Acta Cryst. (1998). C**54**, 995–1000

Two Polymorphs of Bis(4-methoxyphenyl)tellurium(IV) Diiodide†

JOAN FARRAN,[a] ANGEL ALVAREZ-LARENA,[a] MARIO V. CAPPARELLI,[a] JOAN F. PINIELLA,[a] GABRIEL GERMAIN[b] AND LIBARDO TORRES-CASTELLANOS[c]

[a]*Unitat de Cristallografia, Universitat Autònoma de Barcelona, 08193 Bellaterra, Spain,* [b]*Unité de Chimie Physique Moléculaire et de Cristallographie, Université de Louvain, B-1348 Louvain-La-Neuve, Belgium, and* [c]*Departamento de Química, Universidad Nacional de Colombia, Apartado Aéreo 14490, Bogotá DC, Colombia. E-mail: mcappare@quimica.ivic.ve*

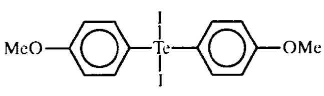
(*Received 4 August 1997; accepted 11 November 1997*)

Abstract

The title compound, $(C_7H_7O)_2TeI_2$ (or $C_{14}H_{14}I_2O_2Te$), crystallizes in space group $P\bar{1}$, either with $Z = 8$, (I*a*), or $Z = 4$, (I*b*). The six independent molecules [four in (I*a*) and two in (I*b*)] have very similar structures. The geometry at the Te atoms is pseudo-trigonal bipyramidal, with the I atoms in the axial positions and the anisyl groups and the lone pair of electrons in the equatorial plane. The Te—C and Te—I distances are in the ranges 2.107 (4)–2.128 (6) and 2.8549 (10)–3.0071 (10) Å, respectively. In both polymorphs, the molecules are associated *via* Te···I secondary bonds [3.6922 (6)–3.9017 (7) Å] to form centrosymmetric tetramers in which the Te_4I_8 cores display step-like geometries. Including the secondary interactions, the coordination about each Te atom is distorted octahedral.

Comment

Within our program of synthetic and structural studies on organotellurium compounds (Farran *et al.*, 1997, and references therein), we prepared several bis-aryltellurium(IV) dihalides, among them bis(*p*-methoxyphenyl)tellurium(IV) diiodide, (I). During crystallization trials of this compound, we noticed that some solvents produced crystals of different colours and/or morphology. This observation prompted a more systematic study of these crystals, which included many solvents (and mixtures of them), unit-cell determinations of some 25 specimens and several structure analyses. These studies revealed that some solvents (*e.g.* acetone, ether, xylene) form red crystals, which are apparently quite stable and contain only the title compound. Other solvents (*e.g.* benzene, toluene, acetonitrile, DMSO), in addition to the red crystals, produce solvated crystals of different appearances, which exhibit a slow decay because of solvent loss. Furthermore, if molecular iodine is present in the solution (from unreacted excess used in the synthesis), some solvents (*e.g.* benzene, chloroform) incorporate it as such into the crystal structure.



(I)

Lattice-parameter measurements revealed that among the red crystals there are two polymorphs, one belonging to space group $P\bar{1}$ with $Z = 8$ [hereafter named (I*a*)] and other also belonging to $P\bar{1}$, but with $Z = 4$ [hereafter named (I*b*)], isostructural with the dichloro (Chadha & Drake, 1984) and dibromo (Farran *et al.*, 1995) analogues of the title compound. We report here the structures of the polymorphs (I*a*) and (I*b*), while those of the co-crystals (I).$0.5C_6H_6$, (I).$0.5CH_3CN$, (I).0.5DMSO and (I).$0.5I_2$, will be published elsewhere (Farran, Alvarez-Larena, Capparelli, Piniella, Germain & Torres-Castellanos, 1998).

The structure analyses showed that (I*a*) and (I*b*) contain only molecules of $(p\text{-}MeOC_6H_4)_2TeI_2$ which, in both polymorphs, are associated into discrete tetramers by means of Te···I interactions. In the two crystal structures there are, in all, six independent molecules of compound (I), which have very similar geometries (Fig. 1). The Te atom displays the expected disphenoidal (*i.e.* pseudo-trigonal bipyramidal) coordination predicted by the valence-shell electron-pair repulsion (VSEPR) model for an AX_4E molecule (Gillespie & Hargittai, 1991, and references therein), in which the I atoms occupy the axial positions, while the organic ligands and the lone pair of electrons lie in the equatorial plane. The range of Te—C distances [2.107 (4)–2.128 (6) Å] is narrow (*ca* 4 s.u.'s) and their values are comparable to 2.116 (20) Å, tabulated by Allen *et al.* (1987) for Te—C(aryl). The range of Te—I distances is much wider (*ca* 152 s.u.'s) due to the influence of the secondary Te···I bonds. The shorter values [2.8549 (10)–2.8766 (11) Å] correspond to I atoms not involved in secondary bonding; bonds of intermediate length [2.8894 (10)–2.9661 (11) Å] are formed by I atoms participating in one secondary bond; the longest Te—I bonds [2.9713 (5)–3.0071 (10) Å] are those in which the I atoms form two secondary bonds. The shorter distances are comparable to the sum of the covalent radii (2.85 Å, using octahedral radius for tellurium; Mangion *et al.*, 1975, and references therein). The range of Te—I distances is similar to those found in other organotellurium iodides with analogous Te···I interactions (Alcock & Harrison, 1984: McCullough *et al.*, 1985, and references therein). It has been suggested that while the individual Te—I bond lengths are greatly affected by secondary bonding, the average value in a

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† Alternative name: diiodobis(4-methoxyphenyl)tellurium(IV).

given I—Te—I system is not (McCullough *et al.*, 1985). Indeed, the range of these averages [2.9167–2.9328 Å] is *ca* 9.5 times smaller than that of the individual values, although in this case, it could simply be because in all six TeI_2 groups of (I*a*) and (I*b*), the halogens participate in two secondary bonds (either 1 + 1 or 0 + 2 bonds per iodine).

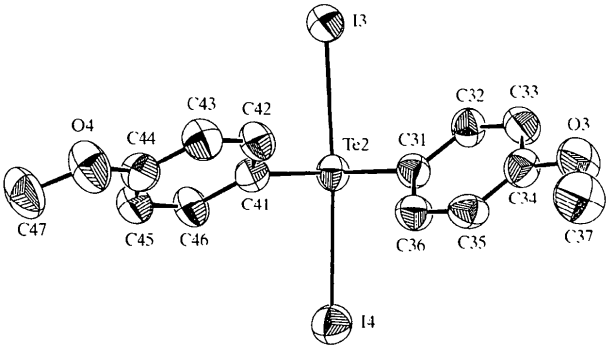

Fig. 1. View of one of the molecules in (I*a*). Displacement ellipsoids are drawn at the 50% probability level.

The C—Te—C angles [range 95.3 (3)–97.9 (2)°] are substantially smaller than 120°, due to the repulsion of the non-bonded pair of electrons on the bonded ones. The I—Te—I groups deviate significantly from linearity [range of angles 174.63 (3)–176.41 (3)°], a feature observed in most disphenoidal R_2TeX_2 organotellurium halides. The sense and magnitude of this deviation depends on the balance between electronic and steric effects (Gillespie, 1961; Ziolo & Troup, 1983), and the angle $\varphi(X—Te—X)$ ranges from $\varphi > 180°$ (towards the organic side) for fluorine to $\varphi < 180°$ (towards the lone pair) for iodine. For instance, in the series Ph_2TeX_2 (X = F, Cl, Br, I), the φ angles are 186.9 (1) (Berry & Edwards, 1980), 184.46 (7) (Alcock & Harrison, 1982), 178.0 (2) (Christofferson & McCullough, 1958), 175.53 (5) (α-form) and 174.32° (β-form, average) (Alcock & Harrison, 1984); while in the series $(p\text{-}Me_2NC_6H_4)_2TeX_2$ (X = F, Cl, Br), the values are 187.71 (7), 176.47 (4) and 174.28 (3)° (Farran, Alvarez-Larena, Capparelli, Piniella & Torres-Castellanos, 1998). In the series $(p\text{-}MeOC_6H_4)_2TeX_2$ (X = Cl, Br, I), the title compound follows the same trend: 181.7 (average) (Chadha & Drake, 1984), 179.28 (average) (Farran *et al.*, 1995), 175.26 [(I*a*), average] and 175.21° [(I*b*), average].

As expected, the I—Te—I and C—Te—C moieties are perpendicular to each other [range of dihedral angles 88.4 (3)–91.1 (3)°]. The aromatic rings are quite planar, but the Te atoms are non-coplanar with the rings [range of deviations 0.0109 (3)–0.1362 (8) Å]. In each molecule, the two rings display a propeller-like arrangement, with ranges of dihedral angles C—Te—C/ring of 28.8 (3)–49.8 (3)° and ring/ring of 50.2 (3)–61.8 (3)°. The methoxy groups are nearly coplanar with the rings [range of C—O—C/ring dihedral angles 1.4 (6)–12.2 (7)°].

In the solid state, organotellurium(IV) halides exhibit a strong tendency to form intermolecular associations, often leading to octahedral environments about the Te atoms (Mangion *et al.*, 1975; McWhinnie & Monsef-Mirzai, 1983). Accordingly, the crystal structures of both polymorphs contain discrete centrosymmetric tetramers (Fig. 2) in which the individual molecules are linked by secondary Te···I bonds (Alcock, 1972, 1990). These tetramers consist of a step-like Te_4I_8 core, with the I—Te—I lines perpendicular to the Te···I···Te···I middle plane and eight *p*-anisyl groups pointing outwards and perpendicularly to the I—Te—I lines.

Tetramers of Te^{IV} halides can display Te_4X_4 cores with cubane- or step-like arrangements. Several compounds are known to adopt the former type of core geometry, for instance $TeCl_4$ (Buss & Krebs, 1971) [and probably $TeBr_4$ (Shoemaker & Abrahams, 1965)], Et_3TeCl (Chadha & Drake, 1986) and Et_3TeBr (Chadha *et al.*, 1984). Aside from the isostructural dichloro and dibromo analogues (Chadha & Drake, 1984; Farran *et al.*, 1995), two organotellurium dichlorides form step-like tetramers, *viz* $(C_6H_5)(p\text{-}BrC_6H_4)TeCl_2$ (Chadha *et al.*, 1983) and $(C_{12}H_8O)TeCl_2$ (Korp *et al.*, 1980), while a triiodide, $(p\text{-}MeOC_6H_4)TeI_3$ (Bird *et al.*, 1980), also displays similar tetramers (not reported as such in the paper). Churchill *et al.* (1976) proposed that (in the case of Cu complexes), the step geometry is most favoured when large halogens or bulky organic ligands are present. Since $(p\text{-}MeOC_6H_4)_2TeX_2$ (X = Cl, Br, I) are isostructural, if that principle were applicable to these compounds it could be concluded that their core geometries are dictated by the size of the *p*-anisyl groups. However, it has been pointed out (Korp *et al.*, 1980) that such an approach, based on size alone, may be too simplistic.

The Te···I secondary bonds span a wide range of distances [3.6922 (6)–3.9017 (7) Å], but even the longest values are significantly shorter than the sum of the van der Waals radii (4.03 Å; Bondi, 1964). Both extreme distances involve the Te2 atom of (I*b*), which displays the most irregular environment (see below). If these values are excluded, the range of intermolecular Te···I distances narrows down considerably (*ca* 1.5 times). If the secondary interactions are taken into account, the environments about the Te atoms are distorted octahedra, with *cis* and *trans* angles in the ranges 75.77 (1)–103.24 (13) and 158.09 (12)–176.2 (2)°, respectively. As indicated above, the octahedron about Te2 of (I*b*) is the most distorted, particularly because of the coordination of $I2^i$ [symmetry code: (i) $1-x$, $2-y$, $1-z$], which forms the extreme angles. Leaving aside these three values, the *cis* and *trans* angles are within 11° of the nominal values. In each Te_4I_8 core, the I···Te···I angle within the middle plane is at least 5° larger than

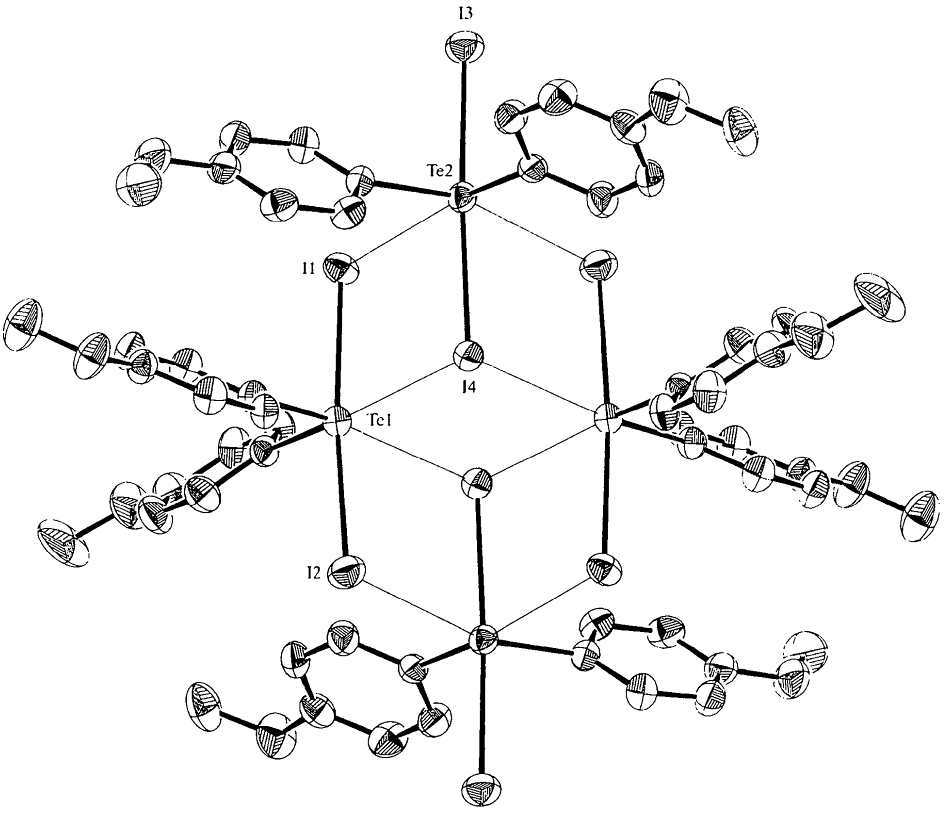

Fig. 2. View of one of the tetramers in (I*b*). Displacement ellipsoids are drawn at the 30% probability level.

that formed by the upper/lower Te atoms, because of the non-linearity of the I—Te—I moieties. As expected, the least-squares lines along the two independent I—Te—I groups of each Te_4I_8 core are nearly parallel [inter-line angles: 3.58 (2) and 3.88 (2)° in (I*a*), and 1.67 (7)° in (I*b*)]. The angle between the two independent cores of (I*a*) is 51.50 (1)°, as measured by the dihedral angle between the middle planes.

Neither crystal structure displays significant I· · ·I interactions, a fact which is consistent with the red colour of the crystals (Dewan & Silver, 1977; McCullough *et al.*, 1985, and references therein).

Polymorphism appears to be a relatively frequent phenomenon (Gavezzotti & Filippini, 1995, and references therein), not uncommon among organotellurium iodides, *e.g.* Me_2TeI_2 (Einstein *et al.*, 1967; Chan & Einstein, 1972), Ph_2TeI_2 (Alcock & Harrison, 1984), $(C_8H_8)TeI_2$ (McCullough *et al.*, 1985) and (o-PhC_6H_4)TeI_3 (McCullough & Knobler, 1976; McCullough, 1977). In the present study, the absence of significant structural differences between the two polymorphs is remarkable, which suggests that they have similar stabilities. Since the specimens of (I*a*) and (I*b*) are indistinguishable in colour and morphology, it is difficult to isolate each crystalline phase and to assess the relative amounts of these phases in the different crystallizations. To address this point, we tried to match the calculated powder patterns of (I*a*) and (I*b*) with experimental data from samples obtained from several solvents. The results were not totally conclusive, due to the complexity of the diffractograms, but seem to indicate that most solvents (*e.g.* acetone, acetonitrile, $CHCl_3$, DMSO, benzene, toluene, xylene) produce a mixture of both polymorphs. However, depending on as yet undetermined factors, in a few cases, we obtained crops which appeared to consist of a single crystalline phase (probably not 100% pure). For instance, two crystallizations, from acetone and acetonitrile, produced the polymorph (I*a*) [m.p.'s 447.1 (2) and 445.6 (2) K, respectively], while another one, from AcOEt/EtOH, gave (I*b*) [m.p. 443.1 (2) K]. The slightly higher values of D_x and melting point of (I*a*) suggest that it could be the more stable polymorph. Furthermore, the powder data seem to indicate that in most crystallizations, (I*a*) is the the most abundant phase.

Experimental

Several synthetic routes to the title compound have been reported (Lederer, 1916; Petragnani & de Moura Campos, 1961; Dorn *et al.*, 1976: Sadekov *et al.*, 1978, 1989; Sadekov & Maksimenko, 1981). The sample used in this work was prepared by the reaction of (p-$MeOC_6H_4$)$_2$Te (Farran *et al.*, 1997) with iodine, as described by Lederer (1916). The specimens used in the X-ray analyses were obtained by slow evaporation of solutions in DMSO/acetone for (I*a*) and in xylene for (I*b*).

Polymorph (I*a*)

Crystal data

$C_{14}H_{14}I_2O_2Te$
$M_r = 595.65$
Triclinic
$P\overline{1}$
$a = 11.822\ (4)$ Å
$b = 14.812\ (5)$ Å
$c = 22.612\ (3)$ Å
$\alpha = 73.57\ (2)°$
$\beta = 75.40\ (2)°$
$\gamma = 67.38\ (3)°$
$V = 3459\ (2)$ Å^3
$Z = 8$
$D_x = 2.287$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 11.5–13.4°$
$\mu = 5.285$ mm^{-1}
$T = 295\ (2)$ K
Red
0.83 × 0.55 × 0.38 mm
Prism

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: empirical from ψ scans (North *et al.*, 1968)
$T_{\min} = 0.073$, $T_{\max} = 0.134$
12 133 measured reflections
12 133 independent reflections

9704 reflections with $I > 2\sigma(I)$
$\theta_{\max} = 25.0°$
$h = -13 \rightarrow 14$
$k = -16 \rightarrow 17$
$l = 0 \rightarrow 26$
3 standard reflections
frequency: 120 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.037$
$wR(F^2) = 0.094$
$S = 1.066$
12 133 reflections
675 parameters
H atoms not refined
$w = 1/[\sigma^2(F_o^2) + (0.0376P)^2 + 13.0277P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.002$
$\Delta\rho_{\max} = 0.79$ e Å^{-3}
$\Delta\rho_{\min} = -1.38$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °) for (Ia)*

Te1—I1	2.8549 (10)	Te3—I5	2.8894 (10)
Te1—I2	3.0071 (10)	Te3—I6	2.9661 (11)
Te1—C11	2.112 (7)	Te3—C51	2.119 (7)
Te1—C21	2.116 (7)	Te3—C61	2.123 (7)
Te2—I3	2.8990 (10)	Te4—I7	2.8766 (11)
Te2—I4	2.9344 (9)	Te4—I8	2.9890 (10)
Te2—C31	2.115 (6)	Te4—C71	2.116 (7)
Te2—C41	2.118 (7)	Te4—C81	2.128 (6)
I1—Te1—I2	176.41 (3)	I5—Te3—I6	174.99 (2)
I1—Te1—C11	91.7 (2)	I5—Te3—C51	92.1 (2)
I1—Te1—C21	92.2 (2)	I5—Te3—C61	90.5 (2)
I2—Te1—C11	91.3 (2)	I6—Te3—C51	92.9 (2)
I2—Te1—C21	89.4 (2)	I6—Te3—C61	89.4 (2)
C11—Te1—C21	96.4 (3)	C51—Te3—C61	95.7 (3)
I3—Te2—I4	174.63 (2)	I7—Te4—I8	174.99 (2)
I3—Te2—C31	91.5 (2)	I7—Te4—C71	92.8 (2)
I3—Te2—C41	89.8 (2)	I7—Te4—C81	92.2 (2)
I4—Te2—C31	93.8 (2)	I8—Te4—C71	89.2 (2)
I4—Te2—C41	90.5 (2)	I8—Te4—C81	92.1 (2)
C31—Te2—C41	96.6 (3)	C71—Te4—C81	95.3 (3)

Table 2. *Contact distances (Å) and contact angles (°) for polymorph (Ia)*

Te1···I4	3.7353 (15)	Te3···I8	3.7962 (14)
Te1···I3^{i}	3.8355 (17)	Te3···I8^{ii}	3.7373 (16)
Te2···I2	3.8127 (15)	Te4···I6	3.7666 (15)
Te2···I2^{i}	3.7520 (16)	Te4···I5^{ii}	3.7915 (17)
I1—Te1···I4	91.76 (3)	I5—Te3···I8	93.33 (2)
I1—Te1···I3^{i}	93.73 (3)	I5—Te3···I8^{ii}	85.61 (3)
I2—Te1···I4	86.52 (3)	I6—Te3···I8	86.99 (3)
I2—Te1···I3^{i}	82.99 (3)	I6—Te3···I8^{ii}	89.39 (3)
I4···Te1···I3^{i}	85.47 (3)	I8···Te3···I8^{ii}	90.78 (3)
C11—Te1···I4	85.1 (2)	C51—Te3···I8	82.8 (2)
C11—Te1···I3^{i}	169.27 (19)	C51—Te3···I8^{ii}	173.0 (2)
C21—Te1···I4	175.69 (18)	C61—Te3···I8	175.95 (19)
C21—Te1···I3^{i}	92.6 (2)	C61—Te3···I8^{ii}	90.91 (19)
I3—Te2···I2	93.68 (3)	I7—Te4···I6	88.18 (3)
I3—Te2···I2^{i}	85.94 (3)	I7—Te4···I5^{ii}	94.39 (3)
I4—Te2···I2	86.12 (3)	I8—Te4···I6	87.21 (3)
I4—Te2···I2^{i}	88.70 (3)	I8—Te4···I5^{ii}	83.29 (3)
I2···Te2···I2^{i}	90.31 (3)	I6···Te4···I5^{ii}	85.39 (3)
C31—Te2···I2	81.9 (2)	C71—Te4···I6	91.2 (2)
C31—Te2···I2^{i}	171.7 (2)	C71—Te4···I5^{ii}	171.92 (17)
C41—Te2···I2	176.21 (18)	C81—Te4···I6	173.40 (18)
C41—Te2···I2^{i}	91.32 (19)	C81—Te4···I5^{ii}	88.02 (18)

Symmetry codes: (i) $-x + 2, -y + 2, -z$; (ii) $-x + 3, -y + 2, -z - 1$.

Polymorph (I*b*)

Crystal data

$C_{14}H_{14}I_2O_2Te$
$M_r = 595.65$
Triclinic
$P\overline{1}$
$a = 10.334\ (1)$ Å
$b = 13.091\ (1)$ Å
$c = 14.588\ (1)$ Å
$\alpha = 110.237\ (7)°$
$\beta = 100.875\ (6)°$
$\gamma = 100.272\ (8)°$
$V = 1753.7\ (2)$ Å^3
$Z = 4$
$D_x = 2.256$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 11.6–14.0°$
$\mu = 5.213$ mm^{-1}
$T = 295\ (2)$ K
Red
0.38 × 0.20 × 0.18 mm
Prism

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: empirical from ψ scans (North *et al.*, 1968)
$T_{\min} = 0.218$, $T_{\max} = 0.391$
6165 measured reflections
6165 independent reflections

4296 reflections with $I > 2\sigma(I)$
$\theta_{\max} = 25.0°$
$h = -12 \rightarrow 11$
$k = -15 \rightarrow 14$
$l = 0 \rightarrow 17$
3 standard reflections
frequency: 120 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.028$
$wR(F^2) = 0.073$
$S = 1.013$
6165 reflections
347 parameters
H atoms not refined
$w = 1/[\sigma^2(F_o^2) + (0.0408P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.002$
$\Delta\rho_{\max} = 0.68$ e Å^{-3}
$\Delta\rho_{\min} = -0.68$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 3. *Selected geometric parameters (Å, °) for (Ib)*

Te1—I1	2.9063 (5)	Te2—I3	2.8688 (5)
Te1—I2	2.9232 (5)	Te2—I4	2.9713 (5)
Te1—C11	2.107 (4)	Te2—C31	2.114 (4)
Te1—C21	2.111 (4)	Te2—C41	2.119 (4)
I1—Te1—I2	174.967 (15)	I3—Te2—I4	175.460 (13)
I1—Te1—C11	91.95 (12)	I3—Te2—C31	90.37 (12)
I1—Te1—C21	91.15 (13)	I3—Te2—C41	92.6 (1)
I2—Te1—C11	90.81 (12)	C31—Te2—I4	90.34 (12)
I2 Te1 C21	92.76 (13)	C41—Te2—I4	91.72 (12)
C11—Te1—C21	95.8 (2)	C31—Te2—C41	97.9 (2)

Table 4. *Contact distances (Å) and contact angles (°) for polymorph (Ib)*

Te1···I4	3.6998 (5)	Te2···I1	3.6922 (6)
Te1···I4^{i}	3.7935 (6)	Te2···I2^{i}	3.9017 (7)
I1—Te1···I4	84.42 (1)	I3—Te2···I1	95.57 (1)
I1—Te1···I4^{i}	92.50 (1)	I3—Te2···I2^{i}	92.99 (1)
I2—Te1···I4	91.56 (1)	I4—Te2···I1	83.68 (1)
I2—Te1···I4^{i}	85.04 (1)	I4—Te2···I2^{i}	82.48 (1)
I4···Te1···I4^{i}	98.02 (1)	I1···Te2···I2^{i}	75.77 (1)
C11—Te1···I4	86.3 (1)	C31—Te2···I1	174.01 (10)
C11—Te1···I4^{i}	174.09 (12)	C31—Te2···I2^{i}	103.24 (13)
C21—Te1···I4	175.16 (11)	C41—Te2···I1	82.61 (11)
C21—Te1···I4^{i}	80.19 (11)	C41—Te2···I2^{i}	158.09 (12)

Symmetry code: (i) $-x + 1, -y + 2, -z + 1$.

The title structures were solved by direct methods. H atoms were placed in calculated positions using a riding model with fixed C—H distances (0.93 Å for C_{sp^2} and 0.96 Å for C_{sp^3}) and $U_{iso} = pU_{eq}$(parent atom) (p = 1.2 for C_{sp^2} and 1.5 for C_{sp^3}). A single orientation parameter was refined for each methyl group [except for C57 and C77 of (I*a*)]. The methoxy groups attached to C54 and C74 of (I*a*) were found to be disordered. Each one was split into two alternative positions, with complementary occupancies, and refined with $U_{iso}(\mathrm{O}n) = U_{iso}(\mathrm{O}n')$ and $U_{iso}(\mathrm{C}n7) = U_{iso}(\mathrm{C}n7')$ (n = 5, 7), and with restrained C*n*4—O*n*, O*n*—C*n*7 and C*n*4—C*n*7 distances, to give similar geometries to both parts. The final occupancy factors for the unprimed atoms were 0.53 (1) in both cases. Powder data were measured using a Philips X'PERT-MPD System and Cu $K\alpha$ radiation. Simulated diffractograms were calculated with the *POWDER CELL* program (Kraus & Nolze, 1996). Melting points were measured by differential scanning calorimetry (DSC), using a Perkin-Elmer DSC7 instrument in continuous heating rate mode (20 K min^{-1}) under an argon atmosphere.

For both compounds, data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989); cell refinement: *CAD*-4 *Software*; data reduction: *CRYSTAN* (Burzlaff *et al.*, 1977); program(s) used to solve structures: *SHELXS*86 (Sheldrick, 1990); program(s) used to refine structures: *SHELXL*93 (Sheldrick, 1993); molecular graphics: *ZORTEP* (Zsolnai & Pritzkow, 1995) and *PLUTON*93 (Spek, 1993); software used to prepare material for publication: *SHELXL*93. Geometric calculations were performed using *PARST*95 (Nardelli, 1995) and *PLATON*94 (Spek, 1994).

We gratefully acknowledge the financial support of the European Economic Community (project CI1*.0574.ES). JF thanks the Generalitat de Catalunya for an FI grant, while MVC and GG thank the Ministerio de Educación y Cultura of Spain for sabbatical grants (projects SAB95-0281 and SAB89-0031). We thank Dr S. Suriñach (Departamento de Física, UAB) for the DSC measurements. The X-ray measurements were carried out at the Servei de Difracció de Raigs X (UAB).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: MU1363). Services for accessing these data are described at the back of the journal.

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3,4,4a,5,6,7,8,8a-Octahydro-8a-hydroxy-2-quinolone and its 8a-Hydroperoxy Derivative

STEFANO ALINI, ATTILIO CITTERIO, ALESSANDRA FARINA, MARIA CRISTINA FOCHI AND LUCIANA MALPEZZI*

Dipartimento di Chimica, Politecnico di Milano, Via Mancinelli 7, 20131 Milano, Italy. E-mail: luci@indigo.chem.polimi.it

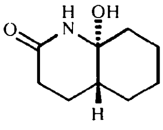
(*Received 1 July 1997; accepted 26 January 1998*)

Abstract

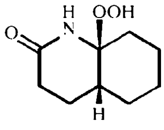
The crystal structures of the title compounds, 3,4,4a,5,6,7,8,8a-octahydro-8a-hydroxy-2-quinolone [$C_9H_{15}NO_2$, (I)] and 3,4,4a,5,6,7,8,8a-octahydro-8a-hydroperoxy-2-quinolone [$C_9H_{15}NO_3$, (II)], show a *trans*- and a *cis*-fused-ring configuration, respectively, with the cyclohexane rings in a chair conformation in both compounds. In (I), the molecules are linked about 2_1 axes *via* intermolecular N—H···O hydrogen bonds, forming an infinite helix; further O—H···O interactions result in a two-dimensional hydrogen-bond network. In (II), the molecules form centrosymmetric dimers *via* pairwise N—H···O interactions, and these dimers are connected by O—H···O hydrogen bonds, giving infinite parallel chains.

Comment

Recently, we reported an efficient new procedure for the synthesis of 6-hydroxy-3,4,5,6-tetrahydro-2-pyridones and 6-hydroperoxy-3,4,5,6-tetrahydro-2-pyridones, by hydration–cyclization of δ-ketonitriles with basic hydrogen peroxide (Citterio *et al.*, 1997). The first class of compounds are useful intermediates in acyliminium chemistry (Murahashi *et al.*, 1993), whereas the latter are quite stable hydroperoxides. Applied to 2-(2-cyanoethyl)cyclohexanone, this procedure affords compounds (I) and (II) as a mixture of the corresponding *cis* and *trans* isomers. The stereochemistry of (I) and (II) was difficult to elucidate by NMR spectroscopy, and in order to confirm their identity and to determine the relative stereochemistry, an X-ray structural investigation was carried out on pure epimers obtained by selective crystallization. In both compounds, the cyclohexane ring adopts a chair conformation. The ring fusion in (I) is *trans*, with a torsion angle O2—C9—C10—H10 of 176.9 (10)° and with the hydroxy substituent in an axial position, which is the only conformation possible for this compound (Fig. 1). In (II), the two rings have a *cis*-fused stereochemistry, with a torsion angle O2—C9—C10—H10 of 54.9 (12)° and the hydroperoxy group in an equatorial position. Within the piperidone rings of both compounds, the carbonyl and the N_{sp^2} groups are nearly coplanar [r.m.s. deviations are 0.045 and 0.021 Å for (I) and (II), respectively], with the C4 and C10 atoms lying below and above the least-squares mean planes, respectively. Bond distances and angles in both compounds are in agreement with the expected values, with the exception of the bond angles around atoms C9 and C10, where significant deviation from C_{sp^3} geometry is observed (Tables 1 and 3), probably due to the different ring junctions. The conformation around the C9—O2 bond is approximately *gauche*. The value of the torsion angles N—C9—O2—H2O for (I) and N—C9—O2—O3 for (II) are, respectively, −46.0 (13) and −57.31 (16)°, slightly smaller than those reported for a similar structural motif (64–67°) in the



(I)



(II)