

Table 5. *Hydrogen-bonded interactions*

The columns labelled x' , y' , z' give the symmetry of the acceptor atom Y' . E.s.d.'s for bonds involving H atoms are not given since the H atoms are geometrically constrained.

X	H	Y'	x'	y'	z'	$X \cdots Y'$	$H \cdots Y'$	$X-H \cdots Y'$
O	H(O)	Br	$1-x$	$\frac{1}{2}+y$	$1-z$	3.415 (9) Å	2.43 Å	180°
N	H(NA)	Br	$1-x$	$-\frac{1}{2}+y$	$1-z$	3.218 (9)	2.22	167
N	N(NB)	Br	$1+x$	y	z	3.332 (9)	2.31	171

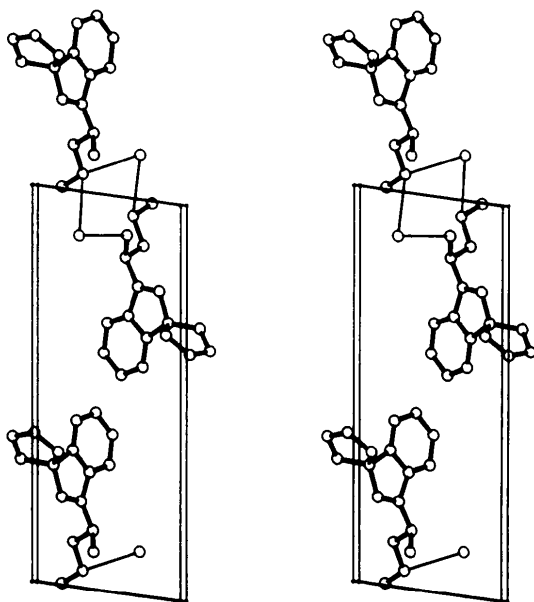


Fig. 2. Stereoscopic drawing of the molecular packing as seen along b . Thin lines represent hydrogen bonds.

The molecular packing and hydrogen-bonding system are shown in Fig. 2 and the hydrogen-bonded interactions are listed in Table 5. The crystal packing fully utilizes the hydrogen-bonding potential of the molecule. N—H \cdots Br and O—H \cdots Br bonds hold the

structure together in the b direction. In the other directions van der Waals contacts are the only intermolecular interactions. No distances violating ordinary packing requirements are found in the structure apart from the hydrogen bonds.

I wish to thank Dr Åke Jönsson for the crystals. My sincere thanks are also due to Professor Diego Carlström and Ingrid Hacksell for valuable help. The investigation was supported by the Swedish Medical Research Council (project No. 144), Karolinska Institutets Fonder and Magnus Bergvalls Stiftelse.

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Acta Cryst. (1981). **B37**, 709–711

4,4,5,5-Tetramethyl-2-phenyl-1,3-dioxolan-2-ylum Dichloroiodate(I)

BY M. R. CAIRA AND J. F. DE WET

Crystallography Group, University of Port Elizabeth, PO Box 1600, Port Elizabeth 6000, South Africa

(Received 22 September 1980; accepted 13 October 1980)

Abstract. C₁₃H₁₇O₂⁺.ICl₂⁻, orthorhombic, *Pnma*, $a = 17.51$ (1), $b = 10.22$ (1), $c = 9.11$ (1) Å, $V = 1630$ Å³, $M_r = 403.1$, $Z = 4$, $D_c = 1.642$, $D_m = 1.66$ Mg m⁻³, $\mu(\text{Mo } K\alpha) = 2.12$ mm⁻¹. Final $R = 0.049$ for 756

reflections. The 4,4,5,5-tetramethyl-2-phenyl-1,3-dioxolan-2-ylum cation is bisected by a crystallographic mirror plane which also contains a linear, symmetrical ICl₂⁻ ion.

Introduction. Halogens and interhalogens oxidize 4,4,5,5-tetramethyl-2-phenyl-1,3-dioxolane to compounds which were proposed to be 4,4,5,5-tetramethyl-2-phenyl-1,3-dioxolan-2-ylum polyhalide salts (Goosen & McClelland, 1979). Since complexes between organic molecules and halogens/interhalogens are well characterized (Hassel & Rømming, 1962; Prout & Wright, 1968), a possibility remained that the products of these reactions were not salts, but intermolecular complexes whose properties could be similar. The compound chosen for X-ray investigation was the product of the addition of ICl to 4,4,5,5-tetramethyl-2-phenyl-1,3-dioxolane.

Systematic absences noted on Weissenberg and precession photographs were $0kl$, $k + l = 2n + 1$, and $h0l$, $h = 2n + 1$ indicating space groups $Pna2_1$ or $Pnam$. Intensities were obtained from a single crystal $0.20 \times 0.12 \times 0.16$ mm mounted on a Philips PW 1100 computer-controlled four-circle diffractometer with graphite-monochromated Mo $K\alpha$ radiation. With the ω - 2θ scan technique (scan width $1.2^\circ\theta$, speed $0.04^\circ\theta$ s^{-1}), the intensities of 1335 reflections were measured in the range $3 < \theta < 23^\circ$. The background was scanned on both sides of the peak for half the time of the peak scan. The intensities of three reference reflections, monitored every 56 min, showed no systematic variation. Of the reflections recorded, 136 were systematically absent and a further 442 with $I < 2\sigma(I)$ were regarded as unobserved. The refinement was based on the remaining 757 observed reflections. Lorentz and polarization but no absorption corrections were applied.

The space group of lower symmetry ($Pna2_1$) was tentatively assumed and the I atom was located from a Patterson synthesis. All the remaining non-hydrogen atoms were revealed in successive difference syntheses. Inspection of the atomic coordinates showed that they were consistent with a model in which the halogen atoms and three C atoms are situated in the mirror planes of $Pnam$, the planar carbo-cation thus lying perpendicular to the mirror. Successful refinement followed with the halogen atoms and C(1), C(6) and C(9) in special positions 4(c) and the remaining atoms in general positions 8(d) of $Pnma$ (*International Tables for X-ray Crystallography*, 1965). After full-matrix least-squares refinement (Sheldrick, 1977) with all non-hydrogen atoms thermally anisotropic, R was 0.054. All H atoms except H(9) were geometrically placed in a riding model (C-H = 1.08 Å) with common isotropic temperature factors for each of the three sets (each unique methyl and phenyl). The position of H(9) was calculated, the constraints of the C-H length and $y[H(9)] = 0.25$ being applied during refinement. During the final refinement in the accelerated full-matrix mode, all the parameters of H(9) were kept constant, including its temperature factor ($U = 0.14$ Å²). The reflection 020 apparently suffered

Table 1. *Positional parameters* ($\times 10^4$) *for non-hydrogen atoms and isotropic temperature factors* ($U_{iso} \times 10^3$)

The equivalent isotropic temperature parameters are defined by

$$U_{iso} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	U_{iso} (Å ²)
I	6291 (1)	2500 (0)	5165 (1)	46
Cl(1)	5304 (2)	2500 (0)	3100 (4)	75
Cl(2)	7308 (3)	2500 (0)	7143 (5)	73
C(1)	3703 (9)	2500 (0)	5250 (14)	47
O(2)	3460 (3)	1431 (6)	4673 (7)	56
C(3)	2941 (5)	1738 (8)	3386 (9)	41
C(4)	2189 (5)	1086 (10)	3763 (9)	56
C(5)	3311 (5)	1091 (10)	2073 (9)	57
C(6)	4203 (8)	2500 (0)	6544 (16)	48
C(7)	4421 (5)	1314 (12)	7133 (11)	61
C(8)	4873 (6)	1335 (15)	8377 (11)	83
C(9)	5084 (12)	2500 (0)	8968 (19)	107

from extinction and was omitted. The quantity minimized* was $\sum w\Delta^2$ ($\Delta = |F_o| - k|F_c|$). Convergence was reached at $R = 0.049$ and $R_w (= \sum w|\Delta| / \sum |F_o|) = 0.039$ with weights $w \propto [\sigma^2(F_o) + gF_o^2]^{-1}$; the constant g was optimized for constancy of the one-way sampling distribution of $\langle w\Delta^2 \rangle$ with $(\sin \theta)/\lambda$ and $[F_o/F_o(\max.)]^{1/2}$ and refined to 1.04×10^{-4} . A final difference map showed no peaks > 0.6 e Å⁻³; the final mean shift/e.s.d. was 0.1. U values for the H atoms refined to 0.078, 0.089 (methyl atoms) and 0.11 Å² (phenyl atoms). Scattering factors were calculated analytically, those for I being corrected for anomalous dispersion (*International Tables for X-ray Crystallography*, 1974). Positional parameters and equivalent U_{iso} values for the non-hydrogen atoms are listed in Table 1.

Discussion. Bond lengths and angles are listed in Tables 2 and 3. Fig. 1 is a perspective view of one formula unit which consists of an essentially planar substituted dioxolanylium cation associated with a symmetrical and nearly linear dichloroiodate anion. The anions lie on crystallographic mirror planes which

* Lists of structure factors, anisotropic thermal parameters and H atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35736 (8 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*

I-Cl(1)	2.555 (4)	C(3)-C(3 ¹)	1.56 (2)
I-Cl(2)	2.533 (4)	C(1)-C(6)	1.47 (2)
O(2)-C(1)	1.29 (1)	C(6)-C(7)	1.38 (1)
O(2)-C(3)	1.52 (1)	C(7)-C(8)	1.38 (1)
C(3)-C(4)	1.52 (1)	C(8)-C(9)	1.36 (1)
C(3)-C(5)	1.51 (1)		

Symmetry code: (i) $x, \frac{1}{2} - y, z$; (ii) $\frac{1}{2} + x, \frac{1}{2} - y, 1\frac{1}{2} - z$.

Table 3. Bond angles ($^{\circ}$) with e.s.d.'s in parentheses

Cl(1)—I—Cl(2)	177.9 (2)	C(3 ^b)—C(3)—C(4)	116.1 (7)
O(2)—C(1)—O(2 ¹)	117 (1)	C(3 ^b)—C(3)—C(5)	116 (1)
O(2)—C(1)—C(6)	121.7 (6)	C(1)—C(6)—C(7)	118.5 (7)
C(1)—O(2)—C(3)	109.8 (8)	C(7)—C(6)—C(7 ^a)	123 (1)
O(2)—C(3)—C(3 ^a)	102.0 (8)	C(6)—C(7)—C(8)	118 (1)
O(2)—C(3)—C(4)	104.8 (7)	C(7)—C(8)—C(9)	120 (2)
O(2)—C(3)—C(5)	105.3 (7)	C(8)—C(9)—C(8 ^a)	123 (2)
C(4)—C(3)—C(5)	111.0 (7)		

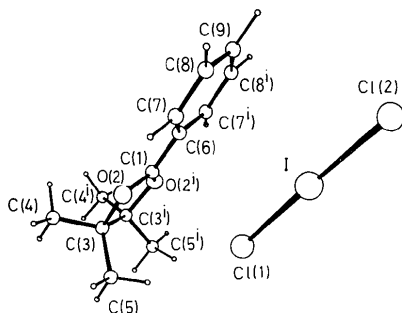


Fig. 1. Perspective view of one formula unit (de Wet, 1980).

also bisect the cations through C(1), C(6), C(9) and H(9). (Intramolecular symmetry necessitates a numbering scheme which differs from that implied in the title.)

Least-squares planes were calculated for the dioxolanylium and phenyl rings, both individually and in combination (Table 4). The dioxolanylium moiety is evidently planar within experimental error and constrains the methyl groups to an eclipsed conformation. This geometry is very similar to that observed in the related 2,4,4,5,5-pentamethyl-1,3-dioxolan-2-yl cation perchlorate (Paulsen & Dammeyer, 1973), but, whereas one pair of *trans*-vicinal CH₃—C bonds is forced to be longer than the other pair in the perchlorate (an effect attributed to relief of steric congestion by bond extension), the CH₃—C lengths observed in the title compound are equal within experimental error.

The length of 1.29 (1) Å for O(2)—C(1) and O(2¹)—C(1) is considerably shorter than the 1.426 ± 0.004 Å typical of 1,3-dioxolanes, being of the same order as the C—O distances in the carbonate ion and in metal acetylacetonates (Sutton, 1965). This is consistent with high double-bond character which could be represented by extensive mesomeric interactions between the electron-deficient C(1) and the bonded O atoms. The phenyl ring shows the same degree of planarity as the dioxolanylium ring, while the combined systems are also rather closely coplanar, though less so. Coplanarity of the two ring systems suggests the possibility of delocalization of positive charge between the dioxolanylium and aromatic π systems, which should result in an increase in the bond order of the connecting σ bond, C(1)—C(6). For σ -bonded trigonal C atoms with increasing degree of π -electron interaction, the bond length l may be related to the π bond order p by the equation $l = 1.51 - 0.17p$ (Coulson,

Table 4. Distances (Å) of atoms from least-squares planes

Values in parentheses indicate the uncertainty in the atomic position at the 5% level (Å).

Plane 1: C(1) 0.006 (0.041); O(2), O(2¹) -0.004 (0.021); C(3) C(3^b) 0.001 (0.029)

Plane 2: C(6) -0.004 (0.040); C(7), C(7^a) 0.002 (0.036); C(8), C(8^a) 0.002 (0.042); C(9) -0.004 (0.054); I* 3.713 (0.004)

Plane 3: C(1) 0.033 (0.041); O(2), O(2¹) 0.005 (0.021); C(3), C(3^b) -0.029 (0.029); C(6) 0.036 (0.040); C(7), C(7^a) 0.023 (0.036); C(8), C(8^a) -0.015 (0.042); C(9) -0.039 (0.054)

* Atom not included in plane calculation.

1970). The bond length of 1.47 (2) Å for C(1)—C(6) is significantly shorter (at the 0.025 level) than the limiting value for a pure σ bond (1.51 Å), but the difference represents a π bond order of only 0.25. Apparently the electron deficiency of the carbonium ion is largely satisfied by mesomeric interactions with the adjacent O atoms, particularly in view of the observed short C—O distances referred to above.

The I atom is 3.71 Å from the mean plane through the phenyl ring and is almost symmetrically located, with non-bonded I...C distances in the range 3.87–4.06 Å (e.s.d.'s ~ 0.02 Å). Intermolecular contacts < 3.5 Å not involving H atoms are those between Cl(1) and C(1) (3.42 Å) and between Cl(2) and C(1^a) (3.41 Å) of an *a*-glide-related carbo-cation.

We thank Dr C. W. McClelland for supplying the crystals and for discussions, and Dr G. Gafner, South African Council for Scientific and Industrial Research, for the services of the national X-ray Data Collection Facility in providing the diffractometer data.

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