with equal weights for all reflexions of magnitude larger than three times the background count. All others (the unobserved) were omitted as suggested by Dunning & Vand (1969). The refined positional and thermal parameters are listed in Table 1. Interatomic distances and bond angles were calculated using the crystallographic program *ORFFE* of Busing, Martin & Levy (1964). The values are given in Tables 2 and 3. The observed and calculated structure factors are listed in Table 4.

Table 2. *Bond distances* (Å)

Standard deviations in parentheses.

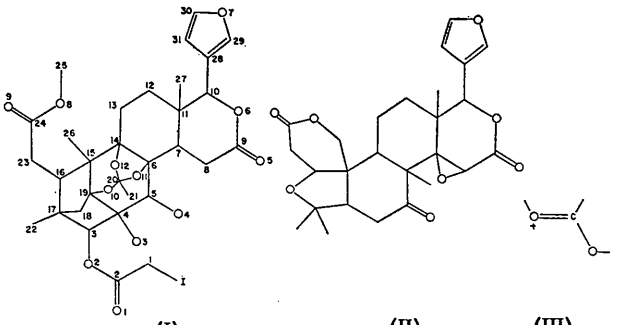
| | | | |
|---|---|---|---|
| C=O bond lengths | | C–C bond lengths | |
| C(2)—O(1) | 1·26 (2) | C(1)—C(2) | 1·46 (2) |
| C(24)–O(9) | 1·22 (1) | C(3)—C(4) | 1·54 (1) |
| C(9)—O(5) | 1·24 (2) | C(3)—C(17) | 1·64 (3) |
| | | C(4)—C(5) | 1·51 (1) |
| –(C)–O bond lengths | | C(4)—C(19) | 1·52 (1) |
| | | C(5)—C(6) | 1·49 (2) |
| C(3)—O(2) | 1·43 (1) | C(6)—C(7) | 1·50 (1) |
| C(4)—O(3) | 1·38 (1) | C(6)—C(14) | 1·51 (1) |
| C(5)—O(4) | 1·53 (2) | C(7)—C(8) | 1·61 (3) |
| C(6)—O(11) | 1·51 (3) | C(7)—C(11) | 1·47 (2) |
| C(10)–O(6) | 1·54 (2) | C(8)—C(9) | 1·46 (2) |
| C(14)–O(12) | 1·40 (2) | C(10)–C(11) | 1·54 (2) |

Table 2 (*cont.*)

| | | | |
|---|---|---|---|
| | | C–C bond lengths | |
| C(19)–O(10) | 1·47 (1) | C(10)–C(28) | 1·47 (2) |
| C(20)–O(10) | 1·37 (2) | C(11)–C(12) | 1·59 (1) |
| C(20)–O(11) | 1·49 (2) | C(11)–C(27) | 1·57 (2) |
| C(20)–O(12) | 1·37 (2) | C(12)–C(13) | 1·63 (3) |
| C(25)–O(8) | 1·45 (2) | C(13)–C(14) | 1·56 (1) |
| | | C(14)–C(15) | 1·61 (2) |
| –(C)–O bond lengths | | C(15)–C(16) | 1·58 (2) |
| C(2)—O(2) | 1·31 (2) | C(15)–C(19) | 1·50 (1) |
| C(9)—O(6) | 1·36 (2) | C(15)–C(26) | 1·59 (2) |
| C(24)–O(8) | 1·33 (2) | C(16)–C(17) | 1·59 (2) |
| | | C(16)–C(23) | 1·62 (3) |
| | | C(17)–C(18) | 1·54 (1) |
| Furan ring | | C(17)–C(22) | 1·47 (2) |
| C(29)–O(7) | 1·32 (2) | C(18)–C(19) | 1·56 (1) |
| C(30)–O(7) | 1·32 (2) | C(20)–C(21) | 1·47 (2) |
| C(28)–C(29) | 1·35 (1) | C(23)–C(24) | 1·47 (2) |
| C(30)–C(31) | 1·35 (1) | | |
| C(28)–C(31) | 1·44 (2) | C–halogen bond lengths | |
| | | C(1)—I | 2·18 (1) |
| | | C(32)–Cl(1) | 1·77 (2) |
| | | C(32)–Cl(2) | 1·79 (2) |

## Discussion

The stereoscopic diagram in Fig. 1 illustrates the molecular geometry while the atomic numbering used is shown in (I). A comparison with the structure of limonin (II) demonstrates that phragmalin possesses the structural features which typify the meliacins.



(I) (II) (III)

The furan ring is a substituent group of the $\delta$-lactone which joins a decalin skeleton similar to limonin. The three oxygen atoms on the carbon atoms 6, 14 and 19 are bonded in the form of an orthoester of acetic acid. In this way a tricyclic system is generated consisting of a seven-membered, a six-membered and a five-membered ring, each having two oxygen atoms in its ring structure.

The respective C–O bond lengths, *viz*, $1{\cdot}51 \pm 0{\cdot}03$ [C(6)–O(11)], $1{\cdot}47 \pm 0{\cdot}01$ [C(19)–O(10) $1{\cdot}37 \pm 0{\cdot}02$ [C(20)–O(10)] $1{\cdot}49 \pm 0{\cdot}02$ [C(20)–O(11)], $1{\cdot}37 \pm 0{\cdot}02$ [C(20)–O(12)] and $1{\cdot}40 \pm 0{\cdot}02$ Å [C(14)–O(12)] give an average value of $1{\cdot}43 \pm 0{\cdot}02$ Å which compares favourably with the value of $1{\cdot}426 \pm 0{\cdot}005$ Å reported for the C–O distance in saturated heterocyclic compounds (Sutton, 1965). The average $sp^3$-carbon–oxygen bond length in the lactone and ester functional groups is $1{\cdot}47 \pm 0{\cdot}02$ Å while the average $sp^2$-carbon–oxygen bond

length is 1·33 ± 0·02 Å. This difference occurs generally in the case of esters and lactones and is attributed to the important contributions made by (III) to the electronic structure (McPhail & Sim, 1966).

Table 3. *Bond angles (degrees)*

Standard deviations in parentheses.

| | | | |
|---|---|---|---|
| I–C(1)–C(2) | 110·2 (4) | C(7)—C(8)—C(9) | 114·4 (5) |
| C(1)—C(2)—O(1) | 124·5 (3) | C(8)—C(9)—O(5) | 123·6 (4) |
| C(1)—C(2)—O(2) | 109·0 (4) | C(8)—C(9)—O(6) | 125·6 (3) |
| O(1)—C(2)—O(2) | 123·9 (3) | O(5)—C(9)—O(6) | 110·4 (2) |
| C(2)—O(2)—C(3) | 119·3 (2) | O(6)—C(10)–C(11) | 109·8 (4) |
| O(2)—C(3)—C(4) | 115·1 (4) | O(6)—C(10)–C(28) | 99·7 (4) |
| O(2)—C(3)—C(16) | 109·6 (4) | C(11)–C(10)–C(28) | 111·4 (3) |
| C(4)—C(3)—C(17) | 103·1 (3) | C(19)–O(10)–C(20) | 113·6 (1) |
| C(3)—C(4)—O(3) | 108·8 (4) | C(7)—C(11)–C(10) | 112·0 (3) |
| C(3)—C(4)—C(5) | 111·9 (3) | C(7)—C(11)–C(27) | 106·3 (2) |
| C(3)—C(4)—C(19) | 102·4 (4) | C(7)—C(11)–C(12) | 110·9 (4) |
| O(3)—C(4)—C(19) | 113·4 (3) | C(10)–C(11)–C(12) | 107·0 (4) |
| O(3)—C(4)—C(5) | 111·4 (4) | C(10)–C(11)–C(27) | 112·2 (4) |
| C(5)—C(4)—C(19) | 108·5 (5) | C(12)–C(11)–C(27) | 108·4 (3) |
| C(4)—C(5)—O(4) | 109·3 (6) | C(6)—O(11)–C(20) | 104·3 (1) |
| C(4)—C(5)—C(6) | 116·2 (4) | C(11)–C(12)–C(13) | 109·7 (6) |
| O(4)—C(5)—C(6) | 112·2 (3) | C(14)–O(12)–C(20) | 102·1 (4) |
| C(5)—C(6)—C(7) | 122·3 (2) | C(12)–C(13)–C(14) | 108·8 (3) |
| C(5)—C(6)—C(14) | 108·9 (2) | O(12)–C(14)–C(15) | 108·5 (3) |
| C(5)—C(6)—O(11) | 99·8 (3) | O(12)–C(14)–C(13) | 101·5 (4) |
| C(14)—C(6)—C(7) | 114·2 (5) | O(12)–C(14)–C(6) | 102·2 (2) |
| C(14)—C(6)—O(11) | 100·4 (2) | C(6)—C(14)–C(15) | 118·2 (5) |
| C(7)—C(6)—O(11) | 107·9 (1) | C(6)—C(14)–C(13) | 111·1 (3) |
| C(10)—O(6)—C(9) | 117·9 (2) | C(13)–C(14)–C(15) | 113·3 (3) |
| C(6)—C(7)—C(8) | 115·9 (5) | C(14)–C(15)–C(19) | 98·8 (3) |
| C(6)—C(7)—C(11) | 113·7 (1) | C(14)–C(15)–C(26) | 106·9 (5) |
| C(8)—C(7)—C(11) | 112·5 (4) | C(14)–C(15)–C(16) | 121·9 (2) |
| C(29)—O(7)—C(30) | 109·7 (2) | C(16)–C(15)–C(26) | 114·5 (2) |
| C(24)—O(8)—C(25) | 119·5 (1) | C(16)–C(15)–C(19) | 100·1 (4) |
| | | C(19)–C(15)–C(26) | 113·2 (2) |
| C(15)—C(16)–C(17) | 100·9 (3) | O(10)–C(20)–C(21) | 111·4 (1) |
| C(17)—C(16)–C(23) | 116·1 (4) | O(10)–C(20)–O(12) | 119·3 (3) |
| C(15)—C(16)–C(23) | 110·4 (4) | O(10)–C(20)–O(11) | 104·4 (5) |
| C(3)—C(17)–C(22) | 112·3 (3) | C(21)–C(20)–O(12) | 115·1 (3) |
| C(3)—C(17)–C(18) | 93·3 (3) | C(21)–C(20)–O(11) | 103·4 (2) |
| C(3)—C(17)–C(16) | 100·1 (4) | O(12)–C(20)–O(11) | 100·4 (2) |
| C(16)—C(17)–C(18) | 106·6 (2) | C(16)–C(23)–C(24) | 107·2 (4) |
| C(16)—C(17)–C(22) | 117·9 (3) | C(23)–C(24)–O(9) | 124·7 (4) |
| C(18)—C(17)–C(22) | 121·9 (4) | C(23)–C(24)–O(8) | 117·7 (1) |
| C(17)—C(18)–C(19) | 94·1 (5) | O(9)—C(24)–O(8) | 117·5 (4) |
| C(15)—C(19)–C(18) | 100·3 (3) | C(10)–C(28)–C(29) | 141·7 (2) |
| C(15)—C(19)–O(10) | 110·7 (4) | C(10)–C(28)–C(31) | 119·7 (4) |
| C(15)—C(19)–C(4) | 114·3 (2) | C(29)–C(28)–C(31) | 98·3 (4) |
| O(10) –C(19)–C(18) | 116·3 (2) | C(28)–C(29)–O(7) | 114·2 (2) |
| O(10) –C(19)–C(4) | 111·7 (1) | O(7)—C(30)–C(31) | 104·6 (4) |
| C(4)—C(19)–C(18) | 103·0 (6) | C(28)–C(31)–C(30) | 112·7 (4) |
| | | Cl(1) –C(32)–Cl(2) | 106·7 (5) |

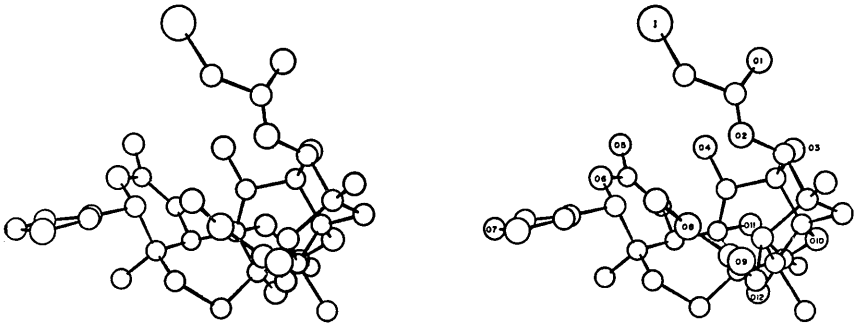



Fig. 1. Stereoscopic drawing of the molecule of phragmalin iodoacetate.

The formation of the orthoester is unique among the known meliacins and furthermore explains the origin of the two 'extra' carbon atoms which distinguish phragmalin from the meliacins. The meliacins all possess a maximum of 26 carbon atoms in their ring skeletons, whereas the free acid from which phragmalin is derived has 28.

Another unexpected feature of the structure of phragmalin is the presence of a norbornane skeleton which is defined by the carbon atoms 3, 4, 19, 15, 16, 17 and 18. The value of 94·1° for the bond angle C(17)–C(18)–C(19) is typical for a methylene bridge angle in this bicyclic arrangement (Wunderlich, 1967; Williams, 1969). The methylene bridge constrains the cyclohexane ring in a boat conformation. A similar situation is observed for the cyclohexane ring consisting of the carbon atoms, 4, 5, 6, 14, 15 and 19 in which case it is the orthoester which imposes the higher energy boat conformation.

The third cyclohexane ring, containing the carbon atoms 6, 7, 11, 12, 13 and 14, is also present in the boat conformation. The atoms C(7) and C(13) are rigidly held by the orthoester bridge and four adjacent carbon atoms in the latter cyclohexane ring are thus constrained to an almost coplanar arrangement. This permits the existence of the boat conformation alone.

Steric considerations appear to play an important role in this instance. The angular methyl group, C(27), occupies a position which involves less steric hindrance from the orthoester than would be the case if

Table 4. *Observed and calculated structure factors*

The columns are $k$, $l$. $F_o \times 10$ and $F_c \times 10$.

H = 0

| | | | |
|---|---|---|---|
| 0 | -8 | 1175 | 1009 |
| 0 | -4 | 294 | 359 |
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| 1 | -9 | 119 | 89 |
| 1 | -7 | 869 | 725 |
| 1 | -6 | 110 | 56 |
| 1 | -5 | 331 | 274 |
| 1 | -4 | 562 | 464 |
| 1 | -3 | 376 | 440 |
| 1 | -2 | 2405 | 2201 |
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| 2 | -8 | 420 | 406 |
| 2 | -7 | 702 | 634 |
| 2 | -6 | 335 | 308 |
| 2 | -5 | 535 | 473 |
| 2 | -4 | 234 | 138 |
| 2 | -3 | 380 | 308 |
| 2 | -2 | 569 | 635 |
| 2 | -1 | 1056 | 1078 |
| 2 | 0 | 1029 | 816 |
| 3 | -10 | 404 | 271 |
| 3 | -9 | 169 | 106 |
| 3 | -8 | 224 | 250 |
| 3 | -7 | 392 | 430 |
| 3 | -6 | 470 | 395 |
| 3 | -5 | 668 | 498 |
| 3 | -3 | 1074 | 943 |
| 3 | -2 | 1345 | 1315 |
| 4 | -10 | 138 | 52 |
| 4 | -9 | 168 | 179 |
| 4 | -8 | 213 | 195 |
| 4 | -7 | 116 | 142 |
| 4 | -6 | 297 | 329 |
| 4 | -5 | 513 | 439 |
| 4 | -4 | 1306 | 1261 |
| 4 | -3 | 453 | 450 |
| 4 | -1 | 751 | 813 |
| 4 | 0 | 1521 | 1515 |
| 5 | -8 | 190 | 215 |
| 5 | -7 | 145 | 137 |
| 5 | -6 | 388 | 347 |
| 5 | -5 | 1393 | 1337 |
| 5 | -3 | 627 | 592 |
| 5 | -2 | 179 | 147 |
| 5 | -1 | 226 | 318 |
| 6 | -9 | 147 | 20 |
| 6 | -8 | 610 | 600 |
| 6 | -7 | 139 | 66 |
| 6 | -5 | 293 | 411 |
| 6 | -4 | 887 | 941 |
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| 6 | -2 | 467 | 439 |
| 6 | -1 | 155 | 252 |
| 6 | 0 | 339 | 536 |
| 7 | -6 | 386 | 403 |
| 7 | -5 | 141 | 128 |
| 7 | -4 | 311 | 228 |
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| 7 | -2 | 796 | 862 |
| 7 | -1 | 784 | 842 |
| 8 | -8 | 203 | 209 |
| 8 | -6 | 223 | 284 |
| 8 | -5 | 568 | 501 |
| 8 | -4 | 658 | 724 |
| 8 | -3 | 410 | 436 |
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| 8 | -1 | 680 | 783 |
| 8 | 0 | 513 | 534 |
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| 9 | -5 | 620 | 515 |
| 9 | -4 | 240 | 220 |
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| 9 | -1 | 313 | 359 |
| 10 | -8 | 182 | 211 |
| 10 | -7 | 449 | 379 |
| 10 | -6 | 217 | 112 |
| 10 | -5 | 474 | 507 |
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| 10 | -1 | 134 | 104 |
| 10 | 0 | 1139 | 1314 |
| 11 | -6 | 252 | 228 |
| 11 | -5 | 317 | 476 |
| 11 | -4 | 225 | 323 |
| 11 | -3 | 545 | 645 |
| 11 | -1 | 384 | 509 |
| 12 | -8 | 218 | 180 |
| 12 | -4 | 253 | 369 |
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| 13 | -7 | 132 | 197 |
| 13 | -3 | 247 | 309 |
| 14 | -7 | 159 | 205 |
| 14 | -5 | 276 | 226 |
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| 14 | -1 | 216 | 364 |
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| 15 | -1 | 113 | 100 |
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| 16 | -1 | 197 | 218 |
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| 17 | -3 | 222 | 251 |
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| 1 | -9 | 407 | 373 |
| 1 | -7 | 351 | 253 |
| 1 | -6 | 948 | 778 |
| 1 | -5 | 188 | 152 |
| 1 | -4 | 194 | 197 |
| 1 | -3 | 969 | 789 |
| 1 | -2 | 1059 | 992 |
| 1 | -1 | 1163 | 1145 |
| 1 | 0 | 1058 | 916 |
| 2 | -10 | 259 | 186 |
| 2 | -8 | 535 | 361 |
| 2 | -7 | 436 | 365 |
| 2 | -6 | 477 | 330 |
| 2 | -5 | 670 | 608 |
| 2 | -4 | 999 | 997 |
| 2 | -3 | 1126 | 1080 |
| 2 | -2 | 297 | 317 |
| 2 | -1 | 1511 | 1548 |
| 2 | 0 | 460 | 327 |
| 3 | -10 | 180 | 162 |
| 3 | -9 | 615 | 503 |
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| 3 | -6 | 362 | 418 |
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| 3 | 0 | 1256 | 1329 |
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| 4 | -8 | 264 | 212 |
| 4 | -7 | 391 | 302 |
| 4 | -6 | 403 | 369 |
| 4 | -5 | 556 | 429 |
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| 4 | -2 | 474 | 578 |
| 4 | -1 | 1108 | 1109 |
| 4 | 0 | 766 | 1109 |
| 5 | -9 | 285 | 177 |
| 5 | -8 | 305 | 276 |
| 5 | -7 | 283 | 291 |
| 5 | -6 | 435 | 418 |
| 5 | -5 | 1521 | 1441 |
| 5 | -4 | 572 | 495 |
| 5 | -3 | 1038 | 1031 |
| 5 | -2 | 1449 | 1417 |
| 5 | -1 | 1725 | 1522 |
| 5 | 0 | 1194 | 1138 |
| 6 | -9 | 381 | 218 |
| 6 | -6 | 188 | 163 |
| 6 | -5 | 536 | 535 |
| 6 | -4 | 401 | 431 |
| 6 | -3 | 832 | 869 |
| 6 | -2 | 682 | 671 |
| 6 | -1 | 535 | 760 |
| 6 | 0 | 99 | 21 |
| 7 | -9 | 245 | 251 |
| 7 | -8 | 277 | 205 |
| 7 | -7 | 498 | 471 |
| 7 | -6 | 374 | 374 |
| 7 | -5 | 307 | 365 |
| 7 | -4 | 1291 | 1226 |
| 7 | -3 | 240 | 266 |
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| 8 | -8 | 218 | 225 |
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| 8 | -3 | 143 | 74 |
| 8 | -2 | 601 | 602 |
| 8 | -1 | 373 | 325 |
| 8 | 0 | 1102 | 1309 |
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| 9 | -7 | 352 | 342 |
| 9 | -6 | 169 | 192 |
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| 9 | -4 | 563 | 547 |
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| 9 | -1 | 264 | 395 |
| 9 | 0 | 224 | 341 |
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| 10 | -7 | 187 | 201 |
| 10 | -6 | 114 | 46 |
| 10 | -5 | 228 | 258 |
| 10 | -4 | 356 | 383 |
| 10 | -3 | 454 | 558 |
| 10 | -1 | 126 | 84 |
| 10 | 0 | 537 | 572 |
| 11 | -8 | 156 | 178 |
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| 11 | -3 | 254 | 323 |
| 11 | -2 | 229 | 441 |
| 11 | -1 | 361 | 403 |
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| 12 | -3 | 341 | 330 |
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| 12 | -1 | 294 | 404 |
| 13 | -7 | 207 | 119 |
| 13 | -6 | 392 | 429 |
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| 13 | -3 | 244 | 316 |
| 13 | -2 | 384 | 406 |
| 13 | -1 | 131 | 242 |
| 14 | -5 | 221 | 174 |
| 14 | -4 | 108 | 140 |
| 14 | -1 | 268 | 259 |
| 15 | -5 | 150 | 247 |
| 15 | -3 | 210 | 108 |
| 15 | -1 | 258 | 243 |
| 16 | -4 | 164 | 237 |
| 16 | -3 | 239 | 180 |
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| 18 | -1 | 193 | 197 |
| 18 | 0 | 235 | 184 |

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| 0 | -4 | 2016 | 1942 |
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| 1 | -8 | 238 | 229 |
| 1 | -7 | 311 | 270 |
| 1 | -6 | 359 | 297 |
| 1 | -5 | 994 | 962 |
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| 1 | -3 | 1384 | 1371 |
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| 1 | -1 | 1132 | 1140 |
| 1 | 0 | 1186 | 1175 |
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| 2 | -6 | 556 | 460 |
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| 2 | -4 | 897 | 862 |
| 2 | -3 | 1316 | 1209 |
| 2 | -2 | 557 | 526 |
| 2 | -1 | 551 | 600 |
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| 3 | -9 | 276 | 155 |
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| 3 | -6 | 547 | 484 |
| 3 | -5 | 499 | 483 |
| 3 | -4 | 188 | 74 |
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| 4 | -9 | 206 | 128 |
| 4 | -8 | 325 | 235 |
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| 4 | -6 | 727 | 630 |
| 4 | -5 | 311 | 291 |
| 4 | -4 | 477 | 449 |
| 4 | -3 | 632 | 536 |
| 4 | -2 | 1088 | 1141 |
| 4 | -1 | 2090 | 2036 |
| 4 | 0 | 1731 | 1766 |
| 5 | -9 | 124 | 105 |
| 5 | -8 | 418 | 349 |
| 5 | -6 | 247 | 267 |
| 5 | -5 | 301 | 389 |
| 5 | -3 | 394 | 424 |
| 5 | -2 | 596 | 453 |
| 5 | -1 | 2011 | 1937 |
| 6 | 0 | 1658 | 1716 |
| 6 | -9 | 151 | 89 |
| 6 | -8 | 709 | 610 |
| 6 | -5 | 593 | 629 |
| 6 | -4 | 565 | 610 |
| 6 | -3 | 720 | 867 |
| 6 | -2 | 433 | 417 |
| 6 | -1 | 1073 | 1134 |
| 6 | 0 | 1253 | 1410 |
| 7 | -8 | 247 | 157 |
| 7 | -7 | 262 | 216 |
| 7 | -6 | 119 | 112 |
| 7 | -5 | 363 | 395 |
| 7 | -4 | 273 | 316 |
| 7 | -3 | 267 | 383 |
| 7 | -2 | 250 | 218 |
| 7 | -1 | 901 | 1055 |
| 7 | 0 | 88 | 172 |
| 8 | -9 | 237 | 224 |
| 8 | -8 | 232 | 190 |
| 8 | -7 | 214 | 237 |
| 8 | -6 | 383 | 359 |
| 8 | -5 | 221 | 274 |
| 8 | -4 | 271 | 277 |
| 8 | -3 | 184 | 315 |
| 8 | -2 | 331 | 471 |
| 8 | -1 | 586 | 751 |
| 8 | 0 | 502 | 522 |
| 9 | -8 | 174 | 175 |
| 9 | -7 | 231 | 238 |
| 9 | -6 | 220 | 260 |
| 9 | -5 | 218 | 242 |
| 9 | -4 | 195 | 167 |
| 9 | -3 | 125 | 187 |
| 9 | -1 | 554 | 625 |
| 9 | 0 | 253 | 206 |
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| 10 | -5 | 179 | 192 |
| 10 | -4 | 363 | 450 |
| 10 | -3 | 526 | 557 |
| 10 | -2 | 405 | 503 |
| 10 | -1 | 328 | 541 |
| 10 | 0 | 307 | 267 |
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| 11 | -5 | 414 | 436 |
| 11 | -4 | 125 | 43 |
| 11 | -3 | 556 | 618 |
| 11 | -2 | 111 | 204 |
| 11 | -1 | 321 | 444 |
| 11 | 0 | 189 | 374 |
| 12 | -4 | 120 | 213 |
| 12 | -3 | 265 | 361 |
| 12 | -2 | 132 | 100 |
| 12 | -1 | 155 | 172 |
| 12 | 0 | 421 | 555 |
| 13 | -4 | 569 | 549 |
| 13 | -3 | 289 | 336 |
| 13 | -2 | 333 | 524 |
| 14 | -4 | 440 | 421 |
| 14 | -3 | 317 | 350 |
| 14 | -2 | 268 | 338 |
| 14 | -1 | 118 | 143 |
| 15 | -3 | 139 | 180 |
| 15 | -2 | 251 | 290 |
| 15 | 0 | 116 | 182 |
| 16 | -5 | 156 | 213 |
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| 16 | 0 | 157 | 131 |
| 17 | -1 | 139 | 168 |
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| 0 | -4 | 212 | 246 |
| 0 | -2 | 938 | 944 |
| 0 | -1 | 575 | 703 |
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| 1 | -7 | 490 | 414 |
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| 1 | -3 | 1250 | 1061 |
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| 1 | -1 | 543 | 628 |
| 1 | 0 | 523 | 480 |
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| 2 | -9 | 364 | 298 |
| 2 | -8 | 441 | 389 |
| 2 | -7 | 246 | 173 |
| 2 | -6 | 128 | 172 |
| 2 | -5 | 378 | 343 |
| 2 | -4 | 557 | 513 |
| 2 | -3 | 1278 | 1179 |
| 2 | -2 | 457 | 596 |
| 2 | -1 | 1335 | 1336 |
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| 3 | -9 | 260 | 213 |
| 3 | -8 | 598 | 464 |
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| 4 | -3 | 374 | 365 |
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| 4 | -1 | 1016 | 1059 |
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| 5 | -8 | 155 | 158 |
| 5 | -7 | 391 | 373 |
| 5 | -6 | 199 | 280 |
| 5 | -5 | 551 | 401 |
| 5 | -4 | 599 | 665 |
| 5 | -3 | 508 | 513 |
| 5 | -2 | 405 | 421 |
| 5 | -1 | 1057 | 1094 |
| 5 | 0 | 1047 | 870 |
| 6 | -10 | 296 | 220 |
| 6 | -9 | 160 | 159 |
| 6 | -7 | 187 | 131 |
| 6 | -6 | 442 | 403 |
| 6 | -5 | 195 | 182 |
| 6 | -4 | 652 | 645 |
| 6 | -3 | 598 | 540 |
| 6 | -2 | 1216 | 1317 |
| 6 | -1 | 420 | 374 |
| 6 | 0 | 353 | 314 |
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| 7 | -8 | 276 | 296 |
| 7 | -7 | 264 | 199 |
| 7 | -6 | 178 | 186 |
| 7 | -5 | 306 | 337 |
| 7 | -4 | 370 | 462 |
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| 7 | -2 | 1012 | 937 |
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| 8 | -4 | 486 | 454 |
| 8 | -3 | 442 | 436 |
| 8 | -2 | 422 | 428 |
| 8 | -1 | 665 | 662 |
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| 9 | -8 | 277 | 187 |
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| 9 | -4 | 242 | 341 |
| 9 | -3 | 259 | 356 |
| 9 | -2 | 256 | 309 |
| 9 | -1 | 416 | 473 |
| 9 | 0 | 1170 | 1205 |
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| 10 | -5 | 154 | 194 |
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| 10 | -1 | 435 | 473 |
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| 12 | -1 | 261 | 270 |
| 12 | 0 | 387 | 574 |
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| 13 | -4 | 188 | 281 |
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| 13 | -2 | 141 | 100 |
| 13 | -1 | 354 | 365 |
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| 14 | -4 | 139 | 189 |
| 14 | -2 | 363 | 275 |
| 14 | 0 | 150 | 132 |
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| 15 | -5 | 141 | 217 |
| 15 | -1 | 319 | 281 |
| 16 | -5 | 173 | 59 |
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| 17 | 0 | 163 | 146 |
| 18 | -1 | 121 | 153 |

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| 1 | -2 | 125 | 197 |
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| 2 | -3 | 513 | 500 |
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| 3 | -8 | 280 | 239 |
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| 4 | -4 | 241 | 270 |
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| 4 | -1 | 687 | 462 |
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| 5 | -8 | 243 | 192 |
| 5 | -7 | 213 | 166 |
| 5 | -6 | 162 | 144 |
| 5 | -4 | 967 | 1015 |
| 5 | -3 | 430 | 401 |
| 5 | -2 | 181 | 234 |
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| 6 | -4 | 216 | 83 |
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| 6 | -1 | 194 | 193 |
| 6 | -5 | 901 | 864 |
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| 6 | -3 | 407 | 554 |
| 6 | -2 | 219 | 235 |
| 6 | -1 | 603 | 606 |
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| 7 | -8 | 183 | 105 |
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| 7 | -5 | 557 | 522 |
| 7 | -4 | 778 | 818 |
| 7 | -3 | 671 | 744 |
| 7 | -2 | 113 | 82 |
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| 8 | -6 | 283 | 330 |
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| 8 | -3 | 341 | 478 |
| 8 | -2 | 451 | 665 |
| 8 | -1 | 145 | 179 |
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| 9 | 0 | 221 | 319 |
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| 11 | -5 | 425 | 417 |
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| 11 | -3 | 315 | 324 |
| 11 | -2 | 262 | 331 |
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| 12 | -3 | 212 | 340 |
| 12 | -1 | 149 | 160 |
| 12 | 0 | 252 | 257 |
| 13 | -6 | 136 | 143 |
| 13 | -5 | 234 | 252 |
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| 13 | -2 | 221 | 172 |
| 13 | -1 | 213 | 235 |
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| 14 | -5 | 315 | 296 |
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| 14 | -2 | 378 | 421 |
| 14 | 0 | 215 | 141 |
| 15 | -5 | 131 | 189 |
| 15 | -4 | 178 | 284 |
| 15 | -3 | 241 | 257 |
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| 17 | -2 | 131 | 123 |
| 18 | 0 | 233 | 196 |

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| 1 | -1 | 930 | 952 |
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| 2 | -6 | 261 | 186 |
| 2 | -5 | 243 | 268 |
| 2 | -4 | 570 | 544 |
| 2 | -3 | 825 | 707 |
| 2 | -2 | 752 | 796 |
| 2 | -1 | 655 | 668 |

Table 4 (*cont.*)

the cyclohexane ring reverted to the alternative boat conformation.

The furan ring is flat with the least-squares plane through the atoms involved given by the equations:

$$0{\cdot}18767\ X + 0{\cdot}86034\ Y - 0{\cdot}47391\ Z - 0{\cdot}13920 = 0^{*} \quad (1)$$

Deviations from this plane are given in Table 5. The values of $1{\cdot}32 \pm 0{\cdot}02$ and $1{\cdot}32 \pm 0{\cdot}02$ Å for the C–O bond lengths in the furan ring show good agreement with corresponding literature values; this also applies to the distances C(28)–C(29), C(30)–C(31) and C(28)–C(31), *viz*, $1{\cdot}35 \pm 0{\cdot}01$, $1{\cdot}35 \pm 0{\cdot}01$ and $1{\cdot}44 \pm 0{\cdot}02$ Å (Grant, Hamilton Hamor, Robinson & Sim, 1963; McPhail & Sim, 1966).

Table 5. *Atomic deviations* ($\sigma$) *from the least-squares planes defined by equations* (1), (2), (3) *and* (4) *respectively*

| | $\sigma$(Å) | Equation of plane |
|---|---|---|
| O(7) | −0·01 | (1) |
| C(28) | −0·04 | (1) |
| C(29) | −0·02 | (1) |
| C(30) | 0·03 | (1) |
| C(31) | 0·04 | (1) |
| C(10) | 0·02 | (1) |
| O(5) | −0·01 | (2) |
| O(6) | −0·01 | (2) |
| C(8) | −0·01 | (2) |
| C(9) | 0·03 | (2) |
| O(1) | 0·01 | (3) |
| O(2) | 0·01 | (3) |
| C(1) | 0·01 | (3) |
| C(2) | −0·03 | (3) |
| O(8) | 0·01 | (4) |

* *X*, *Y* and *Z* (in Å units) refer to the crystallographic axes *a*, *b* and *c* respectively.

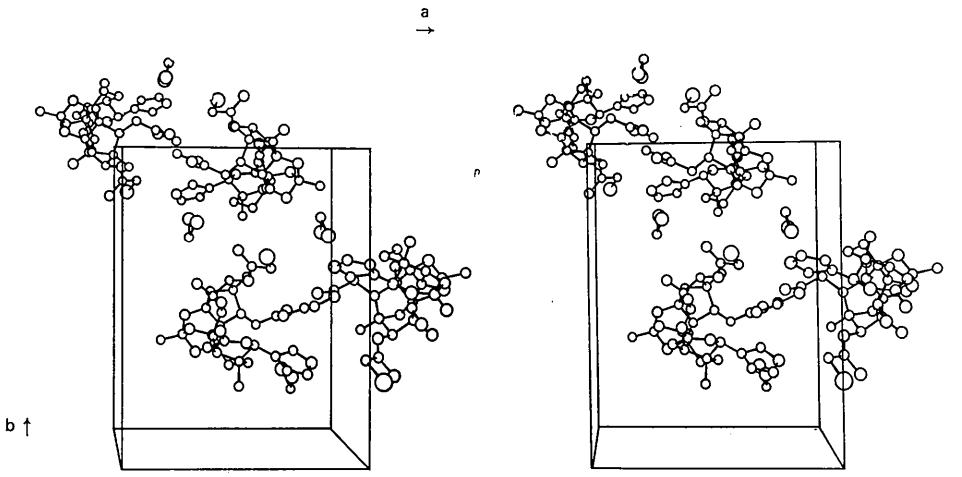


Fig. 2. Stereoscopic diagram of the molecular packing in the unit cell viewed along the *c* axis.

Table 5 (*cont.*)

| | σ(Å) | Equation of plane |
|---|---|---|
| O(9) | 0·01 | (4) |
| C(23) | 0·01 | (4) |
| C(24) | −0·02 | (4) |

A total of three carbonyl functions are incorporated in the structure of phragmalin iodoacetate showing C=O bond lengths of 1·26±0·02 [C(2)–O(1)] 1·22±0·01 [C(24)–O(9)] and 1·24±0·02 Å [C(9)–O(5)] which fall within the accepted range for this distance (Sutton, 1965). The best planes passing through each trigonally hybridized carbonyl carbon atom and its three bonded neighbours are given by the following equations:

$$0{\cdot}09514\,X+0{\cdot}83289\,Y+0{\cdot}54521\,Z-6{\cdot}54674=0^{*} \quad (2)$$

$$0{\cdot}58055\,X+0{\cdot}47265\,Y+0{\cdot}66300\,Z-5{\cdot}93134=0 \quad (3)$$

$$-0{\cdot}36677\,X+0{\cdot}92598\,Y+0{\cdot}08971\,Z+0{\cdot}76306=0 \quad (4)$$

Deviations from these planes are listed in Table 5 and show each carbonyl group to be coplanar with the two carbon atoms bonded to it. The average $sp^3$C–$sp^3$C single bond length is 1·55±0·02 Å which is in good agreement with the value of 1·545 Å in diamond.

Fig. 2 shows the molecular packing in the unit cell viewed along the *c* axis. One molecule of methylene chloride is incorporated in the unit cell for each molecule of phragmalin iodoacetate. The rapid decay of the crystalline material is a probable consequence of the loss of these $CH_2Cl_2$ molecules from the crystal lattice on exposure to the atmosphere.

The closest approach of two atoms in neighbouring molecules is 3·28±0·02 Å and occurs between the atoms C(1) and O(9), the parent molecules of which are related by a *c*-screw axis at $a=0{\cdot}25$. The closest approach of a chlorine atom to an atom in the molecule of phragmalin iodoacetate is 3·53±0·03 Å and is found between Cl(2) and O(7). The latter oxygen atom belongs to an asymmetric unit displaced by one unit-cell translation in the **c** direction with respect to the chlorine atom in the tabulated asymmetric unit.

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