

the aromaticity of the oxopyrimidine ring. Experiments have shown that only (III) and (IV) undergo isomerization (Bobrański, 1977), which means that substantial differences in the isomerization rate are due to small changes in the aromaticity of the oxopyrimidine ring. The greater value of HOMA for (III) than for (IV) shows that a cyclohexyl substituent crowds the adjacent carbamido groups more than a *p*-bromophenyl group does and that it also has a stronger influence on the oxopyrimidine-ring conformation and resonance.

It is worth noting that the *p*-bromophenyl group in (III) is not only a hindrance, but that it is also partially conjugated with the lone pair at N(1). This is evident from the shortening of the N(1)–C(1) bond. However, as can be seen from a comparison of the HOMA indexes for compounds (III) and (IV), this conjugation influences the oxopyrimidine-ring resonance much less than the *p*-bromophenyl-group steric effect.

The molecules are hydrogen bonded into dimers across centers of symmetry. The N(2)–H(20)···O(3¹) hydrogen bond is characterized by the following parameters: N(2)···O(3¹) = 2.877 (5), N(2)–H(20) = 0.874, H(20)···O(3¹) = 2.010 Å; N(2)–H(20)–O(3) = 171.2°. The symmetry operation relating O(3) to O(3¹) is $-x, 2 - y, -z$. The packing of the molecules in the unit cell is shown in Fig. 3.

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(±)-*erythro*-Methyl 3-*tert*-Butoxy-2-iodo-3-(*p*-methoxyphenyl)propionate

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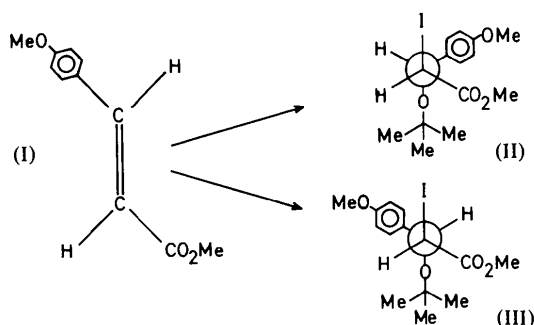
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Abstract. C₁₅H₂₁IO₄, triclinic, $P\bar{1}$, $a = 8.49$ (1), $b = 10.07$ (1), $c = 10.94$ (1) Å, $\alpha = 113.36$ (5), $\beta = 101.23$ (5), $\gamma = 83.45$ (5)°, $V = 841.3$ Å³, $M_r = 392.2$, $Z = 2$, $D_c = 1.548$, $D_m = 1.46$ Mg m⁻³ (flotation in aqueous KI); $\mu(\text{Mo } K\alpha) = 0.177$ mm⁻¹. The compound, synthesized by the ionic addition of *tert*-butyl hypoiodite to (*E*)-methyl *p*-methoxycinnamate, is in the *erythro* form. This establishes the mode of addition to the olefin as *trans*.

Introduction. The aim of this analysis was to determine the mode of ionic addition of *tert*-butyl hypoiodite (Bu^tOI) to the olefin (*E*)-methyl *p*-methoxycinnamate (I). The scheme below illustrates the two

alternative configurations, *threo* (II) or *erythro* (III), expected on the basis of *cis* or *trans* addition respectively.



For cyclic olefins, addition of Bu^tOI yields products whose configurations can be readily determined from NMR coupling constants between the vicinal H atoms. Since there is free rotation in the title compound, the NMR technique is not applicable and an X-ray investigation was therefore undertaken. This study shows that the product has the (*erythro*) structure (III), proving that *trans* addition of Bu^tOI has occurred.

Synthesis of the compound has been reported elsewhere (Glover, 1980). The colourless crystals, grown from *n*-hexane, generally occurred as laminae of too poor quality for single-crystal analysis. Nevertheless, it was possible to cleave these into fragments which were then spherically ground to minimize absorption. The crystals develop a faint yellow colour on prolonged exposure to Cu K α radiation ($\lambda = 1.5418$ Å). Preliminary Weissenberg and precession photographs showed that the crystals belong to the triclinic system. A spherical specimen of mean radius 0.09 mm was sealed in a Lindemann capillary and mounted on a Philips PW 1100 computer-controlled four-circle diffractometer. The intensities of 2332 reflections were measured in the range $3 < \theta < 23^\circ$ with graphite-monochromated Mo K α radiation ($\lambda = 0.7107$ Å). The ω - 2θ technique was used (scan width $1.2^\circ \theta$, speed $0.04^\circ \theta \text{ s}^{-1}$) and the background was measured on both sides of the peak for a total time equal to the peak scan time. The intensities of three reference reflections, monitored periodically during data collection, decreased very slowly, but all remained within 2% of their respective mean values. With the criterion $I_{\text{rel}} > 2\sigma(I_{\text{rel}})$ for an observed reflection, 940 reflections were classified as unobserved and the remaining 1392 were corrected for Lorentz and polarization effects and used in the final refinement. No absorption corrections were applied ($\mu R \sim 0.16$).

The space group $P\bar{1}$ was assumed and a sharpened Patterson map (Sheldrick, 1977) was interpreted accordingly to locate the I atom. The remaining non-hydrogen atoms were revealed by standard heavy-atom procedures. After full-matrix least-squares refinement with I thermally anisotropic and all other non-hydrogen atoms isotropic, R was 0.068 and most of the H atoms were revealed in a difference map. Because of limited computer memory, subsequent refinement was carried out with a blocked-matrix technique with anisotropic thermal parameters assigned to all the atoms. H atoms were included at geometrically calculated positions and refined in a riding model (C-H 1.08 Å). They were divided into seven groups (five methyl, one phenyl and one tertiary C-H), the atoms of each group being assigned a common isotropic temperature factor which was initially allowed to refine. Further refinement of these parameters produced rather high values in some cases, so that in the final cycles the U_{iso} values were kept constant in the range 0.075 to 0.12 Å². The function minimized was

Table 1. Fractional atomic coordinates ($\times 10^4$) for non-hydrogen atoms and equivalent isotropic thermal parameters U_{eq} (Å² $\times 10^3$) with e.s.d.'s in parentheses

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
I	3078 (1)	1652 (1)	4512 (1)	73 (1)
C(1)	1125 (11)	1052 (9)	2821 (10)	57 (6)
C(2)	306 (10)	-292 (9)	2667 (11)	48 (5)
C(3)	14 (13)	2379 (10)	3078 (12)	61 (6)
C(4)	-574 (13)	4514 (11)	2643 (13)	89 (8)
C(5)	-2346 (11)	-1184 (10)	1357 (11)	53 (6)
C(6)	-3169 (13)	-1356 (13)	-76 (11)	81 (7)
C(7)	-2040 (12)	-2670 (10)	1457 (11)	73 (6)
C(8)	-3375 (12)	-185 (11)	2368 (11)	75 (6)
C(9)	1480 (10)	-1578 (9)	2518 (11)	45 (5)
C(10)	1922 (11)	-2126 (10)	3527 (10)	51 (5)
C(11)	3009 (11)	-3282 (10)	3396 (11)	53 (6)
C(12)	3685 (11)	-3903 (10)	2227 (13)	54 (6)
C(13)	3281 (11)	-3379 (9)	1223 (11)	52 (6)
C(14)	2209 (11)	-2234 (10)	1354 (11)	54 (6)
C(15)	5098 (12)	-5731 (11)	2995 (12)	85 (7)
O(2)	-871 (7)	-513 (6)	1474 (6)	50 (4)
O(3)	-1028 (9)	2692 (7)	3768 (8)	74 (5)
O(4)	356 (8)	3161 (7)	2440 (8)	75 (4)
O(5)	4783 (8)	-5066 (7)	2027 (8)	74 (4)

$\sum w\Delta^2$ ($\Delta = |F_o| - |kF_c|$) with w proportional to $[gF_o^2 + \sigma^2(F_o)]^{-1}$; final convergence yielded $R = 0.052$, $R_w = 0.044$, and g refined to 3.59×10^{-4} . The latter was optimized for constancy of the sampling distribution of $\langle w\Delta^2 \rangle$ with $(\sin \theta)/\lambda$ and $[F_o/F_o(\text{max})]^{1/2}$. The maximum shift in the atomic parameters on the final cycle was 0.06σ and the largest peak in the final difference map had a height of $0.65 \text{ e } \text{Å}^{-3}$, located 1.1 Å from the I atom.* Scattering factors and anomalous-dispersion corrections were taken from *International Tables for X-ray Crystallography* (1974). Fractional coordinates of the non-hydrogen atoms are listed in Table 1.

Discussion. Bond lengths and angles are listed in Tables 2 and 3. Atomic nomenclature is shown in Fig. 1, a stereoscopic view of the enantiomer for which coordinates have been listed. As expected, the bulky

* Lists of structure factors, anisotropic thermal parameters and H atom positions have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35153 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Bond lengths (Å) with e.s.d.'s in parentheses

C(1)-I	2.164 (9)	C(5)-C(8)	1.51 (1)
C(1)-C(2)	1.53 (1)	C(2)-C(9)	1.52 (1)
C(1)-C(3)	1.51 (1)	C(9)-C(10)	1.39 (2)
C(3)-O(3)	1.21 (2)	C(10)-C(11)	1.38 (1)
C(3)-O(4)	1.33 (2)	C(11)-C(12)	1.39 (2)
O(4)-C(4)	1.45 (1)	C(12)-C(13)	1.37 (2)
C(2)-O(2)	1.44 (1)	C(13)-C(14)	1.36 (1)
O(2)-C(5)	1.45 (1)	C(14)-C(9)	1.41 (2)
C(5)-C(6)	1.54 (2)	C(12)-O(5)	1.38 (1)
C(5)-C(7)	1.53 (2)	O(5)-C(15)	1.43 (2)

iodo and *tert*-butoxy substituents are situated *trans* to one another with respect to C(1)–C(2) [torsion angle I–C(1)–C(2)–O(2) is -177.5°]. Of chemical significance is the fact that the molecule possesses the *erythro* structure. The term *erythro*, though not strictly applicable in this context, has been used (Glover, 1980) for clarity to describe the relative configurations of the substituents at C(1) and C(2). Structurally, the *erythro* and *threo* diastereomers are in this case characterized by ideal torsion angles of 180 and 60° respectively for C(3)–C(1)–C(2)–C(9). The calculated torsion angle is -175.6° and it may therefore be deduced that the reaction between Bu^tOI and the parent olefin to yield the title compound proceeds *via trans* addition.

The C(1)–I length, 2.164 (9) Å, is in the range of paraffinic C–I distances and compares favourably with the 2.18 (1) Å in phragmalin iodoacetate (Coetzer, Baxter & Gafner, 1971). All other bond lengths are in the expected ranges.

There is evidence of steric strain in the molecule due to the proximity of the bulky iodo, *tert*-butoxy and *p*-methoxyphenyl substituents. This strain can be partly relieved by rotation of the *tert*-butoxy group about C(2)–O(2) so as to avoid close contacts with the phenyl ring. Thus, the C(2)–O(2)–C(5)–C(6) chain is extended, but the plane of this chain is not parallel to the plane through I, C(1), C(2) and O(2). Rotation about C(2)–O(2) results in a torsion angle C(9)–

Table 4. *Least-squares planes and deviations (Å) of atoms from the planes*

Equations are of the form $AX_o + BY_o + CZ_o = D$ and refer to a right-handed orthogonal system with $Z_o \parallel c$, $X_o \parallel a^*$.

Plane 1:	$-0.6463 X_o + 0.5553 Y_o + 0.5234 Z_o = 1.2359$		
Plane 2:	$0.6679 X_o + 0.5076 Y_o + 0.5443 Z_o = 2.4290$		
Plane 3:	$0.7461 X_o + 0.6640 Y_o + 0.0490 Z_o = 0.1445$		
Plane 1			
I	-0.015 (0.003)‡	O(2)	-0.021 (0.021)
C(1)	0.018 (0.034)	†C(5)	0.601 (0.037)
C(2)	0.017 (0.035)		
Plane 2			
C(3)	0.009 (0.040)‡	C(4)	0.004 (0.042)
O(3)	-0.005 (0.027)	†C(1)	0.059 (0.034)
O(4)	-0.008 (0.026)		
Plane 3			
C(9)	-0.006 (0.035)‡	C(14)	0.005 (0.037)
C(10)	0.003 (0.035)	†C(2)	0.019 (0.035)
C(11)	0.001 (0.037)	†O(5)	-0.005 (0.026)
C(12)	-0.002 (0.040)	†C(15)	-0.149 (0.040)
C(13)	-0.001 (0.035)		

† Atoms not included in plane calculation.

‡ Uncertainty in the atomic position (Å) at the 5% level.

C(2)–O(2)–C(5) of 89.2° and C(5) is displaced 0.6 Å from the plane through I, C(1), C(2) and O(2) (see Table 4 for relevant least-squares-plane data). Furthermore, C(1)–C(2)–O(2) (102.2°) is considerably smaller than the ideal tetrahedral angle, the difference being taken up by the opening of C(1)–C(2)–C(9) (112.1°) and C(9)–C(2)–O(2) (112.6°). Some short intramolecular contacts are: I...C(9) 3.38, C(5)...C(9) 3.29, C(2)...C(7) 3.00 and C(7)...C(9) 3.14 Å. There are no abnormally short intermolecular contacts. The closest approach of two I atoms is 4.67 Å (equivalent position for the second I atom: $1 - x, -y, 1 - z$).

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Table 3. *Bond angles (°) with e.s.d.'s in parentheses*

I–C(1)–C(2)	112.2 (7)	C(8)–C(5)–C(7)	112 (1)
I–C(1)–C(3)	105.1 (6)	C(8)–C(5)–C(6)	109.5 (8)
C(2)–C(1)–C(3)	113.3 (8)	C(7)–C(5)–C(6)	110.1 (8)
C(1)–C(3)–O(3)	125 (1)	C(2)–C(9)–C(10)	122 (1)
C(1)–C(3)–O(4)	110 (1)	C(2)–C(9)–C(14)	121 (1)
O(3)–C(3)–O(4)	124.9 (9)	C(10)–C(9)–C(14)	117.4 (8)
C(3)–O(4)–C(4)	116.2 (9)	C(9)–C(10)–C(11)	122 (1)
C(1)–C(2)–C(9)	112.1 (8)	C(10)–C(11)–C(12)	119 (1)
C(1)–C(2)–O(2)	102.2 (9)	C(11)–C(12)–O(5)	122 (1)
C(9)–C(2)–O(2)	112.6 (7)	C(11)–C(12)–C(13)	120.6 (9)
C(2)–O(2)–C(5)	117.9 (9)	O(5)–C(12)–C(13)	118 (1)
O(2)–C(5)–C(8)	111.1 (7)	C(12)–C(13)–C(14)	121 (1)
O(2)–C(5)–C(7)	112.5 (8)	C(13)–C(14)–C(9)	121 (1)
O(2)–C(5)–C(6)	102 (1)	C(12)–O(5)–C(15)	118.6 (9)

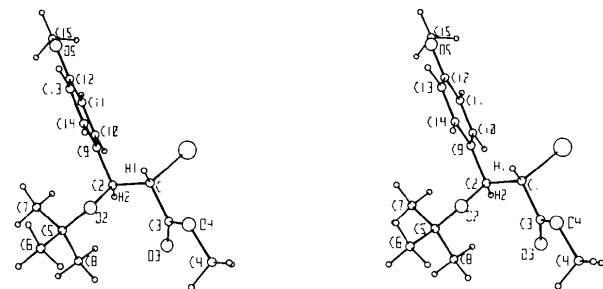


Fig. 1. Stereoscopic view of one enantiomer of the title compound (drawn with CRISTEP; de Wet, 1980).

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