

Tableau 2. Paramètres géométriques (Å, °)

C1—C2	1,520 (3)	C6—C7	1,531 (3)
C1—C6	1,545 (3)	C7—C8	1,515 (3)
C1—C11	1,563 (3)	C7—C13	1,471 (4)
C2—C3	1,467 (2)	C7—O17	1,462 (3)
C2—O16	1,458 (2)	C8—C9	1,525 (3)
C3—C4	1,504 (3)	C9—C10	1,528 (3)
C3—C12	1,509 (4)	C10—C11	1,543 (3)
C3—O16	1,451 (2)	C11—C14	1,531 (3)
C4—C5	1,521 (3)	C11—C15	1,539 (3)
C5—C6	1,540 (3)	C13—O17	1,426 (4)
C2—C1—C6	112,5 (1)	C6—C7—C13	117,9 (2)
C2—C1—C11	112,5 (1)	C6—C7—O17	114,3 (2)
C6—C1—C11	116,6 (2)	C8—C7—C13	118,0 (2)
C1—C2—C3	123,0 (2)	C8—C7—O17	110,8 (2)
C1—C2—O16	116,1 (1)	C13—C7—O17	58,2 (2)
C3—C2—O16	59,5 (1)	C7—C8—C9	113,2 (2)
C2—C3—C4	119,0 (2)	C8—C9—C10	115,5 (2)
C2—C3—C12	119,9 (2)	C9—C10—C11	118,1 (2)
C2—C3—O16	60,0 (1)	C1—C11—C10	113,4 (2)
C4—C3—C12	116,8 (2)	C1—C11—C14	109,8 (2)
C4—C3—O16	113,4 (2)	C1—C11—C15	107,3 (2)
C12—C3—O16	114,2 (2)	C10—C11—C14	110,6 (2)
C3—C4—C5	112,8 (2)	C10—C11—C15	106,8 (2)
C4—C5—C6	111,6 (2)	C14—C11—C15	108,7 (2)
C1—C6—C5	107,6 (2)	C7—C13—O17	60,6 (2)
C1—C6—C7	116,9 (2)	C2—O16—C3	60,6 (1)
C5—C6—C7	112,2 (2)	C7—O17—C13	61,2 (2)
C6—C7—C8	120,6 (2)		
C6—C1—C2—C3	14,9 (1)	C1—C6—C7—C8	-20,2 (1)
C1—C2—C3—C4	1,2 (1)	C6—C7—C8—C9	77,0 (2)
C2—C3—C4—C5	16,7 (1)	C7—C8—C9—C10	-76,4 (2)
C3—C4—C5—C6	-51,6 (1)	C8—C9—C10—C11	58,6 (2)
C4—C5—C6—C1	67,3 (1)	C9—C10—C11—C1	-64,1 (2)
C5—C6—C1—C2	-46,8 (1)	C10—C11—C1—C6	81,2 (1)
C1—C2—C3—C12	-154,6 (2)	C5—C6—C7—C13	-53,8 (2)
C1—C2—C3—O16	103,0 (2)	C9—C8—C7—O17	-60,4 (2)
C11—C1—C6—C7	-51,8 (1)		

Les listes des facteurs de structure, des facteurs d'agitation thermique anisotrope, des coordonnées des atomes d'hydrogène, et des distances et angles des atomes d'hydrogène ont été déposées au dépôt d'archives de la British Library Document Supply Centre (Supplementary Publication No. SUP 55157: 8 pp.). On peut en obtenir des copies en s'adressant à: The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, Angleterre. [Référence de CIF: PA1001]

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## Enantiomerically Pure $\alpha$ -Haloketals: Structure and Conformation of (2'S,4'R,5'R)-Dimethyl 2'-Halo-1',2',3',4'-tetrahydro-spiro[1,3-dioxolane-2,1'-naphthalene]-4,5-dicarboxylates (Halo = Cl, Br, I)

SANDRA IANELLI AND MARIO NARDELLI \*

*Istituto di Chimica Generale ed Inorganica, Università degli Studi di Parma, Centro di Studio CNR per la Strutturistica Diffraattometrica, Viale delle Scienze 78, I-43100 Parma, Italy*

CLAUDIO GIORDANO, LAURA COPPI AND ANGELO RESTELLI

*Istituto di Ricerca Chimica 'G. Zambon', Zambon Group SpA, Via Cimabue 26-28, I-20032 Cormano, Milano, Italy*

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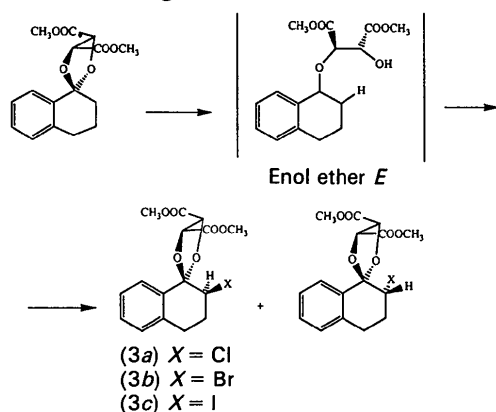
## Abstract

The title compounds were prepared during the course of research into diastereofacial selectivity in the halogenation of enol ethers. Crystals of the title compounds, which belong to the orthorhombic space group  $P2_12_12_1$ , are isostructural; the enantiomers have the *R,R* configuration at the tartrate moiety and the *S* configuration at C2'. The absolute configurations of the Br and I derivatives have been checked by means of Bijvoet pairs. The geometries and conformations of the three molecules are compared, paying particular attention to the orientations of the two methoxycarbonyl moieties which are determined mainly by packing effects.

## Comment

(2'S,4'R,5'R)-Dimethyl 2'-halo-1',2',3',4'-tetrahydro-spiro[1,3-dioxolane-2,1'-naphthalene]-4,5-dicarboxylates are the main reaction products obtained from a new, highly diastereoselective halogenation reaction of the enol ether *E*, generated under the reaction conditions from dimethyl 1',2',3',4'-tetrahydro-spiro[1,3-dioxolane-2,1'-naphthalene]-4,5-dicarboxylate (Giordano, Coppi & Rest-

elli, 1990), according to the scheme:



These findings are important in understanding the mechanism of bromination of (4*R*,5*R*)-dimethyl 2-aryl-1,3-dioxolane-4,5-dicarboxylate (Castaldi, Cavicchioli, Giordano & Uggeri, 1986, 1987), which is the key step in the industrial asymmetric synthesis of (*S*)-(+)-2-(6-methoxy-2-naphthyl)propanoic acid (naproxen) (Giordano, Castaldi, Cavicchioli & Villa, 1989; Elks & Gamellin, 1990).

The present paper reports the results of the crystal structure analyses that allowed the configuration at the halogen-substituted C atom of the main reaction product to be determined.

Bond distances and angles are compared in Table 2 where the weighted means are also given. The *ORTEP* drawings of the molecules of the three derivatives are shown in Fig. 1; the figure suggests that as the configurations at C11 and C12 are *R,R*, the configuration at C9 is *S*. This is the most important result obtained from the X-ray analysis as it allows the determination of the configuration of the epimer formed with higher yield in the halogenation of the enol ether *E* (Giordano, Coppi & Restelli, 1990).

From the values of bond distances and angles (Table 2), it can be seen that the change of the halogen substituent does not significantly influence the geometry of the molecule. This is true not only of bond distances and angles, but also torsion angles and puckering parameters (Table 2).

Consideration of the average values of the C—C distances in the benzene moiety suggests that fusion with the cyclohexene ring causes some tendency for the double bonds to be alternately localized at C1—C6, C2—C3 and C4—C5. The average length of the shorter sides [1.382(3) Å] is significantly less than the average length of the longer sides [1.402(3) Å], with a  $\Delta/\sigma$  value of 4.7. No significant asymmetry is observed in the two exocyclic angles at the C1—C6 junction. With regard to the C—O distances in the dioxolane ring, it should be noted that the O2—C10 bond is significantly longer than O2—C12 ( $\Delta/\sigma = 6.8$ ), while the difference between O1—C10 and O1—C11 is not significant ( $\Delta/\sigma = 0.5$ ); there is no apparent explanation for this finding.

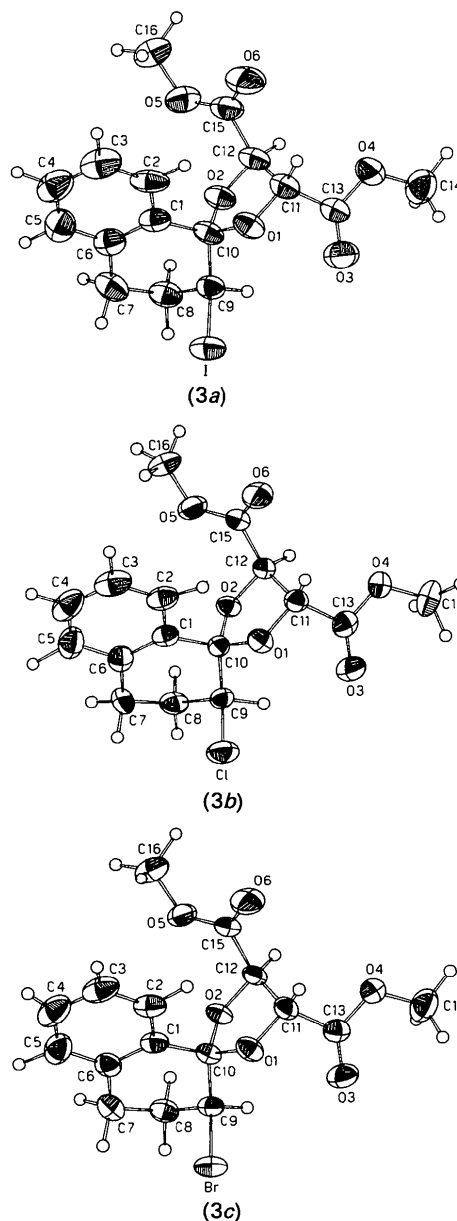


Fig. 1. *ORTEP* (Johnson, 1965) drawings of the three compounds with ellipsoids at 50% probability.

The C—X distances agree quite well with the averaged values of corresponding structures retrieved from the Cambridge Structural Database (Allen, Kennard, Watson, Brammer, Orpen & Taylor, 1987); C—Cl was found to be 1.807(6) compared with 1.803(3) Å in the literature, C—Br 1.973(3) compared with 1.966(29) Å and C—I 2.180(5) compared with 2.162(15) Å. The corresponding C—C—X angles are equal in the three compounds and quite near to the tetrahedral value.

The orientation of the two methoxycarbonyl groups is defined by the O—C—C—O torsion angles (Table 2) and illustrated by the Newman projections (Fig. 2) which

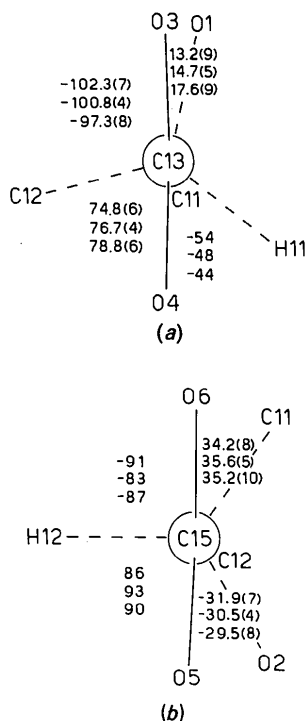


Fig. 2. Newman projections along (a) the C13—C11 bond and (b) the C15—C12 bond showing the orientation of the acetoxy groups.

show that the situation of the two groups is not the same. This different situation is confirmed by the analysis of the non-bonded potential-energy profiles obtained by rotating these groups about the C—C bonds, showing that packing interactions are the most important factors determining the conformation of these groups in the crystal.

The most significant results of an anisotropic atomic displacement analysis are quoted in Table 3. The analysis, performed using *THMV* (Trueblood, 1984), was carried out in terms of the LST rigid-body model (Schomaker & Trueblood, 1968; Trueblood, 1978), considering also the internal motions according to Dunitz & White (1973). These results, together with the ellipsoids shown in Fig. 1, suggest that the displacements are similar in the three kinds of molecule and that internal motions (or static displacements) must have some importance, especially in the halogens and some atoms of the benzo and methoxycarbonyl groups.

Packing is determined mainly by van der Waals interactions and the volume occupied by the molecule in the crystal,  $V_m = V/Z$ , increases with the atomic number of the halogen substituent according to the increase of its van der Waals and covalent radii. If Pauling's (1942) values for the van der Waals radii ( $r$ ) are assumed, the observed C—X distances and the calculated molecular volumes are in good agreement with those obtained experimentally from the unit-cell volumes.

	$r$ (Å)	$V_m$ (Å <sup>3</sup> )	$V_m$ (calc.) (Å <sup>3</sup> )
(3a)	1.80	397.6	398.7
(3b)	1.95	404.8	405.6
(3c)	2.15	418.3	416.4

The differences do not exceed 0.5%.

## Experimental

### Compound (3a)

#### Crystal data

C<sub>16</sub>H<sub>17</sub>ClO<sub>6</sub>  
 $M_r = 340.76$   
 Orthorhombic  
*P*2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>  
 $a = 14.932$  (3) Å  
 $b = 14.850$  (2) Å  
 $c = 7.173$  (2) Å  
 $V = 1590.5$  (0.6) Å<sup>3</sup>  
 $Z = 4$   
 $D_x = 1.423$  Mg m<sup>-3</sup>

#### Data collection

Nonius CAD-4 diffractometer  
 $\theta$ - $2\theta$  scans  
 Absorption correction: not applied  
 1637 measured reflections  
 1027 observed reflections  
 $[I > 2\sigma(I)]$

#### Refinement

Refinement on  $F$   
 Final  $R = 0.0318$   
 $wR = 0.0407$   
 $S = 0.4548$   
 1027 reflections  
 208 parameters  
 H-atom parameters not refined  
 $w = 1/[\sigma^2(F_o) + 0.005F_o^2]$

Mo  $K\alpha_1$  radiation  
 $\lambda = 0.709300$  Å  
 Cell parameters from 25 reflections  
 $\theta = 12$ – $17^\circ$   
 $\mu = 0.2639$  mm<sup>-1</sup>  
 $T = 293$  (2) K  
 Prismatic crystals  
 $0.53 \times 0.32 \times 0.28$  mm  
 Colourless

$\theta_{\max} = 25^\circ$   
 $h = 0 \rightarrow 17$   
 $k = 0 \rightarrow 17$   
 $l = 0 \rightarrow 8$   
 1 standard reflection  
 frequency: 160 min  
 intensity variation: within statistical fluctuation

$(\Delta/\sigma)_{\max} = 0.032$   
 $\Delta\rho_{\max} = 0.09$  e Å<sup>-3</sup>  
 $\Delta\rho_{\min} = -0.10$  e Å<sup>-3</sup>  
 Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Tables 2.2A, 2.2C and 2.3.1)

### Compound (3b)

#### Crystal data

C<sub>16</sub>H<sub>17</sub>BrO<sub>6</sub>  
 $M_r = 385.21$   
 Orthorhombic  
*P*2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>  
 $a = 15.054$  (3) Å  
 $b = 14.924$  (2) Å  
 $c = 7.207$  (2) Å  
 $V = 1619.2$  (6) Å<sup>3</sup>  
 $Z = 4$   
 $D_x = 1.580$  Mg m<sup>-3</sup>

Cu  $K\alpha_1$  radiation  
 $\lambda = 1.540562$  Å  
 Cell parameters from 30 reflections  
 $\theta = 26$ – $52^\circ$   
 $\mu = 3.729$  mm<sup>-1</sup>  
 $T = 293$  (2) K  
 Prismatic crystals  
 $0.41 \times 0.33 \times 0.21$  mm  
 Colourless

**Data collection**

Siemens-AED diffractometer

 $\theta$ -2 $\theta$  scans

Absorption correction:

not applied

3451 measured reflections

2808 observed reflections

 $[I > 2\sigma(I)]$  $R_{\text{int}} = 0.0344$  $\theta_{\text{max}} = 70^\circ$ **Refinement**Refinement on  $F^2$ Final  $R = 0.0431$  $wR = 0.0558$  $S = 0.7118$ 

2808 reflections

261 parameters

All H-atom parameters re-  
fined $w = 1/[\sigma^2(F_o) + 0.005F_o^2]$  $h = -17 \rightarrow 17$  $k = 0 \rightarrow 17$  $l = 0 \rightarrow 8$ 

1 standard reflection

monitored every 50

reflections

intensity variation: within

statistical fluctuation

 $(\Delta/\sigma)_{\text{max}} = 0.003$  $\Delta\rho_{\text{max}} = 0.66 \text{ e } \text{\AA}^{-3}$  $\Delta\rho_{\text{min}} = -1.7 \text{ e } \text{\AA}^{-3}$ 

Atomic scattering factors

from *International Tables*for *X-ray Crystallogra-**phy* (1974, Vol. IV, Tables

2.2A, 2.2C and 2.3.1)

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters ( $\text{\AA}^2$ )*

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

	$x$	$y$	$z$	$U_{\text{eq}}$
(3a)				
Cl	0.1500 (1)	0.5481 (1)	0.2148 (3)	0.0623 (6)
O1	0.1362 (3)	0.7486 (2)	0.1490 (6)	0.0438 (13)
O2	0.0342 (3)	0.7742 (2)	0.3807 (5)	0.0380 (12)
O3	-0.0093 (3)	0.7097 (3)	-0.0811 (7)	0.0614 (17)
O4	-0.0312 (3)	0.8566 (3)	-0.1230 (6)	0.0568 (16)
O5	0.0783 (3)	0.9342 (3)	0.5368 (7)	0.0549 (17)
O6	0.1204 (4)	0.9879 (3)	0.2605 (8)	0.0728 (20)
C1	0.1840 (4)	0.7290 (4)	0.4702 (9)	0.0379 (20)
C2	0.2431 (4)	0.8016 (4)	0.4522 (11)	0.0541 (27)
C3	0.3043 (4)	0.8204 (4)	0.5919 (14)	0.0658 (33)
C4	0.3060 (5)	0.7664 (6)	0.7490 (12)	0.0712 (31)
C5	0.2492 (5)	0.6930 (5)	0.7669 (12)	0.0664 (31)
C6	0.1880 (4)	0.6737 (4)	0.6221 (9)	0.0433 (22)
C7	0.1292 (4)	0.5923 (4)	0.6425 (10)	0.0527 (24)
C8	0.0482 (4)	0.5929 (4)	0.5185 (10)	0.0458 (23)
C9	0.0697 (4)	0.6233 (3)	0.3210 (9)	0.0393 (19)
C10	0.1093 (4)	0.7179 (3)	0.3292 (8)	0.0346 (19)
C11	0.0790 (4)	0.8186 (3)	0.0879 (9)	0.0390 (19)
C12	0.0348 (4)	0.8519 (3)	0.2670 (8)	0.0358 (19)
C13	0.0087 (4)	0.7856 (4)	-0.0503 (9)	0.0451 (22)
C14	-0.1027 (5)	0.8398 (5)	-0.2554 (11)	0.0734 (25)
C15	0.0841 (4)	0.9322 (4)	0.3531 (10)	0.0430 (24)
C16	0.1247 (5)	1.0060 (4)	0.6266 (12)	0.0733 (30)
(3b)				
Br	0.15288 (3)	0.54124 (2)	0.21313 (7)	0.0553 (1)
O1	0.1338 (2)	0.7483 (2)	0.1487 (4)	0.0450 (8)
O2	0.0330 (2)	0.7756 (2)	0.3804 (4)	0.0367 (6)
O3	-0.0135 (2)	0.7110 (2)	-0.0767 (5)	0.0611 (10)
O4	-0.0300 (2)	0.8589 (2)	-0.1264 (5)	0.0561 (9)
O5	0.0794 (2)	0.9344 (2)	0.5329 (4)	0.0543 (9)
O6	0.1181 (3)	0.9888 (2)	0.2554 (5)	0.0729 (13)
C1	0.1816 (2)	0.7311 (2)	0.4672 (6)	0.0402 (9)
C2	0.2424 (2)	0.8018 (3)	0.4450 (7)	0.0504 (13)
C3	0.3030 (3)	0.8220 (3)	0.5824 (9)	0.0672 (19)
C4	0.3048 (3)	0.7702 (4)	0.7443 (8)	0.0713 (18)
C5	0.2480 (3)	0.6981 (4)	0.7625 (7)	0.0618 (16)
C6	0.1853 (2)	0.6776 (3)	0.6259 (6)	0.0438 (10)
C7	0.1266 (3)	0.5972 (3)	0.6490 (6)	0.0516 (12)
C8	0.0455 (2)	0.5961 (2)	0.5238 (6)	0.0441 (10)
C9	0.0680 (2)	0.6254 (2)	0.3280 (5)	0.0383 (9)
C10	0.1072 (2)	0.7195 (2)	0.3282 (5)	0.0347 (9)
C11	0.0775 (2)	0.8186 (2)	0.0870 (5)	0.0401 (10)
C12	0.0347 (2)	0.8532 (2)	0.2668 (5)	0.0388 (9)
C13	0.0078 (2)	0.7873 (2)	-0.0477 (6)	0.0427 (10)
C14	-0.1028 (3)	0.8408 (5)	-0.2555 (8)	0.0725 (16)
C15	0.0839 (3)	0.9329 (2)	0.3495 (6)	0.0448 (11)
C16	0.1254 (4)	1.0072 (3)	0.6254 (8)	0.0713 (18)
(3c)				
I	0.15803 (3)	0.53481 (2)	0.21680 (7)	0.0641 (1)
O1	0.1307 (3)	0.7484 (3)	0.1498 (7)	0.0566 (13)
O2	0.0337 (3)	0.7792 (2)	0.3822 (7)	0.0506 (12)
O3	-0.0166 (4)	0.7138 (3)	-0.0670 (9)	0.0765 (18)
O4	-0.0258 (4)	0.8609 (3)	-0.1271 (9)	0.0722 (17)
O5	0.0816 (4)	0.9362 (3)	0.5253 (8)	0.0713 (18)
O6	0.1185 (5)	0.9888 (4)	0.2495 (11)	0.0980 (27)
C1	0.1800 (3)	0.7347 (4)	0.4656 (10)	0.0517 (18)
C2	0.2414 (4)	0.8032 (4)	0.4388 (13)	0.0651 (25)
C3	0.3021 (5)	0.8237 (6)	0.5727 (16)	0.0832 (35)
C4	0.3028 (5)	0.7737 (6)	0.7372 (15)	0.0845 (32)
C5	0.2448 (5)	0.7046 (6)	0.7613 (12)	0.0729 (27)
C6	0.1825 (4)	0.6858 (4)	0.6271 (11)	0.0584 (20)
C7	0.1235 (4)	0.6073 (5)	0.6605 (12)	0.0658 (22)
C8	0.0447 (4)	0.6035 (4)	0.5322 (10)	0.0569 (18)
C9	0.0662 (3)	0.6292 (3)	0.3367 (9)	0.0489 (16)
C10	0.1055 (3)	0.7223 (3)	0.3310 (8)	0.0472 (17)
C11	0.0771 (4)	0.8195 (4)	0.0874 (10)	0.0546 (18)
C12	0.0357 (4)	0.8546 (4)	0.2659 (10)	0.0559 (18)
C13	0.0074 (4)	0.7888 (4)	-0.0463 (10)	0.0552 (20)

**Compound (3c)****Crystal data** $\text{C}_{16}\text{H}_{17}\text{IO}_6$  $M_r = 432.21$ 

Orthorhombic

 $P2_12_12_1$  $a = 15.317 (3) \text{ \AA}$  $b = 15.056 (2) \text{ \AA}$  $c = 7.255 (2) \text{ \AA}$  $V = 1673.1 (0.6) \text{ \AA}^3$  $Z = 4$  $D_x = 1.716 \text{ Mg m}^{-3}$ Cu  $K\alpha_1$  radiation $\lambda = 1.540562 \text{ \AA}$ 

Cell parameters from 28

reflections

 $\theta = 26-40^\circ$  $\mu = 15.441 \text{ mm}^{-1}$  $T = 293 (2) \text{ K}$ 

Prismatic crystals

0.163 mm (radius)

Colourless

**Data collection**

Siemens-AED diffractometer

 $\theta$ -2 $\theta$  scans

Absorption correction:

spherical

6917 measured reflections

2699 observed reflections

 $[I > 2\sigma(I)]$  $R_{\text{int}} = 0.0323$  $\theta_{\text{max}} = 70^\circ$ **Refinement**Refinement on  $F^2$ Final  $R = 0.0377$  $wR = 0.0587$  $S = 0.8421$ 

2699 reflections

258 parameters

H-atom parameters not re-  
fined $w = 1/[\sigma^2(F_o) + 0.005F_o^2]$  $(\Delta/\sigma)_{\text{max}} = 0.12$  $h = -21 \rightarrow 21$  $k = -20 \rightarrow 20$  $l = 0 \rightarrow 11$ 

1 standard reflection

monitored every 50

reflections

intensity variation: within

statistical fluctuation

 $\Delta\rho_{\text{max}} = 0.33 \text{ e } \text{\AA}^{-3}$  $\Delta\rho_{\text{min}} = -0.99 \text{ e } \text{\AA}^{-3}$ Extinction correction: not  
applied

Atomic scattering factors

from *International Tables*for *X-ray Crystallogra-**phy* (1974, Vol. IV, Tables

2.2A, 2.2C and 2.3.1)

C14	-0.0975 (6)	0.8435 (7)	-0.2537 (13)	0.0842 (30)
C15	0.0851 (5)	0.9346 (4)	0.3448 (12)	0.0642 (24)
C16	0.1256 (8)	1.0085 (6)	0.6193 (16)	0.0915 (35)

Table 2. Comparison of relevant structural parameters ( $\text{\AA}$ ,  $^\circ$ ) with e.s.d.'s in parentheses

$Q_T$  is the total puckering amplitude ( $\text{\AA}$ ) (Cremer & Pople, 1975) and ADP denotes asymmetry displacement parameters (Nardelli, 1983b).

	(3a)	(3b)	(3c)	Av.
X-C9	1.807 (6)	1.973 (3)	2.180 (5)	—
O1-C10	1.427 (7)	1.420 (4)	1.425 (8)	1.422 (3)
O1-C11	1.415 (7)	1.421 (4)	1.423 (7)	1.420 (3)
O2-C10	1.447 (7)	1.445 (4)	1.443 (6)	1.445 (3)
O2-C12	1.413 (6)	1.418 (4)	1.414 (7)	1.416 (3)
O3-C13	1.179 (7)	1.201 (5)	1.197 (8)	1.194 (7)
O4-C13	1.319 (7)	1.337 (5)	1.334 (8)	1.332 (5)
O4-C14	1.451 (9)	1.463 (6)	1.456 (11)	1.459 (4)
O5-C15	1.321 (9)	1.323 (5)	1.311 (10)	1.321 (4)
O5-C16	1.425 (8)	1.450 (6)	1.450 (11)	1.442 (8)
O6-C15	1.192 (8)	1.192 (5)	1.186 (10)	1.191 (4)
C1-C2	1.400 (8)	1.406 (5)	1.409 (8)	1.405 (4)
C1-C6	1.365 (9)	1.396 (6)	1.384 (10)	1.386 (9)
C1-C10	1.514 (8)	1.513 (5)	1.513 (8)	1.513 (4)
C2-C3	1.385 (11)	1.379 (7)	1.379 (12)	1.380 (5)
C3-C4	1.384 (12)	1.400 (9)	1.411 (15)	1.400 (6)
C4-C5	1.387 (11)	1.381 (7)	1.379 (12)	1.382 (5)
C5-C6	1.413 (10)	1.398 (6)	1.393 (10)	1.400 (5)
C6-C7	1.501 (8)	1.499 (5)	1.507 (9)	1.501 (4)
C7-C8	1.501 (9)	1.519 (6)	1.526 (10)	1.516 (6)
C8-C9	1.521 (10)	1.516 (6)	1.507 (10)	1.515 (5)
C9-C10	1.526 (7)	1.523 (4)	1.526 (7)	1.524 (3)
C11-C12	1.527 (8)	1.536 (5)	1.536 (10)	1.534 (4)
C11-C13	1.525 (9)	1.504 (5)	1.515 (9)	1.510 (6)
C12-C15	1.531 (8)	1.523 (5)	1.533 (9)	1.527 (4)

C10-O1-C11	110.2 (4)	109.9 (3)	110.2 (4)	110.1 (2)
C10-O2-C12	108.6 (4)	108.0 (3)	107.9 (4)	108.1 (2)
C13-O4-C14	117.0 (5)	116.1 (4)	114.8 (6)	116.1 (6)
C15-O5-C16	115.8 (5)	116.6 (3)	117.7 (6)	116.6 (4)
C6-C1-C10	120.0 (5)	120.4 (3)	120.1 (5)	120.2 (2)
C2-C1-C10	119.1 (5)	119.5 (3)	120.3 (6)	119.5 (3)
C2-C1-C6	120.6 (6)	119.8 (3)	119.2 (6)	119.8 (3)
C1-C2-C3	120.3 (6)	120.9 (4)	121.1 (7)	120.8 (3)
C2-C3-C4	119.0 (6)	119.3 (4)	118.8 (7)	119.1 (3)
C3-C4-C5	121.3 (7)	119.8 (5)	120.3 (9)	120.3 (5)
C4-C5-C6	119.1 (7)	121.5 (5)	120.4 (8)	120.6 (7)
C1-C6-C5	119.6 (6)	118.6 (4)	120.2 (6)	119.2 (5)
C5-C6-C7	118.0 (6)	119.7 (4)	117.2 (7)	118.8 (7)
C1-C6-C7	122.4 (6)	121.7 (3)	122.5 (6)	122.0 (2)
C6-C7-C8	114.1 (5)	114.6 (3)	114.0 (6)	114.4 (2)
C7-C8-C9	112.6 (5)	111.7 (3)	113.0 (5)	112.2 (4)
C8-C9-C10	108.6 (5)	110.6 (3)	110.3 (5)	110.1 (6)
X-C9-C8	110.4 (4)	110.6 (2)	110.5 (4)	110.6 (2)
X-C9-C10	109.2 (4)	109.7 (2)	109.5 (3)	109.6 (2)
C1-C10-C9	114.2 (5)	113.1 (3)	113.2 (5)	113.4 (3)
O2-C10-C9	104.0 (4)	103.6 (2)	103.8 (4)	103.7 (2)
O2-C10-C1	109.7 (4)	109.5 (3)	109.6 (4)	109.6 (2)
O1-C10-C9	111.6 (5)	112.8 (3)	112.7 (5)	112.5 (3)
O1-C10-C1	111.3 (4)	111.1 (3)	110.9 (4)	111.1 (2)
O1-C10-O2	105.3 (4)	106.3 (3)	106.2 (4)	106.0 (3)
O1-C11-C13	112.4 (4)	112.9 (3)	112.4 (5)	112.7 (2)
O1-C11-C12	103.8 (4)	103.5 (3)	103.2 (5)	103.5 (2)
C12-C11-C13	110.7 (5)	110.9 (3)	110.7 (5)	110.8 (2)
O2-C12-C11	102.9 (4)	102.8 (3)	103.7 (4)	103.0 (3)
C11-C12-C15	112.6 (5)	112.8 (3)	112.4 (5)	112.7 (2)
O2-C12-C15	113.9 (5)	114.9 (3)	114.7 (5)	114.6 (3)
O4-C13-C11	108.1 (5)	108.8 (3)	107.5 (5)	108.4 (4)
O3-C13-C11	125.9 (6)	126.3 (3)	125.8 (6)	126.2 (2)
O3-C13-O4	125.9 (6)	124.8 (4)	126.5 (6)	125.5 (5)
O6-C15-C12	122.3 (6)	122.3 (4)	122.4 (8)	122.3 (3)
O5-C15-C12	112.9 (5)	112.3 (3)	111.6 (6)	112.3 (3)
O5-C15-O6	124.8 (6)	125.3 (4)	125.9 (7)	125.3 (3)

O1-C11-C13-O4	-169.6 (5)	-167.7 (3)	-166.4 (5)	-167.8 (7)
O2-C12-C15-O5	-31.9 (7)	-30.5 (4)	-29.5 (8)	-30.6 (5)

#### Puckering parameters

C1, C6, C7, C8, C9, C10 ring				
$Q_T$	0.466 (6)	0.460 (4)	0.450 (6)	0.459 (4)
ADP $D_2(C8-C9)$	0.028 (3)	0.030 (2)	0.044 (2)	0.035 (5)
$D_2(C9)$	0.076 (3)	0.070 (2)	0.049 (3)	0.066 (7)
C10, O1, C11, C12, O2 ring				
$Q_T$	0.283 (5)	0.292 (3)	0.279 (5)	0.287 (4)
ADP $D_2(C12)$	0.010 (3)	0.006 (2)	0.005 (3)	0.007 (2)

Table 3. Analysis of the anisotropic atomic displacements in terms of LST rigid-body motion and internal motions

PN1 is a point on the normal to the mean plane through the C11, C13, O3, O4 group, PN2 is a point on the normal to the mean plane through the C12, C15, O5, O6 group, PZ is the normal to the benzene plane at C6.  $\Delta$  is the mean difference of the mean-square vibrational amplitudes along the interatomic directions for all pairs of atoms,  $\Delta U = U_{ij}(\text{obs.}) - U_{ij}(\text{calc.})$ ,  $R_{wU} = [\sum(w\Delta U)^2 / \sum(wU_o)^2]^{1/2}$ ,  $\sigma(w\Delta U) = [\sum(w\Delta U)^2 / \sum w^2]^{1/2}$ ,  $\sigma(U_o)$  is the mean e.s.d. of  $U_o$ 's.

Derivative	Treatment	$\Delta \times 10^4 (\text{\AA})$	$\sigma(w\Delta U) \times 10^4$	$\sigma(U_o) \times 10^4$	$R_{wU}$
(3a)	Rigid-body	80 (106)	61	—	0.169
	Internal motions	—	53	39	0.146
(3b)	Rigid-body	67 (93)	33	—	0.104
	Internal motions	—	31	19	0.097
(3c)	Rigid-body	89 (120)	23	—	0.064
	Internal motions	—	21	34	0.061

Group librating	Libration along	Libration amplitude ( $^\circ$ )		
		(3a)	(3b)	(3c)
X	C9-C10	4.5 (8)	3.8 (7)	3.2 (8)
C1, C2, C3, C4, C5	C6-PZ	3.1 (8)	1.0 (27)	—
C14	C13-PN1	1.2 (37)	—	—
C16	C15-PN2	2.4 (20)	1.2 (82)	—

The integrated intensities were measured using a modified version (Belletti, Ugozzoli, Cantoni & Pasquinelli, 1979) of the Lehmann & Larsen (1974) peak-profile analysis procedure. Corrections were applied for Lorentz and polarization effects but absorption was only considered for (3c) for which a crystal sample ground to a sphere of radius 0.163 mm was used. Secondary extinction was considered according to Zachariasen (1963) for (3b) only [ $g = 1.20(9) \times 10^{-7}$ ].

The structure of (3a) was determined by direct methods using SHELXS86 (Sheldrick, 1986). The atomic coordinates from this analysis were then used as starting data for the refinement of the other structures as they are isostructural. Refinement for all three compounds was by anisotropic full-matrix least squares on  $F$  using SHELX76 (Sheldrick, 1976). In the case of (3a), the H atoms were found but not refined and in that of (3b), the H atoms were found and refined with the exception of those of the C8 methylene and both methyl groups, which were placed at calculated positions riding on the attached C atoms. This treatment was applied to all the H atoms of (3c).

The absolute configuration was determined for (3b) and (3c) by refining the structures of the first assumed model and of its enantiomorph until complete convergence, and then comparing the  $wR$  values using Hamilton's (1965) test. In order to obtain additional evidence, the Bijvoet differences  $[\Delta F(\text{obs.}) = |F(\text{obs.,H})| - |F(\text{obs.,-H})|]$  of the observed values were compared with the differences  $[\Delta F(\text{calc.}) = |F(\text{calc.,H})| - |F(\text{calc.,-H})|]$  of the calculated values for the model and its enantiomorph, according to Noordik, Beurskens & Tjhuis (1978). The following results were obtained. For (3b),  $wR(\text{model}) = 0.0558$ ,  $wR'(\text{enant.}) = 0.0763$ ,  $R = wR'/wR = 1.367$ ,  $R(1,2547,0.005) = 1.002$ , model  $\Sigma \Delta F(\text{obs.}) \Delta F(\text{calc.}) = 696(2)$ , enantiomorph  $\Sigma \Delta F(\text{obs.}) \Delta F(\text{calc.}) = -690(2)$  on 1254 Bijvoet pairs. For (3c),  $wR(\text{model}) = 0.0587$ ,  $wR'(\text{enant.}) = 0.1121$ ,  $R = wR'/wR = 1.910$ ,  $R(1,2441,0.005) = 1.002$ , model

$\Sigma\Delta F(\text{obs.})\Delta F(\text{calc.}) = 10025(29)$ , enantiomorph  $\Sigma\Delta F(\text{obs.}) \times \Delta F(\text{calc.}) = -9742(29)$  on 1104 Bijvoet pairs. The results indicate that the model corresponds to the correct configuration, with the same *2R,3R* configuration for the tartaric moiety as that of the tartaric acid used in the synthesis.

Throughout this paper, the averaged values are means weighted according to the reciprocals of the largest 'external' and internal standard deviations (Topping, 1960).

The calculations were carried out on the ENCORE-GOULD-POWERNODE 6040 computer of the 'Centro di Studio per la Strutturistica Diffraattometrica del CNR (Parma)'. In addition to the quoted programs, *LQPARM* (Nardelli & Mangia, 1984), *PARST* (Nardelli, 1983a), and *ORTEP* (Johnson, 1965) were also used.

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Lists of structure factors, anisotropic thermal parameters, H-atom coordinates, complete geometry and non-bonded energy profiles have been deposited with the British Library Centre as Supplementary Publication No. SUP 55190 (57 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: KA1004]

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## Structure and Conformation of 1'-Phenylindan-2-spiro-4'-piperidin-1-one

SANDRA IANELLI AND MARIO NARDELLI

*Istituto di Chimica Generale ed Inorganica, Università degli Studi di Parma, Centro di Studio CNR per la Strutturistica Diffraattometrica, Viale delle Scienze 78, I-43100 Parma, Italy*

D. BELLETTI

*Istituto di Strutturistica Chimica, Università degli Studi di Parma, Centro di Studio CNR per la Strutturistica Diffraattometrica, Viale delle Scienze, I-43100 Parma, Italy*

BRIGITTE JAMART-GRÉGOIRE, HERVÉ FORCONI AND PAUL CAUBÈRE

*Laboratoire de Chimie Organique I, UA CNRS 457, Université de Nancy I, BP 239, 54506 Vandoeuvre-Les-Nancy CEDEX, France*

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## Abstract

The title compound was obtained, amongst other products, by the condensation of quinuclidinone enolate with bromobenzene in the presence of the  $\text{NaNH}_2 \cdot t\text{BuONa}$  complex base. X-ray analysis proved the only way of successfully identifying its structure. Its formation suggests a new mechanism of arylic condensation. The spiro addition of piperidine to the indanone system does not modify the geometry of the two moieties significantly. It is possible that some degree of conjugation between the N lone pair and the phenyl  $\pi$  system determines the conformation about the N-Ph bond, which itself seems mainly influenced by packing interactions.

## Comment

The condensation of ketone enolates with aryl halides in the presence of  $\text{NaNH}_2 \cdot \text{RONa}$  complex bases is now a well established procedure which allows the synthesis of a wide variety of compounds (Caubère, 1974; Carré, Jamart-Grégoire, Geoffroy, Caubère, Ianelli & Nardelli, 1988, and references cited therein). In order to develop research into this kind of reaction, we have been studying the condensation of ketones containing functional groups for some time. As part of this work, we carried out the condensation of the enolate of quinuclidinone with bromobenzene.

Amongst the products isolated was one that we were unable to identify by the usual spectroscopic methods and