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3-Chloro- and 3-Bromo-2-oxopropyl *p*-Toluenesulfonate

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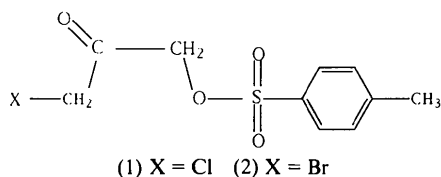
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Abstract

The crystal structures of 3-chloro-2-oxopropyl *p*-toluenesulfonate, $C_{10}H_{11}ClO_4S$, and 3-bromo-2-oxopropyl *p*-toluenesulfonate, $C_{10}H_{11}BrO_4S$, were determined at 150 and 293 K, respectively. They have essentially identical molecular structures and conformations, but different, though closely related, crystal structures. The Cl(or Br)—CH₂—CO—CH₂—O chain has an almost planar conformation.

Comment

The title compounds 3-chloro- (1) and 3-bromo-2-oxopropyl *p*-toluenesulfonate (2) are of interest as intermediates in a recently developed synthesis of isotopically labelled epichlorohydrins (O'Hagan, White & Jones, 1994). In order to provide additional insight into the potential reactivity of these molecules, we undertook structural studies.



The molecular structures of (1) and (2) in the crystalline form are essentially identical (Fig. 1). An interesting feature to emerge was the conformation of the O1, C8, C9, O4, C10, X moiety (X = Cl or Br), which is planar to within 0.11 Å for (1) and 0.05 Å for (2). The planes of this moiety and the benzene ring form

dihedral angles of 93.9 (1) and 91.5 (1)° with each other in (1) and (2), respectively, and both are approximately perpendicular to the O1, S, C1 plane. This apparently unfavourable conformation, on steric grounds, may be eased by hyperconjugation in the planar moiety, or by donation from the lone pair of O1 onto the σ^* orbital of the X—C10 bond [in both molecules, O1...C10 2.68 Å]. The latter explanation, however, seems less likely as the X—C10 bonds are not weakened, but rather are shorter than the average Cl—CH₂ and Br—CH₂ bond lengths of 1.790 (7) and 1.966 (29) Å, respectively (Allen, Kennard, Watson, Brammer, Orpen & Taylor, 1987), and the S—O1 bond is not lengthened. The *cis*-planar orientation of the halogen and O4 atoms is quite common for α -halogenoketones and can be attributed to O...Cl charge-transfer bonds (e.g. Sørensen, 1974; Watson, Go & Purdy, 1973).

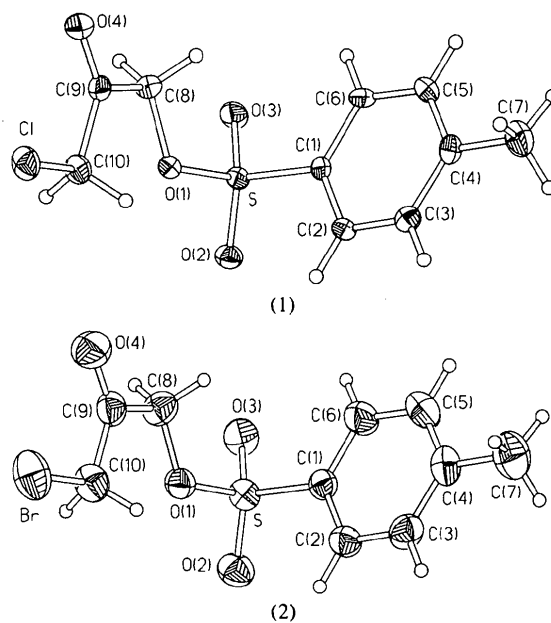


Fig. 1. Molecular structures of compounds (1) and (2), showing 50% probability displacement ellipsoids.

It is noteworthy that the deviation of the C1—S—O1—C8 torsion angle from 0 or 180° makes the molecular conformation chiral and the actual conformations of (1) and (2) are those of maximum chirality.

With the van der Waals radii of Cl and Br being similar (1.75 versus 1.85 Å; see Bondi, 1964), crystals of (1) and (2) might be expected to be isomorphous. In fact, (1) forms chiral crystals (space group $P2_1$) with the polarity along the 2_1 axis defined by parallel orientation of S(=O)₂ groups along this axis, while (2) crystallizes in space group $P2_1/c$ (Fig. 2) with the unit cell equal to that of (1) with the *c* parameter doubled. The latter contains enantiomers differing by rotation of *ca* 160° around the S—O1 bond and oriented antiparallel along

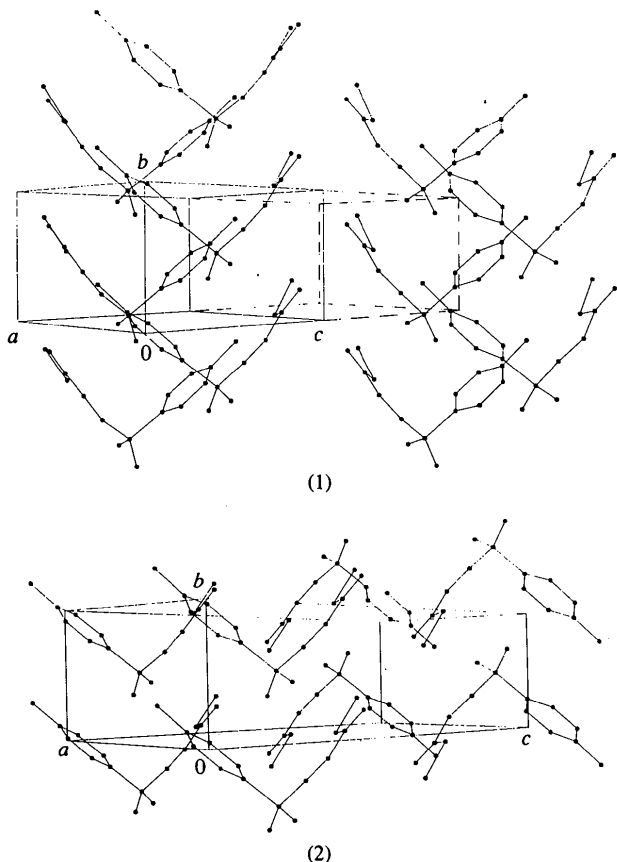


Fig. 2. Crystal packing of (1) and (2), projected on the (10 $\bar{1}$) and (10 $\bar{2}$) planes, respectively.

the 2₁ axis. Secondary halogen-halogen interactions do not exist in either structure, the shortest Cl...Cl (4.35 Å) and Br...Br (3.97 Å) distances being greater than van der Waals distances (Bondi, 1964).

The crystal lattices of both (1) and (2) can be converted into pseudo-orthorhombic by transformations $2a + c \rightarrow a'$, $2a - c \rightarrow c'$ for (1), and $a + c \rightarrow a'$, $a - c \rightarrow c'$ for (2), but the structures possess neither strict nor approximate symmetry corresponding to any orthorhombic space group. The crystal of (2) is pseudo-isostructural with the normal (ambient-temperature) phase of 4,4'-dichlorobiphenyl sulfone (3), known for the stability of its incommensurate phase below 150 K (Zúñiga, Pérez-Mato & Breczewski, 1993), and also with 4,4'-dibromo- (4) and 4,4'-diiodobiphenyl sulfone (5) (Sime & Woodhouse, 1974). Unit-cell parameters of compounds (3)–(5) in the $I2/a$ setting are similar to those of (2) in the $P2_1/a$ setting, with essentially the same packing motif. The molecules of (3)–(5) occupy special positions with S atoms on the $[\frac{1}{4} y 0]$ twofold axis; a similar pseudo-axis exists in the crystal of (2), 'linking' the 4-methylphenyl- and BrCH₂COCH₂O moieties, which have rather similar van der Waals shapes.

Experimental

Compound (1)

Crystal data

C₁₀H₁₁ClO₄S
M_r = 262.70
 Monoclinic
*P*2₁
a = 10.888 (8) Å
b = 5.095 (3) Å
c = 10.923 (8) Å
 β = 111.16 (5)°
V = 565.1 (7) Å³
Z = 2
D_x = 1.544 Mg m⁻³

Mo K α radiation

λ = 0.71073 Å
 Cell parameters from 22 reflections
 θ = 13–14°
 μ = 0.517 mm⁻¹
T = 150 (2) K
 Tetragonal prism
 0.48 × 0.13 × 0.11 mm
 Colourless

Data collection

Rigaku AFC-6S four-circle diffractometer
 2 θ/ω scans
 Absorption correction: analytical, six faces indexed
T_{min} = 0.9158, *T_{max}* = 0.9539
 1182 measured reflections
 1118 independent reflections

1022 observed reflections [*I* > 2 σ (*I*)]
R_{int} = 0.0341
 θ_{\max} = 27.31°
h = 0 → 12
k = 0 → 6
l = -13 → 13
 3 standard reflections monitored every 150 reflections
 intensity variation: none

Refinement

Refinement on *F*²
R[*F*² > 2 σ (*F*²)] = 0.0341
wR(*F*²) = 0.0905
S = 1.072
 1116 reflections
 149 parameters
 $w = 1/[\sigma^2(F_o^2) + (0.0491P)^2 + 0.5576P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.522 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.494 \text{ e \AA}^{-3}$
 Extinction correction: none
 Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)
 Absolute configuration: Flack (1983)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²) for (1)

$$U_{eq} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*a_i \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U_{eq}</i>
Cl	0.17189 (11)	0.2010 (3)	0.04095 (10)	0.0302 (3)
S	0.21188 (10)	0.9788 (2)	0.46500 (9)	0.0172 (3)
O1	0.1747 (3)	0.8044 (7)	0.3369 (3)	0.0189 (7)
O2	0.2973 (3)	1.1728 (7)	0.4447 (3)	0.0217 (7)
O3	0.0927 (3)	1.0568 (7)	0.4827 (3)	0.0238 (8)
O4	-0.0181 (3)	0.2578 (8)	0.1743 (3)	0.0269 (8)
C1	0.3006 (4)	0.7649 (10)	0.5913 (4)	0.0191 (10)
C2	0.4303 (4)	0.7003 (11)	0.6077 (4)	0.0202 (10)
C3	0.4966 (4)	0.5219 (9)	0.7032 (4)	0.0196 (10)
C4	0.4373 (4)	0.4061 (10)	0.7843 (4)	0.0220 (11)
C5	0.3094 (4)	0.4787 (13)	0.7670 (4)	0.0262 (10)
C6	0.2398 (4)	0.6541 (10)	0.6716 (4)	0.0223 (11)
C7	0.5105 (5)	0.2046 (12)	0.8853 (4)	0.0325 (12)
C8	0.0625 (4)	0.6268 (11)	0.3077 (4)	0.0233 (11)
C9	0.0649 (4)	0.4267 (10)	0.2068 (4)	0.0194 (10)
C10	0.1729 (4)	0.4601 (12)	0.1503 (4)	0.0246 (11)

Table 2. Selected geometric parameters (Å, °) for (1)

Cl—C10	1.778 (5)	O1—C8	1.460 (5)
S—O2	1.428 (3)	O4—C9	1.205 (6)
S—O3	1.436 (3)	C8—C9	1.509 (7)
S—O1	1.582 (3)	C9—C10	1.522 (6)
S—C1	1.750 (5)		
O2—S—O3	120.1 (2)	O1—C8—C9	110.1 (3)
O2—S—O1	102.9 (2)	O4—C9—C8	119.3 (4)
O3—S—O1	108.6 (2)	O4—C9—C10	124.6 (4)
O1—S—C1	103.8 (2)	C8—C9—C10	116.1 (4)
C8—O1—S	117.9 (3)	C9—C10—C1	111.8 (4)
C6—C1—C2	120.8 (4)		
C2—C1—S—O1	75.4 (4)	O1—C8—C9—C10	-4.2 (6)
C1—S—O1—C8	80.3 (3)	C8—C9—C10—C1	176.2 (3)
S—O1—C8—C9	-164.2 (3)		

Compound (2)*Crystal data*C₁₀H₁₁BrO₄S*M_r* = 307.16

Monoclinic

*P*2₁/*c**a* = 11.002 (2) Å*b* = 5.160 (2) Å*c* = 22.490 (3) Å β = 110.48 (3)°*V* = 1196.3 (3) Å³*Z* = 4*D_x* = 1.706 Mg m⁻³*Data collection*

Rigaku AFC-6S four-circle diffractometer

2 θ / ω scans

Absorption correction:

analytical, six faces

indexed

T_{min} = 0.4143, *T_{max}* = 0.7165

2893 measured reflections

2752 independent reflections

*Refinement*Refinement on *F*²*R*[*F*² > 2 σ (*F*²)] = 0.0401*wR*(*F*²) = 0.0877*S* = 1.117

2751 reflections

149 parameters

w = 1/[$\sigma^2(F_o^2) + (0.0362P)^2$ + 1.0468*P*]where *P* = (*F_o*² + 2*F_c*²)/3Mo *K* α radiation λ = 0.71073 Å

Cell parameters from 24

reflections

 θ = 13.5–14.5° μ = 3.606 mm⁻¹*T* = 293 (2) K

Plate

0.51 × 0.22 × 0.10 mm

Colourless

1550 observed reflections

[*I* > 2 σ (*I*)]*R_{int}* = 0.0288 θ_{max} = 27.50°*h* = -14 → 0*k* = -6 → 0*l* = -27 → 29

3 standard reflections

monitored every 150

reflections

intensity variation: 0.2%

(Δ/σ)_{max} = -0.009 $\Delta\rho_{max}$ = 0.344 e Å⁻³ $\Delta\rho_{min}$ = -0.340 e Å⁻³

Extinction correction: none

Atomic scattering factors

from *International Tables*for *Crystallography* (1992,

Vol. C, Tables 4.2.6.8 and

6.1.1.4)

Table 3. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²) for (2)
$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U_{eq}</i>
Br	0.16417 (5)	0.19840 (11)	0.01966 (2)	0.0619 (2)
S	0.21392 (9)	0.9838 (2)	0.23277 (5)	0.0327 (2)
O1	0.1776 (2)	0.8066 (5)	0.17120 (11)	0.0351 (6)
O2	0.2994 (3)	1.1711 (5)	0.22244 (13)	0.0425 (7)
O3	0.0971 (3)	1.0660 (6)	0.24121 (13)	0.0418 (7)
O4	-0.0184 (3)	0.2805 (6)	0.09153 (15)	0.0559 (9)

C1	0.2986 (3)	0.7725 (7)	0.2942 (2)	0.0306 (9)
C2	0.4257 (4)	0.7088 (8)	0.3032 (2)	0.0364 (9)
C3	0.4901 (4)	0.5343 (9)	0.3502 (2)	0.0420 (10)
C4	0.4289 (4)	0.4246 (9)	0.3889 (2)	0.0418 (10)
C5	0.3028 (4)	0.4939 (10)	0.3798 (2)	0.0512 (12)
C6	0.2356 (4)	0.6669 (9)	0.3323 (2)	0.0450 (11)
C7	0.4994 (5)	0.2299 (10)	0.4393 (2)	0.0639 (14)
C8	0.0665 (4)	0.6369 (8)	0.1575 (2)	0.0404 (10)
C9	0.0660 (4)	0.4416 (8)	0.1073 (2)	0.0370 (10)
C10	0.1735 (4)	0.4637 (8)	0.0809 (2)	0.0435 (11)

Table 4. Selected geometric parameters (Å, °) for (2)

Br—C10	1.920 (4)	O1—C8	1.447 (5)
S—O2	1.424 (3)	O4—C9	1.204 (5)
S—O3	1.428 (3)	C8—C9	1.512 (5)
S—O1	1.590 (3)	C9—C10	1.501 (5)
S—C1	1.750 (4)		
O2—S—O3	119.8 (2)	O1—C8—C9	110.2 (3)
O2—S—O1	103.1 (2)	O4—C9—C10	124.7 (4)
O3—S—O1	108.9 (2)	O4—C9—C8	118.7 (4)
O1—S—C1	103.4 (2)	C10—C9—C8	116.5 (4)
C8—O1—S	118.0 (2)	C9—C10—Br	112.2 (3)
C2—C1—C6	120.9 (4)		
C2—C1—S—O1	76.9 (3)	O1—C8—C9—C10	-1.6 (5)
C1—S—O1—C8	80.6 (3)	C8—C9—C10—Br	178.2 (3)
S—O1—C8—C9	-166.7 (3)		

Varied-temperature experiments were carried out using a Cryostream (Oxford Cryosystems) liquid-nitrogen cooling device. For (1), at room temperature *a* = 10.984 (2), *b* = 5.161 (1), *c* = 10.988 (2) Å, β = 110.82 (1)°, *V* = 582.2 (2) Å³ and no phase transition was detected between this temperature and that of data collection (150 K). For (1), the absolute configuration could not be estimated unequivocally, the Flack parameter (Flack, 1983) converged to -0.07 (14) for the 'direct' and to 0.27 (14) for the inverted structure, and *R* factors were only marginally higher for the latter [*wR*(all) = 0.1063, *wR*(obs) = 0.0982, *R*(all) = 0.0427, *R*(obs) = 0.0344, *S* = 1.181]. All non-H atoms were refined with anisotropic displacement parameters. All H atoms were found by difference Fourier synthesis, but included in the refinement as part of a rigid-body (methyl) or riding model (for CH₃ and CH₂, *U* refined).

MSC/AF C Diffractometer Control Software (Molecular Structure Corporation, 1988) was used for data collection and cell determination, and *TEXSAN* software (Molecular Structure Corporation, 1989) for data reduction and absorption correction (De Meulenaer & Tompa, 1965). The latter gave negligible improvement for (1), but a significant improvement for (2) [without correction, *R*(obs) = 0.056, $\Delta\rho_{max}$ = 0.93, $\Delta\rho_{min}$ = -0.91 e Å⁻³]. Both structures were solved by direct methods using *SHELXS86* programs (Sheldrick, 1990) and refined using *SHELXL93* programs (Sheldrick, 1994). Material was prepared for publication with *SHELXL93* and molecular graphics were obtained using *SHELXTL-Plus* software (Sheldrick, 1991).

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Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: HU1109). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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A Novel Bis-Tetrahydronaphthyl Thiosemicarbazone

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Abstract

In an attempt to produce 2-methylene-1-tetralone thiosemicarbazone, the reaction of 2-methylene-1-tetralone with thiosemicarbazide in ethanol containing catalytic quantities of acetic acid afforded the title compound, 2-[2-(2-hydroxy-1-oxo-1,2,3,4-tetrahydro-2-naphthyl)ethyl]-1,2,3,4-tetrahydronaphthalen-1-one 1-thiosemicarbazone, C₂₃H₂₅N₃O₂S, whose structure is reported here. The configuration of the carbimino group

is *E* and the bond lengths in the thiosemicarbazone groups indicate delocalization of the electrons of the N atoms. The planes of the aryl groups are approximately parallel to each other. One of the two cyclohexenone rings is in a twist-chair conformation and the other is in a twist-boat conformation.

Comment

Recently, the anticonvulsant activity of a number of Mannich bases has been described (Dimmock, Jonnalagadda, Phillips, Erciyas, Shyam & Semple, 1992). These compounds are known to undergo facile demethylation, producing the corresponding α,β -unsaturated ketones (Tramontini & Angiolini, 1990) which may be the moieties responsible for bioactivity. Since various thiosemicarbazones have displayed anticonvulsant properties (Dimmock, McColl, Wonko, Thayer & Hancock, 1991), the synthesis of thiosemicarbazones of conjugated enones such as (2) was considered with the aim of producing novel, prototypic anticonvulsant agents. However, reaction of (1) with thiosemicarbazide produced (3) as indicated in the scheme below. The structure of (3) is reported here and Fig. 1 shows an *ORTEPII* (Johnson, 1976) diagram of this compound.

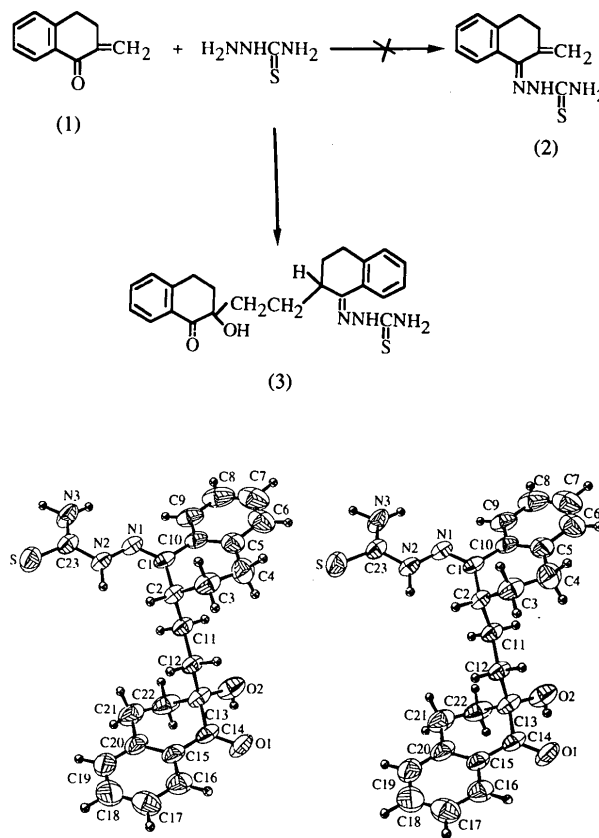


Fig. 1. A stereoscopic *ORTEPII* (Johnson, 1976) view of the title compound. Displacement ellipsoids are plotted at the 50% probability level.