

Fig. 2. The contents of the unit cell projected along *c*. Circles denote iodide ions.

Table 4. The shorter intermolecular contacts (Å) excluding hydrogen atoms; *e.s.d.*'s are ca 0.08 Å

C(21)···O(1 <sup>l</sup> )	3.46	O(2)···C(13 <sup>l</sup> )	3.67
C(20)···C(18 <sup>ll</sup> )	3.54	C(21)···C(15 <sup>l</sup> )	3.68
C(4)···C(4 <sup>lll</sup> )	3.63	C(22)···O(1 <sup>l</sup> )	3.69
C(22)···C(10 <sup>lv</sup> )	3.64	O(2)···C(6 <sup>l</sup> )	3.70

Symmetry code

- |                                                |                                             |
|------------------------------------------------|---------------------------------------------|
| (i) $-\frac{1}{2} + x, y, 1\frac{1}{2} - z$    | (iii) $1 - x, -y, 2 - z$                    |
| (ii) $\frac{1}{2} + x, \frac{1}{2} - y, 1 - z$ | (iv) $-\frac{1}{2} + x, y, \frac{1}{2} - z$ |

chloride. The orientation of the ring substituents about C(1)—C(13) and C(7)—C(13) is, however, different, although in both structures they are steeply inclined to one another and to the plane of the ester moiety.

C(*sp*<sup>3</sup>)—C(*sp*<sup>3</sup>) lengths range from 1.43 (5) to 1.64 (4) Å, mean 1.57 Å, and the four C—N<sup>+</sup> lengths are in the range 1.53 (3)—1.57 (3) Å, mean 1.54 Å.

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## The Crystal Structure of 3-(*p*-Chlorophenyl)-3a-methyl-4-oxo-5,6,6a-triphenyl-3a,4-dihydrocyclopenta[2,3-*d*]isoxazoline

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### Abstract

The crystal structure of 3-(*p*-chlorophenyl)-3a-methyl-4-oxo-5,6,6a-triphenyl-3a,4-dihydrocyclopenta[2,3-*d*]isoxazoline, C<sub>31</sub>H<sub>22</sub>ClNO<sub>2</sub>, has been determined from three-dimensional data, measured with an automated Philips PW 1100 single-crystal diffractometer (915 independent non-zero reflexions). The cell constants, obtained by least-squares calculations from direct  $\theta$ -value measurements on the diffractometer, are  $a =$

0567-7408/80/010102-06\$01.00

None of the individual bond lengths differs significantly from standard values. The C—O bonds of the ester group also agree to within the limits of experimental error with expected values.

The packing is shown in Fig. 2, and the shorter intermolecular contacts are in Table 4. None of these is shorter than the sum of the van der Waals radii. The closest contact involving the I<sup>-</sup> ion is 3.90 Å to C(21) of the cation at  $\frac{1}{2} + x, \frac{1}{2} - y, 1 - z$ .

I thank Dr R. B. Barlow for supplying the sample, the University of Birmingham for funds to purchase the diffractometer, and the staff of the Computer Centre for their assistance.

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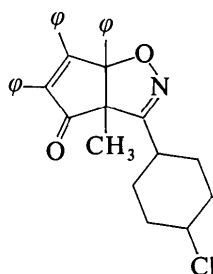
14.0021 (2),  $b = 10.6218$  (10),  $c = 9.5188$  (8) Å,  $\alpha = 64.89$  (1),  $\beta = 101.62$  (1),  $\gamma = 100.68$  (1)°,  $Z = 2$ ; the space group is  $P\bar{1}$ . The structure was solved by direct phase determination with *MULTAN*. The positional and vibrational parameters, with anisotropic temperature factors for the non-hydrogen atoms, were refined by full-matrix least-squares calculations to a final  $R = 0.097$ . The molecule of the compound has a cyclopentenone-isoxazoline structure. To the two central five-membered isoxazoline and cyclopentenone

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rings at an angle of  $107.9^\circ$  are linked four benzene rings and one methyl group with different orientations. As in other isoxazoline derivatives, the characteristic feature is the coplanar system formed by the isoxazoline ring and the *p*-substituted benzene ring.

### Introduction

In recent papers (Rodiou, Kokkou & Rentzeperis, 1978; Stergiou, Kokkou & Rentzeperis, 1978, 1979), the structures of three new isoxazoline derivatives, prepared at the Laboratory of Organic Chemistry of Aristotle University of Thessaloniki (Alexandrou & Argyropoulos, 1977), were reported. The present structure determination of 3-(*p*-chlorophenyl)-3a-methyl-4-oxo-5,6,6a-triphenyl-3a,4-dihydrocyclopenta[2,3-*d*]-isoxazoline (CPMCI) is the fourth of the series under investigation.



### Experimental

Pure, colourless CPMCI crystals, in the form of triclinic plates, were kindly provided by Professor N. E. Alexandrou and Dr N. Argyropoulos. A transparent crystal  $0.10 \times 0.25 \times 0.30$  mm was selected and centred on our computer-controlled Philips PW 1100 four-circle single-crystal diffractometer. With Mo *K* $\alpha$  radiation ( $\lambda = 0.71069$  Å) the  $\theta$  angles of 95 strong reflexions with large  $\theta$  values were directly measured on the diffractometer and subsequently processed with the least-squares program *PARAM* [part of the XRAY system of crystallographic programs (Stewart, Kruger,

Ammon, Dickinson & Hall, 1976)]. The final values obtained for the reduced-cell parameters are included in Table 1. Intensity statistics indicated the presence of a symmetry centre and so the space group *P* $\bar{1}$  was assumed; this was confirmed by the structure determination. The density of the crystals was measured by flotation in a potassium bromide solution.

Three-dimensional intensity data were collected with a scintillation counter on the PW 1100 diffractometer in the  $\omega$ -scan mode, using Mo *K* $\alpha$  radiation, monochromatized with a graphite monochromator. The intensities of 2853 independent reflexions up to  $2\theta = 43^\circ$  (maximum  $h, k, l = 14, \pm 10, \pm 9$  respectively) were examined and measured. Those with intensities greater than  $2\sigma$ , 915 in all, were considered as observed and included in the subsequent computations.

Integrated intensities were converted to  $|F_o|$  values in the usual way, using the special measurement-treatment program *DATRED* (Main, 1970). Since  $\mu$  is very small, no absorption correction was applied. For further calculations the programs of the *MULTAN* (Main, Woolfson, Lessinger, Germain & Declercq, 1974) and XRAY systems were used.

### Determination of the structure and refinement

The structure was solved by direct phase determination with the *MULTAN* system. The phases of 280 strong reflexions were determined and on the resulting *E* map it was possible to locate all the non-hydrogen atoms of the asymmetric unit. A structure factor calculation at this stage, with an overall  $B = 2.96$  Å<sup>2</sup>, gave  $R = 0.266$ .

Refinement of the structure was carried out by full-matrix least-squares calculations. The atomic scattering factors for Cl, O, N and C were from Cromer & Waber (1965), and for H from Stewart, Davidson & Simpson (1965). Anomalous-dispersion corrections for Cl were taken from *International Tables for X-ray Crystallography* (1968). A single scale factor was used for the whole set of reflexion data.

Refinement with individual isotropic temperature factors and then with anisotropic temperature coefficients reduced  $R$  to 0.103, but nine C atoms showed non-positive-definite temperature factors. In view of the rather limited set of reflexions (915) in comparison with the number of parameters to be determined (317), this was not surprising. In order to increase the number of reflexions in the refinement set, 1006 reflexions with  $\sigma < I < 2\sigma$  were included, but although various weighting schemes were tried neither the structure nor the accuracy of the atomic parameters would improve. A similar situation arose when only reflexions with  $1.7\sigma < I < 2\sigma$  were included (779). Since the other alternative was to reduce the number of variables, some of the nine C atoms were included in

Table 1. *Crystal data for CPMCI*

Here and throughout this paper the e.s.d.'s are given in parentheses and refer to the last digit.

$C_{31}H_{22}ClNO_2$	$M_r = 475.5$
Triclinic	Space group <i>P</i> $\bar{1}$
$a = 14.0021$ (12) Å	$Z = 2$
$b = 10.6218$ (10)	$F(000) = 496$
$c = 9.5188$ (8)	$\rho_{\text{calc}} = 1.265$ Mg m <sup>-3</sup>
$\alpha = 64.89$ (1) $^\circ$	$\rho_{\text{meas}} = 1.267$
$\beta = 101.62$ (1)	m.p. = 449–452 K
$\gamma = 100.68$ (1)	$\mu = 0.186$ mm <sup>-1</sup>
$V = 1247.53$ Å <sup>3</sup>	$\lambda(\text{Mo } K\alpha) = 0.71069$ Å

subsequent refinement cycles with individual isotropic temperature factors. Systematic calculations showed that six C atoms could be refined only isotropically. The H atoms of the phenyl rings were then located with the help of the program *BONDAT* of the XRAY system, but those of the methyl group were found on a difference Fourier map. They were included in three further refinement cycles with their positional parameters constant and isotropic temperature factors assigned to them (equal to those of the corresponding C atoms to which they are bonded); *R* reduced to 0.100. At this stage a systematic weight analysis was carried out, which led to the following weighting scheme:  $w = 1/\{1 + [(F - B)/A]^2\}$  with  $A = 60$  and  $B = 130$ . Convergence was reached at  $R = 0.097$  ( $R_w = 0.085$ ). The average shift/error ratio of the last cycle was less than 0.18.

The final positional parameters and equivalent isotropic temperature factors for the non-hydrogen atoms are given in Table 2. The final coordinates and isotropic temperature factors for the H atoms are

Table 2. Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic temperature factors for the non-hydrogen atoms in CPMCI

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (Å <sup>2</sup> )
Cl(1)	6759 (6)	1397 (8)	8868 (8)	7.7
N(1)	2513 (15)	2896 (18)	9617 (22)	4.3
O(1)	1794 (11)	3157 (13)	286 (16)	3.4
O(2)	4174 (10)	1364 (14)	4550 (15)	3.5
C(1)	3274 (17)	2648 (21)	653 (25)	2.7
C(2)	3220 (14)	2812 (19)	2124 (21)	1.8
C(3)	3398 (16)	1496 (20)	3638 (23)	2.1
C(4)	2548 (16)	474 (21)	3775 (22)	3.0
C(5)	1769 (14)	1103 (19)	2821 (22)	1.6
C(6)	2056 (14)	2724 (20)	1951 (23)	2.3
C(7)	4155 (16)	2431 (23)	206 (23)	3.6
C(8)	4133 (16)	2463 (24)	8673 (26)	4.5
C(9)	4947 (16)	2198 (21)	8269 (23)	3.4
C(10)	5781 (17)	1817 (25)	9390 (25)	5.1
C(11)	5797 (17)	1700 (25)	886 (27)	4.9
C(12)	5017 (16)	1997 (21)	1273 (24)	3.3
C(13)	3822 (16)	4172 (22)	2182 (26)	4.7
C(14)	2505 (16)	8987 (20)	4840 (22)	3.3
C(15)	3325 (19)	8314 (23)	4990 (23)	4.7
C(16)	3329 (20)	6892 (30)	6008 (32)	5.5
C(17)	2536 (26)	6182 (27)	6861 (29)	6.3
C(18)	1793 (23)	6884 (24)	6694 (26)	4.9
C(19)	1725 (17)	8282 (23)	5714 (24)	4.3
C(20)	775 (15)	556 (21)	2361 (22)	2.6
C(21)	579 (17)	9266 (21)	2195 (21)	2.6
C(22)	9635 (21)	8733 (24)	1792 (27)	4.8
C(23)	8886 (19)	9422 (26)	1638 (27)	4.6
C(24)	8999 (16)	704 (26)	1722 (24)	4.2
C(25)	9958 (14)	1227 (22)	2113 (24)	3.9
C(26)	1689 (18)	3605 (22)	2493 (29)	4.2
C(27)	1672 (16)	3237 (22)	4067 (27)	4.4
C(28)	1347 (19)	4080 (25)	4618 (27)	5.3
C(29)	1003 (15)	5363 (21)	3553 (24)	3.0
C(30)	987 (20)	5746 (26)	1980 (25)	6.5
C(31)	1330 (17)	4879 (25)	1480 (27)	5.0

Table 3. Atomic coordinates ( $\times 10^3$ ) and isotropic temperature factors for the hydrogen atoms in CPMCI

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (Å <sup>2</sup> )
H(C8)	346	267	781	4.5
H(C9)	498	234	707	3.4
H(C11)	643	127	182	4.9
H(C12)	506	196	247	3.3
H1(C13)	333	483	214	4.7
H2(C13)	434	400	325	4.7
H3(C13)	423	475	119	4.7
H(C15)	394	888	432	4.7
H(C16)	392	630	615	5.5
H(C17)	253	502	772	6.3
H(C18)	115	633	736	4.9
H(C19)	111	883	562	4.3
H(C21)	121	865	245	2.6
H(C22)	952	779	155	4.8
H(C23)	811	892	149	4.6
H(C24)	839	136	138	4.2
H(C25)	7	220	229	3.9
H(C27)	192	221	490	4.4
H(C28)	141	375	589	5.3
H(C29)	73	602	400	3.0
H(C30)	70	673	111	6.5
H(C31)	133	523	19	5.0

Table 4. Interatomic distances (Å) in CPMCI

O(1)—N(1)	1.42 (3)	C(14)—C(15)	1.41 (4)
N(1)—C(1)	1.28 (3)	C(15)—C(16)	1.41 (3)
C(1)—C(2)	1.50 (4)	C(16)—C(17)	1.41 (4)
C(2)—C(6)	1.59 (3)	C(17)—C(18)	1.34 (5)
C(1)—C(7)	1.47 (4)	C(18)—C(19)	1.39 (3)
C(2)—C(13)	1.55 (3)	C(19)—C(14)	1.41 (3)
C(6)—C(26)	1.45 (4)	C(20)—C(21)	1.41 (3)
C(6)—O(1)	1.44 (2)	C(21)—C(22)	1.39 (3)
		C(22)—C(23)	1.34 (4)
C(2)—C(3)	1.54 (2)	C(23)—C(24)	1.38 (4)
C(3)—O(2)	1.24 (2)	C(24)—C(25)	1.39 (3)
C(3)—C(4)	1.44 (3)	C(25)—C(20)	1.39 (3)
C(4)—C(5)	1.35 (3)		
C(4)—C(14)	1.47 (3)	C(26)—C(27)	1.38 (4)
C(5)—C(6)	1.57 (3)	C(27)—C(28)	1.39 (4)
C(5)—C(20)	1.46 (3)	C(28)—C(29)	1.41 (3)
		C(29)—C(30)	1.37 (3)
C(7)—C(8)	1.44 (4)	C(30)—C(31)	1.39 (5)
C(8)—C(9)	1.38 (4)	C(31)—C(26)	1.40 (3)
C(9)—C(10)	1.40 (4)		
C(10)—Cl(1)	1.73 (3)		
C(10)—C(11)	1.37 (4)		
C(11)—C(12)	1.35 (4)		
C(12)—C(7)	1.42 (3)		

shown in Table 3. Interatomic distances and bond angles for the non-hydrogen atoms are given in Tables 4 and 5.\*

\* Lists of structure factors, anisotropic thermal parameters for the non-hydrogen atoms, C—H bond distances, C—C—H bond angles and least-squares planes through the benzene rings have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34779 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

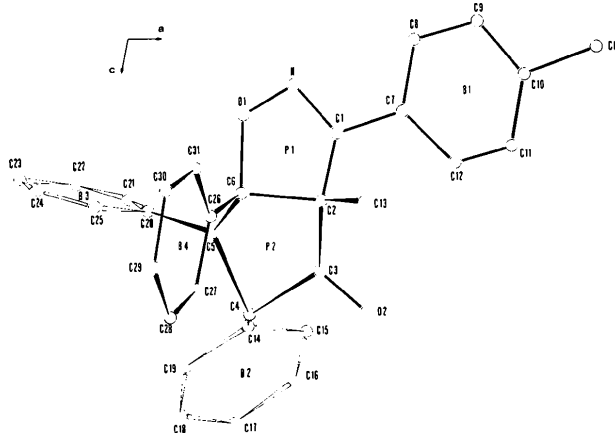
Table 5. Bond angles ( $^{\circ}$ ) in CPMCI

C(6)–O(1)–N(1)	111.4 (1.5)	C(8)–C(9)–C(10)	119.7 (2.2)
O(1)–N(1)–C(1)	106.4 (2.0)	C(9)–C(10)–Cl(1)	118.2 (2.0)
N(1)–C(1)–C(2)	116.3 (2.3)	Cl(1)–C(10)–C(11)	120.9 (1.7)
N(1)–C(1)–C(7)	117.1 (2.3)	C(9)–C(10)–C(11)	120.7 (2.5)
C(2)–C(1)–C(7)	126.0 (1.8)	C(10)–C(11)–C(12)	119.8 (2.1)
C(1)–C(2)–C(6)	97.6 (1.6)	C(11)–C(12)–C(7)	123.5 (2.3)
C(1)–C(2)–C(13)	112.4 (1.6)		
C(1)–C(2)–C(3)	114.4 (1.9)	C(4)–C(14)–C(15)	115.6 (1.9)
C(13)–C(2)–C(6)	117.1 (1.9)	C(4)–C(14)–C(19)	122.8 (2.2)
C(2)–C(6)–C(26)	115.8 (1.8)	C(15)–C(14)–C(19)	121.6 (1.8)
C(2)–C(6)–O(1)	101.2 (1.6)	C(14)–C(15)–C(16)	118.1 (2.2)
C(5)–C(6)–O(1)	110.4 (1.7)	C(15)–C(16)–C(17)	120.0 (2.8)
C(26)–C(6)–O(1)	111.0 (1.6)	C(16)–C(17)–C(18)	119.0 (2.3)
		C(17)–C(18)–C(19)	124.9 (2.6)
C(3)–C(2)–C(6)	99.6 (1.4)	C(18)–C(19)–C(14)	116.3 (2.5)
C(3)–C(2)–C(13)	114.1 (1.6)		
C(2)–C(3)–C(4)	109.7 (1.6)	C(5)–C(20)–C(21)	121.8 (2.1)
C(13)–C(3)–O(2)	123.4 (1.6)	C(5)–C(20)–C(25)	122.9 (2.2)
O(2)–C(3)–C(4)	126.9 (1.6)	C(21)–C(20)–C(25)	115.3 (1.9)
C(3)–C(4)–C(5)	109.5 (1.6)	C(20)–C(21)–C(22)	121.7 (2.3)
C(3)–C(4)–C(14)	126.2 (1.8)	C(21)–C(22)–C(23)	118.9 (2.6)
C(14)–C(4)–C(5)	124.2 (1.9)	C(22)–C(23)–C(24)	123.8 (2.3)
C(4)–C(5)–C(6)	110.9 (1.6)	C(23)–C(24)–C(25)	116.1 (2.3)
C(4)–C(5)–C(20)	132.5 (1.8)	C(24)–C(25)–C(20)	123.9 (2.4)
C(20)–C(5)–C(6)	116.3 (1.5)		
C(5)–C(6)–C(2)	101.4 (1.5)	C(6)–C(26)–C(27)	121.7 (1.9)
C(5)–C(6)–C(26)	115.8 (1.8)	C(6)–C(26)–C(31)	123.1 (2.3)
		C(26)–C(27)–C(28)	122.8 (2.0)
C(1)–C(7)–C(8)	120.2 (1.8)	C(27)–C(28)–C(29)	119.9 (2.2)
C(1)–C(7)–C(12)	123.6 (2.1)	C(28)–C(29)–C(30)	118.8 (2.6)
C(8)–C(7)–C(12)	115.6 (2.3)	C(29)–C(30)–C(31)	119.3 (2.1)
C(7)–C(8)–C(9)	120.5 (1.9)	C(30)–C(31)–C(26)	123.9 (2.4)

## Description of the structure and discussion

Fig. 1 shows in projection the structural and conformational features of the CPMCI molecule, from which it is clear that the compound is a cyclopentenone–isoxazoline derivative.

As expected, the CPMCI molecule shows close similarity to that of 3-(*p*-chlorophenyl)-4-oxo-3a,5,6,6a-tetraphenyl-3a,4-dihydrocyclopenta[2,3-*d*]-isoxazoline (CPCI in the following; Rodiou, Kokkou & Rentzeperis, 1978), from which it differs only in that it contains one methyl group in the place of a benzene

Fig. 1. Projection of the asymmetric unit of CPMCI parallel to *b*.

ring. This substitution, however, results in a halving of the monoclinic cell of CPCI and renders it triclinic, with two molecules of CPMCI instead of four (*cf.* the unit cell of CPCI:  $a = 14.373$ ,  $b = 21.084$ ,  $c = 9.261$  Å,  $\beta = 99.27^{\circ}$ ,  $V = 2769.91$  Å<sup>3</sup> with the values for CPMCI given in Table 1).

The characteristics of the CPMCI molecule are as follows: To the two central five-membered isoxazoline (*P1*) and cyclopentenone (*P2*) rings, at an angle of  $107.9^{\circ}$  with each other, which almost coincides with the angle of  $107^{\circ}$  in CPCI, are linked four benzene rings with different orientations and one methyl group (Fig. 1). All the benzene rings are planar to a good approximation, whereas the five-membered rings deviate considerably from ideal planarity. In Table 6 are listed the least-squares planes through *P1* and *P2*, together with the dihedral angles between them and the planes of the benzene rings.

As in other isoxazoline derivatives investigated so far (Rodiou, Kokkou & Rentzeperis, 1978; Stergiou, Kokkou & Rentzeperis, 1978), the main feature of the molecule is the coplanar system formed by the isoxazoline ring *P1* and the benzene ring *B1* ( $B1 \wedge P1 = 8.0^{\circ}$ ) (Fig. 1). The system is due to the conjugation of the C(1)=N double bond with the benzene ring and is almost parallel to (010). A somewhat less pro-

Table 6. Least-squares planes in CPMCI, with displacements of atoms from the planes (Å)

The equation for a plane is in the form  $AX + BY + CZ = D$  and refers to an orthogonal system of axes, with  $X \parallel a$ ,  $Y$  in the  $ab$  plane,  $Z \parallel c^*$  and  $D$ , the distance of the plane from the origin, in Å. Daggers indicate atoms not included in the calculation of the plane. Mean estimated standard deviations of the atoms defining a plane are given in parentheses following the distance of the first atom.

Plane *P1*: five-membered isoxazoline ring

$$0.12334X + 0.98939Y + 0.07674Z = 3.20363$$

C(1)	-0.08 (13)	N(1)	-0.03
C(2)	0.13	C(7)†	-0.16
C(6)	-0.16	C(8)†	-0.21
O(1)	0.13	C(12)†	-0.37

Plane *P2*: five-membered cyclopentenone ring

$$-0.34326X + 0.28359Y + 0.89540Z = 2.55848$$

C(2)	-0.18 (15)	C(6)	0.16
C(3)	0.15	O(2)†	0.51
C(4)	-0.04	C(20)†	-0.41
C(5)	-0.08	C(26)†	1.45

Dihedral angles between planes ( $^{\circ}$ ) (*B1*, *B2*, *B3* and *B4* are the benzene rings; see Fig. 1)

<i>B1</i> $\wedge$ <i>B2</i>	65.3	<i>B2</i> $\wedge$ <i>B3</i>	52.3	<i>B3</i> $\wedge$ <i>B4</i>	80.3
<i>B1</i> $\wedge$ <i>B3</i>	64.7	<i>B2</i> $\wedge$ <i>B4</i>	53.4	<i>B3</i> $\wedge$ <i>P1</i>	64.1
<i>B1</i> $\wedge$ <i>B4</i>	45.8	<i>B2</i> $\wedge$ <i>P1</i>	68.6	<i>B3</i> $\wedge$ <i>P2</i>	45.8
<i>B1</i> $\wedge$ <i>P1</i>	8.0	<i>B2</i> $\wedge$ <i>P2</i>	35.0		
<i>B1</i> $\wedge$ <i>P2</i>	73.9				
<i>B4</i> $\wedge$ <i>P1</i>	53.8	<i>P1</i> $\wedge$ <i>P2</i>	107.9		
<i>B4</i> $\wedge$ <i>P2</i>	84.7				

nounced conjugation is formed by the cyclopentenone ring *P2* and the benzene ring *B2* ( $35.0^\circ$ ). Owing to steric inhibition, caused by the neighbouring benzene rings and the O(2) atom, the ring *B2* is turned by an angle of  $35.0^\circ$  from the plane of ring *P2*. The two benzene rings *B3* and *B4* are almost perpendicular to each other ( $78.2^\circ$ ). The plane formed by the atoms N—C(4)—C(14) roughly bisects the two five-membered rings *P1* and *P2*, being approximately normal to them ( $79.2$  and  $78.5^\circ$  respectively).

The carbonyl O(2) occupies a prominent position in the molecule: it lies at almost equal distances from C(12), C(15) and C(13), belonging to the two benzene rings *B1*, *B2* and the methyl group respectively [O(2)—C(12) = 3.31 (3), O(2)—C(15) = 3.12 (3) and O(2)—C(13) = 2.93 (3) Å].

The geometrical features of the benzene rings are in good agreement with the usually accepted values. Mean bond lengths of the rings *B1*, *B2*, *B3* and *B4* are 1.39 (4), 1.39 (4), 1.38 (4), and 1.39 (4) Å respectively.

The Cl atom lies on the plane of the *B1* benzene ring (deviation: 0.041 Å). The Cl—C<sub>ar</sub> bond length, 1.735 Å, and the corresponding endocyclic angle,  $120.7^\circ$ , compare well with the values 1.755 Å and  $121.2^\circ$  found in CPCI (Rodiou, Kokkou & Rentzeperis, 1978) and also with the mean values 1.7404 (11) Å and  $121.37$  (9) $^\circ$  deduced by Domenicano, Vaciago & Coulson (1975) for a number of *p*-substituted chlorobenzenes.

The general features of the five-membered isoxazoline and cyclopentenone rings are normal. The C(3)=O(2) bond distance of the cyclopentenone ring is 1.24 Å, close to the usually accepted mean value of 1.23 (1) Å (*International Tables*, 1968). The rather short C(3)—C(4), 1.44 Å, may be attributed to the influence of the conjugated system O(2)=C(3)—C(4)=C(5) and the proximity of the benzene ring *B2*.

The intramolecular contact distances O(1)···H(C31) = 2.37 (2) Å, O(2)···H(C12) = 2.34 (2) Å and O(2)···H2(C13) = 2.52 (2) Å differ slightly from the sum of the van der Waals radii of the corresponding atoms, while the distances Cl···H(C9) = 2.81 (2) Å and Cl···H(C11) = 2.88 (1) Å almost coincide with the calculated ones (Bondi, 1964). All other contact distances are within the expected values.

Fig. 2 is a clinographic projection of the structure showing the molecular packing of CPMCI in the unit cell. The various intermolecular distances are normal. Some interesting intermolecular distances are shown in Table 7. They compare well with the sum of the van der Waals radii of the corresponding atoms.

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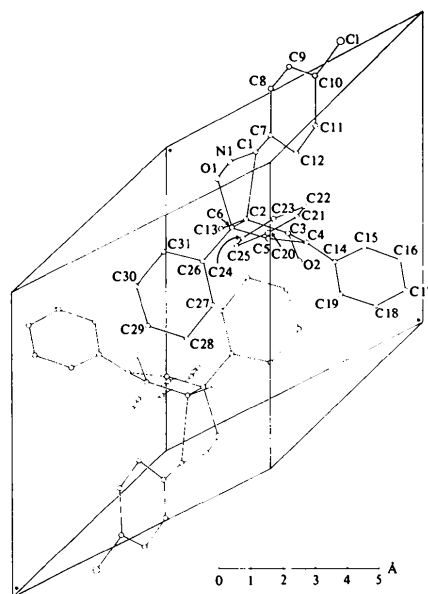


Fig. 2. Clinographic projection of the unit cell, showing the molecular packing.

Table 7. Intermolecular distances (Å)

Cl(1)···H(C24) <sup>I</sup>	2.94 (2)	Symmetry code
Cl(1)···H(C15) <sup>II</sup>	3.12 (1)	
O(2)···H(C9) <sup>III</sup>	2.95 (2)	(I) 1 + x, y, z
O(2)···H(C15) <sup>IV</sup>	2.66 (2)	(II) 1 - x, -y, -z
O(1)···H(C17) <sup>V</sup>	2.67 (2)	(III) x, y, 1 + z
		(IV) 1 - x, -y, 1 - z
		(V) x, 1 + y, z - 1

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## The Crystal Structure of Benzyloxycarbonyl-( $\alpha$ -aminoisobutyryl)<sub>2</sub>-L-Alanyl Methyl Ester

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### Abstract

Crystals of the title compound, C<sub>20</sub>H<sub>29</sub>N<sub>3</sub>O<sub>6</sub>, are monoclinic, space group *P2*<sub>1</sub>, with  $a = 8.839$  (3),  $b = 10.818$  (3),  $c = 11.414$  (2) Å,  $\beta = 95.69$  (2)°,  $Z = 2$ ; final  $R = 0.053$ . The molecular conformation is defined by the following angles ( $\phi, \psi$ ): Aib-1 58.1, 36.8; Aib-2 68.3, 18.6; Ala-3 ( $\phi$ ) -136.2°. The molecule adopts a type III'  $\beta$ -turn conformation stabilized by an intramolecular hydrogen bond between the CO of the benzyloxycarbonyl group and the NH of the alanyl residue. The hydrogen-bond parameters are N...O 2.904 Å and  $\angle$ NH...O 156.9°.

### Introduction

$\alpha$ -Aminoisobutyric acid (Aib) is an important constituent of the membrane-modifying polypeptide alamethicin and related microbial peptides (Martin & Williams, 1976; Pandey, Carter Cook & Rinehart, 1977). The conformational behaviour of Aib-containing peptides has been studied to establish conformation–function correlations for these polypeptides. The presence of *gem*-dialkyl substituents at the C $\alpha$  atom greatly restricts conformational freedom at Aib residues and thus permits the observation of well defined conformations in solution, which may then be compared with the solid-state structures (Nagaraj, Shamala & Balaram, 1979). In this paper we describe the molecular structure of the tripeptide ester benzyloxycarbonyl-Aib-Aib-Ala-OMe, which is shown to adopt a type III'  $\beta$ -turn structure, stabilized by a 4 $\rightarrow$ 1 intramolecular hydrogen bond.

### Experimental

Z-Aib-Aib-Ala-OMe was synthesized from Z-Aib-Aib-OH and Ala-OMe with dicyclohexylcarbodiimide,

followed by work up (Nagaraj, Shamala & Balaram, 1979).

Crystals of Z-Aib-Aib-Ala-OMe (C<sub>20</sub>H<sub>29</sub>N<sub>3</sub>O<sub>6</sub>,  $M_r = 407$ ) belonging to the monoclinic system were obtained by slow evaporation of a chloroform solution. Cell dimensions were obtained from  $2\theta$  measurements both on photographs and on a diffractometer. Crystal data are: space group *P2*<sub>1</sub>,  $a = 8.839$  (3),  $b = 10.818$  (3),  $c = 11.414$  (2) Å,  $\beta = 95.69$  (2)°,  $Z = 2$ ,  $V = 1086$  Å<sup>3</sup>. The density determined in a KCl–water mixture by flotation is 1.23 Mg m<sup>-3</sup> and the calculated density is 1.24 Mg m<sup>-3</sup>. Intensities of 2655 reflections were measured on a CAD-4 diffractometer with Cu  $K\alpha$  radiation and an  $\omega$ - $2\theta$  scan. Two standard reflections were measured after every 100 reflections and there was no significant change in their intensities. The intensities were corrected for Lorentz and polarization factors but not for absorption, since the crystal was 0.4  $\times$  0.3  $\times$  0.1 mm.

### Structure determination and refinement

The structure was solved by direct methods (Karle & Karle, 1966) with *MULTAN* (Germain, Main & Woolfson, 1971). The normalized structure factors (Karle & Hauptman, 1956) were obtained with the overall temperature factor ( $B = 3.36$  Å<sup>2</sup>) and scale factor (0.129) determined from a Wilson (1942) plot. *E* maps were computed with 300 reflections having  $E \geq 1.5$ . Twenty-three non-hydrogen atoms out of 29 could be located in an *E* map corresponding to the highest figure of merit. Calculated structure factors for the trial coordinates of the partial structure gave  $R = 0.41$ . After refinement of positional and isotropic thermal parameters by block-diagonal least squares (R. Shiono, personal communication) *R* converged to 0.36. A difference map computed at this stage revealed the positions of the remaining six atoms. Further refine-