

Table 1. Selected geometric parameters (Å, °)

| | | | |
|----------|-------------|-----------|-------------|
| S—C1 | 1.683 (2) | C2—C3 | 1.394 (2) |
| N1—C2 | 1.329 (2) | C3—C4 | 1.374 (2) |
| N1—C6 | 1.345 (2) | C4—C5 | 1.375 (3) |
| N2—C1 | 1.380 (2) | C5—C6 | 1.366 (3) |
| N2—C2 | 1.396 (2) | C7—C8 | 1.515 (2) |
| N3—C1 | 1.324 (2) | C7—C9 | 1.524 (2) |
| N3—C7 | 1.484 (2) | C7—C10 | 1.515 (3) |
| C1—N2—C2 | 130.00 (12) | N3—C7—C9 | 104.65 (13) |
| C1—N3—C7 | 130.05 (13) | N3—C7—C10 | 110.39 (14) |
| N3—C1—N2 | 116.46 (13) | C8—C7—C9 | 109.04 (16) |
| N3—C1—S | 126.36 (11) | C10—C7—C8 | 111.13 (16) |
| N2—C1—S | 117.19 (10) | C10—C7—C9 | 110.10 (16) |
| N3—C7—C8 | 111.32 (14) | | |

Table 2. Hydrogen-bonding geometry (Å, °)

| D—H...A | D—H | H...A | D...A | D—H...A |
|-------------------------|------|-------|-----------|---------|
| N2—HN2...S ⁱ | 0.86 | 2.62 | 3.454 (1) | 163 |
| N3—HN3...N1 | 0.86 | 1.94 | 2.668 (2) | 142 |

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

The structure was solved by direct methods. All non-H atoms were refined anisotropically and H atoms were geometrically constrained with isotropic displacement parameters.

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1992). Data reduction: *SDP/PDP* (Enraf–Nonius, 1985). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997). Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *KAPPA* (Macíček, 1992).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1341). Services for accessing these data are described at the back of the journal.

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Three 3-arylsulfonyl-1,3-oxazolidines

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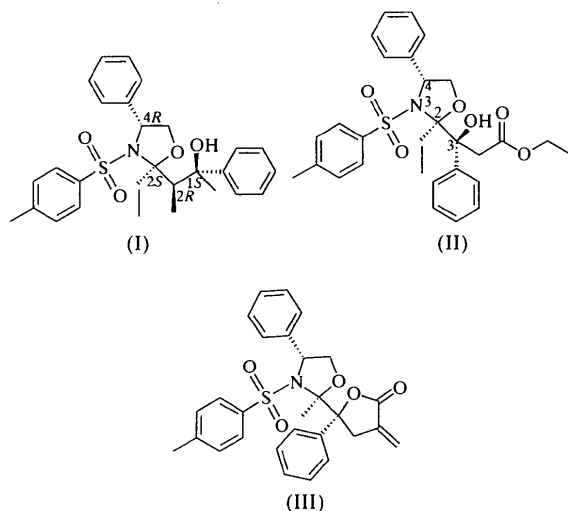
(Received 5 August 1998; accepted 30 September 1998)

Abstract

The structure determinations of (1*S*,2*R*)-2-[(2*S*,4*R*)-2-ethyl-4-phenyl-3-tosyl-1,3-oxazolidin-2-yl]-1-methyl-1-phenylpropanol, C₂₈H₃₃NO₄S, (I), ethyl (3*R*)-3-[(2*S*,4*R*)-2-ethyl-4-phenyl-3-tosyl-1,3-oxazolidin-2-yl]-3-hydroxy-3-phenylpropanoate, C₂₉H₃₃NO₆S, (II), and (1*R*)-2,3,4,5-tetrahydro-5-[(2*S*,4*R*)-2-methyl-4-phenyl-3-tosyl-1,3-oxazolidin-2-yl]-3-methylene-5-phenylfuran-2-one, C₂₈H₂₇NO₅S, (III), were undertaken in order to determine the absolute configuration of the chiral centres. The oxazolidine rings of (I) and (II) exhibit a twist, whereas the oxazolidine ring of (III) adopts an envelope conformation. The hydroxyl groups of (I) and (II) form intramolecular hydrogen bonds.

Comment

Various methods for asymmetric synthesis are based on the utilization of chiral 1,3-oxazolidines. Stereochemically homogeneous 3-arenesulfonyl-1,3-oxazolidines, readily available from enantiomerically pure β -amino-alkanols, are powerful chiral templates for auxiliary-directed asymmetric synthesis (Hoppe *et al.*, 1989, 1990; Hoffmann *et al.*, 1993). They readily add nucleophiles to the carbonyl group, and the attack can be directed selectively from either of its diastereotopic faces (Conde Frieboes *et al.*, 1993; Harder *et al.*, 1994). We have determined the crystal structures of three arylsulfonyl-oxazolidines, in order to establish unambiguously the absolute configuration of the reaction products. In all three cases, the newly formed chiral centre [C22 in (I), C21 in (II) and (III)] shows the *R* configuration.



The geometric parameters of all three compounds (Figs. 1, 2 and 3) agree well with those of the statistical investigations of Herbst-Irmer (1990) and Belvisi *et al.* (1994). The sum of the bond angles at N3 [355.5, 356.5 and 359.0° in (I), (II) and (III), respectively] shows that in all three structures the N atom is in a nearly trigonal planar environment. The tosyl groups of all three compounds adopt a folded conformation, in which the phenyl ring shields the oxazolidine ring. The dihedral angles between these two rings are similar in all three structures: 72.60 (9) in (I), 79.7 (1) in (II) and 72.95 (8)° in (III). The conformation of the sulfonyl groups is such that one of the O atoms nearly lies in the plane of the aromatic ring, whereas the other O atom is nearly *syn*-periplanar with C2 of the oxazolidine ring (see Tables 1, 3 and 5). The oxazolidine rings of (I) and (II) adopt a twist conformation [$Q_2 = 0.206$ and 0.297 Å, and $\varphi_2 = 274.92$ and 302.36° , for (I) and (II), respectively (Cremer & Pople, 1975)], but whereas in (I), N3 [-0.114 (6) Å] and C4 [0.227 (7) Å] deviate from the plane formed by the remaining three atoms, in (II), the atoms C4 [0.30 (1) Å] and C5 [-0.20 (1) Å] deviate from the plane of O1, C2 and N3. The oxazolidine ring of (III) adopts an envelope conformation ($Q_2 = 0.388$ Å, $\varphi_2 = 181.24^\circ$), with O1 deviating by 0.504 (3) Å from the plane of the remaining four atoms (r.m.s. deviation 0.007 Å). The tetrahydrofuran ring in (III) appears in a twist conformation ($Q_2 = 0.241$ Å, $\varphi_2 = 243.69^\circ$), with C21 and C22 deviating by 0.102 (6) and -0.299 (7) Å, respectively, from the plane of the remaining three atoms. A search of the Cambridge Structural Database (Allen & Kennard, 1993; Version 5.12, April 1998) revealed that the oxazolidine ring is a very flexible fragment. It appears in both envelope and twist conformations, with different atoms deviating from the mean ring plane. We did not find any obvious relationship between the nature of the substituents to the oxazolidine ring and its conformation. The molecular

conformations of (I) and (II) are stabilized by an intramolecular hydrogen bond; details are given in Tables 2 and 4.

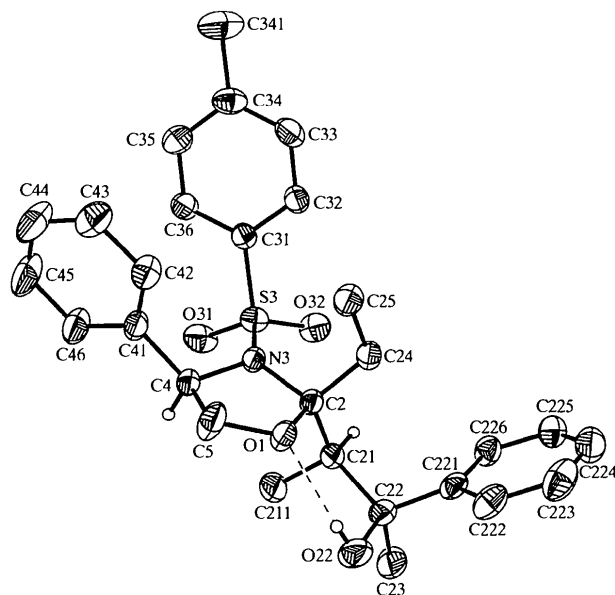


Fig. 1. A perspective view of (I), with the atom-numbering scheme. Only tertiary and hydroxyl-H atoms are shown; displacement ellipsoids are at the 50% probability level.

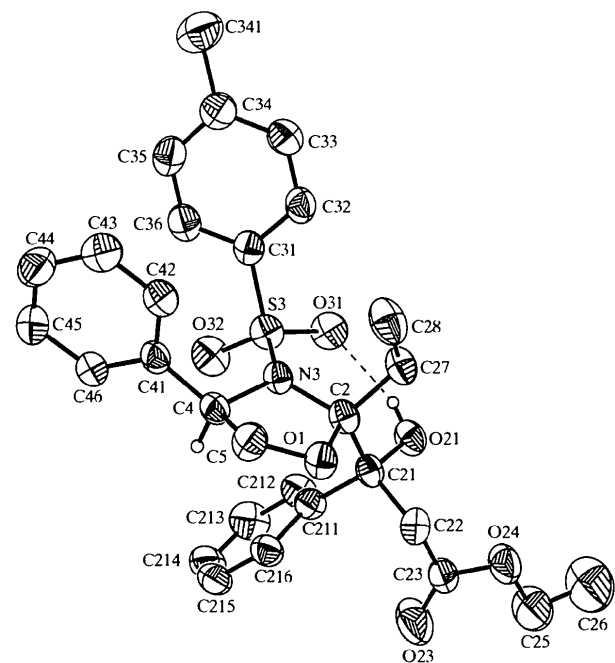


Fig. 2. A perspective view of (II), with the atom-numbering scheme. Only tertiary and hydroxyl-H atoms are shown; displacement ellipsoids are at the 50% probability level.

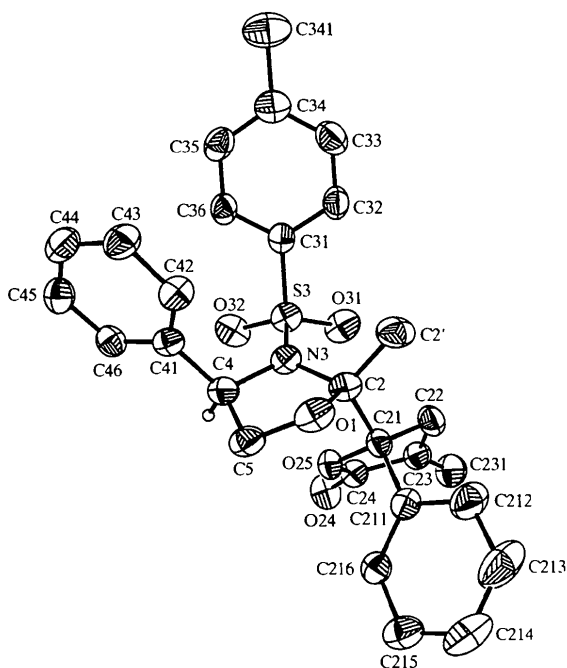


Fig. 3. A perspective view of (III), with the atom-numbering scheme. Only tertiary H atoms are shown; displacement ellipsoids are at the 50% probability level.

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.031$
 $wR(F^2) = 0.085$
 $S = 1.051$
 4411 reflections
 310 parameters
 H atoms: see below
 $w = 1/[\sigma^2(F_o^2) + (0.0498P)^2 + 0.3322P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.003$
 $\Delta\rho_{\max} = 0.156 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.180 \text{ e } \text{\AA}^{-3}$

Extinction correction:
 SHELXL97 (Sheldrick, 1997)
 Extinction coefficient:
 0.00174 (16)
 Scattering factors from
International Tables for Crystallography (Vol. C)
 Absolute structure:
 Flack (1983)
 Flack parameter = 0.009 (15)

Table 1. Selected geometric parameters (\AA , $^\circ$) for (I)

| | | | |
|--------------|-------------|----------------|-------------|
| O1—C5 | 1.403 (2) | S3—O32 | 1.4243 (14) |
| O1—C2 | 1.4274 (19) | S3—O31 | 1.4297 (15) |
| C2—N3 | 1.506 (2) | S3—C31 | 1.7642 (18) |
| N3—C4 | 1.479 (2) | C4—C5 | 1.518 (3) |
| N3—S3 | 1.6368 (13) | | |
| C4—N3—C2 | 111.44 (12) | O31—S3—N3 | 108.09 (8) |
| C4—N3—S3 | 119.77 (12) | O32—S3—C31 | 107.43 (9) |
| C2—N3—S3 | 124.29 (10) | O31—S3—C31 | 106.72 (9) |
| O32—S3—O31 | 120.17 (10) | N3—S3—C31 | 106.90 (8) |
| O32—S3—N3 | 106.87 (7) | | |
| C2—N3—S3—O32 | -3.9 (2) | O31—S3—C31—C36 | 14.9 (2) |

Table 2. Hydrogen-bonding geometry (\AA , $^\circ$) for (I)

| D—H...A | D—H | H...A | D...A | D—H...A |
|--------------|------|-------|-------------|---------|
| O22—H22...O1 | 0.82 | 1.98 | 2.6825 (19) | 143.5 |

Experimental

Compound (I) was synthesized according to Harder *et al.* (1994); (II) and (III) were synthesized according to Conde Frieboes *et al.* (1993). (I) and (II) were crystallized from ethanol, and (III) from an ethyl acetate/cyclohexane solution.

Compound (I)

Crystal data

C₂₈H₃₃NO₄S
 $M_r = 479.61$
 Orthorhombic
 $P2_12_12_1$
 $a = 8.1110 (10) \text{ \AA}$
 $b = 13.449 (2) \text{ \AA}$
 $c = 24.090 (5) \text{ \AA}$
 $V = 2627.9 (7) \text{ \AA}^3$
 $Z = 4$
 $D_x = 1.212 \text{ Mg m}^{-3}$
 D_m not measured

Cu $K\alpha$ radiation
 $\lambda = 1.5418 \text{ \AA}$
 Cell parameters from 25 reflections
 $\theta = 30\text{--}35^\circ$
 $\mu = 1.354 \text{ mm}^{-1}$
 $T = 293 (2) \text{ K}$
 Block
 $0.35 \times 0.30 \times 0.25 \text{ mm}$
 Colourless

Data collection

Enraf–Nonius CAD-4 four-circle diffractometer
 ω scans
 Absorption correction: empirical, measuring nine ψ scans (North *et al.*, 1968)
 $T_{\min} = 0.649$, $T_{\max} = 0.728$
 4809 measured reflections
 4411 independent reflections

4221 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.014$
 $\theta_{\max} = 64.95^\circ$
 $h = -9 \rightarrow 0$
 $k = -15 \rightarrow 13$
 $l = -28 \rightarrow 0$
 3 standard reflections
 frequency: 92 min
 intensity decay: 9.70%

Compound (II)

Crystal data

C₂₉H₃₃NO₆S
 $M_r = 523.62$
 Orthorhombic
 $P2_12_12_1$
 $a = 8.9010 (10) \text{ \AA}$
 $b = 11.935 (2) \text{ \AA}$
 $c = 25.898 (2) \text{ \AA}$
 $V = 2751.2 (6) \text{ \AA}^3$
 $Z = 4$
 $D_x = 1.264 \text{ Mg m}^{-3}$
 D_m not measured

Cu $K\alpha$ radiation
 $\lambda = 1.54180 \text{ \AA}$
 Cell parameters from 25 reflections
 $\theta = 35\text{--}40^\circ$
 $\mu = 1.395 \text{ mm}^{-1}$
 $T = 293 (2) \text{ K}$
 Block
 $0.5 \times 0.3 \times 0.2 \text{ mm}$
 Colourless

Data collection

Enraf–Nonius CAD-4 four-circle diffractometer
 ω scans
 Absorption correction: empirical, measuring nine ψ scans (North *et al.*, 1968)
 $T_{\min} = 0.542$, $T_{\max} = 0.768$
 4256 measured reflections
 4256 independent reflections

3905 reflections with $I > 2\sigma(I)$
 $\theta_{\max} = 65.04^\circ$
 $h = -9 \rightarrow 10$
 $k = 0 \rightarrow 14$
 $l = 0 \rightarrow 30$
 3 standard reflections
 frequency: 92 min
 intensity decay: 10.50%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.042$
 $wR(F^2) = 0.109$
 $S = 1.048$
 4256 reflections
 337 parameters
 H atoms: see below
 $w = 1/[\sigma^2(F_o^2) + (0.0497P)^2 + 0.7913P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.010$
 $\Delta\rho_{\max} = 0.280 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.216 \text{ e } \text{Å}^{-3}$

Table 3. Selected geometric parameters (Å , $^\circ$) for (II)

| | | | |
|--------------|-------------|----------------|-------------|
| O1—C5 | 1.409 (4) | S3—O32 | 1.417 (2) |
| O1—C2 | 1.428 (3) | S3—O31 | 1.429 (2) |
| C2—N3 | 1.502 (3) | S3—C31 | 1.755 (3) |
| N3—C4 | 1.489 (3) | C4—C5 | 1.515 (4) |
| N3—S3 | 1.629 (2) | | |
| C4—N3—C2 | 110.76 (19) | O31—S3—N3 | 106.69 (12) |
| C4—N3—S3 | 118.53 (17) | O32—S3—C31 | 107.16 (15) |
| C2—N3—S3 | 127.16 (16) | O31—S3—C31 | 106.69 (14) |
| O32—S3—O31 | 119.61 (15) | N3—S3—C31 | 107.06 (12) |
| O32—S3—N3 | 109.01 (13) | | |
| C2—N3—S3—O31 | -4.5 (3) | O32—S3—C31—C36 | 11.0 (3) |

Table 4. Hydrogen-bonding geometry (Å , $^\circ$) for (II)

| $D-H \cdots A$ | $D-H$ | $H \cdots A$ | $D \cdots A$ | $D-H \cdots A$ |
|-----------------------|-------|--------------|--------------|----------------|
| O21—H21O \cdots O31 | 0.82 | 1.94 | 2.724 (3) | 158.7 |

Compound (III)

Crystal data

$C_{28}H_{27}NO_5S$
 $M_r = 489.57$
 Orthorhombic
 $P2_12_12_1$
 $a = 11.054 (1) \text{ Å}$
 $b = 14.824 (3) \text{ Å}$
 $c = 15.250 (3) \text{ Å}$
 $V = 2498.9 (7) \text{ Å}^3$
 $Z = 4$
 $D_x = 1.301 \text{ Mg m}^{-3}$
 D_m not measured

Cu $K\alpha$ radiation
 $\lambda = 1.5418 \text{ Å}$
 Cell parameters from 25 reflections
 $\theta = 30\text{--}35^\circ$
 $\mu = 1.472 \text{ mm}^{-1}$
 $T = 293 \text{ K}$
 Block
 $0.6 \times 0.4 \times 0.3 \text{ mm}$
 Colourless

Data collection

Enraf–Nonius CAD-4 four-circle diffractometer
 ω scans
 Absorption correction: empirical, measuring nine ψ scans (North *et al.*, 1968)
 $T_{\min} = 0.557$, $T_{\max} = 0.643$
 2462 measured reflections
 2443 independent reflections

2381 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.029$
 $\theta_{\max} = 64.95^\circ$
 $h = 0 \rightarrow 12$
 $k = 0 \rightarrow 17$
 $l = -17 \rightarrow 1$
 3 standard reflections
 frequency: 92 min
 intensity decay: 1.20%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.029$
 $wR(F^2) = 0.084$
 $S = 1.060$
 2442 reflections
 318 parameters
 H atoms: see below
 $w = 1/[\sigma^2(F_o^2) + (0.0503P)^2 + 0.2923P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.139 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.139 \text{ e } \text{Å}^{-3}$

Table 5. Selected geometric parameters (Å , $^\circ$) for (III)

| | | | |
|--------------|-------------|----------------|-------------|
| O1—C2 | 1.413 (3) | S3—O31 | 1.423 (2) |
| O1—C5 | 1.424 (4) | S3—O32 | 1.433 (2) |
| C2—N3 | 1.482 (3) | S3—C31 | 1.759 (3) |
| N3—C4 | 1.482 (3) | C4—C5 | 1.523 (3) |
| N3—S3 | 1.629 (2) | | |
| C2—N3—C4 | 111.0 (2) | O32—S3—N3 | 106.01 (12) |
| C2—N3—S3 | 128.1 (2) | O31—S3—C31 | 106.99 (12) |
| C4—N3—S3 | 119.8 (2) | O32—S3—C31 | 106.96 (12) |
| O31—S3—O32 | 119.78 (14) | N3—S3—C31 | 108.20 (10) |
| O31—S3—N3 | 108.46 (11) | | |
| C2—N3—S3—O31 | 22.5 (2) | O32—S3—C31—C36 | 25.6 (2) |

H atoms were located by difference Fourier synthesis and refined with fixed individual displacement parameters [$U(H) = 1.5U_{\text{eq}}(O)$, $1.5U_{\text{eq}}(C_{\text{methyl}})$ or $1.2U_{\text{eq}}(C)$] using a riding model with $O-H = 0.82$, $C-H_{\text{methyl}} = 0.96$, $C-H_{\text{secondary}} = 0.97$, $C-H_{\text{tertiary}} = 0.98$ or $C_{\text{sp}^2}-H = 0.93 \text{ Å}$. The methyl groups attached to the aromatic rings were allowed to rotate about their local threefold axis, and the torsion angles about the O—C bonds of the hydroxyl groups were also refined. The displacement ellipsoid of C5 in (I) is slightly elongated perpendicular to the plane of the oxazolidine ring, which might indicate some disorder. The C25—C26 and C23—O24 bond lengths in (II) are rather short. This is due to disorder in the entire ethyl ester group, as can be seen by inspecting the anisotropic displacement parameters of the corresponding atoms. Since the residual electron density was less than $0.3 \text{ e } \text{Å}^{-3}$ in the final difference map, and it was impossible to refine a disordered model for this group, it was refined employing an ordered model.

For all compounds, data collection: *SDP* (Enraf–Nonius, 1985); cell refinement: *SDP*; data reduction: *SDP*; program(s) used to solve structures: *SHELXS86* (Sheldrick, 1990); program(s) used to refine structures: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP (SHELXTL-Plus)*; Sheldrick, 1991)

We thank Professor Dr D. Hoppe, University of Münster, for providing us with the samples.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1328). Services for accessing these data are described at the back of the journal.

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cis-1,2,3,6-Tetrahydrophthalic anhydride at 173 K

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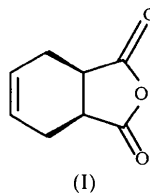
Abstract

The title compound, C₈H₈O₃, (I), crystallizes with two nearly identical molecules in the asymmetric unit. Each molecule has a boat conformation and non-crystallographic mirror symmetry. The structure was determined in connection with a study of the possible chemical decomposition of the compound in different solvents and in contact with the atmosphere. A similar boat conformation was found in five of six structures retrieved from the Cambridge Structural Database which contain (I) as a moiety. The present structure exhibits nearly the same packing motif as the recently found monoclinic polymorph [Ben Fredj, Ben Redjeb, Ben Amor & Driss (1998). *Acta Cryst.* **C54**, 1710–1712].

Comment

The structure of the title compound, (I), was determined by X-ray structure analysis during investigations on

the possibility of chemical decomposition in solution, especially hydrolysis. Solutions of (I) in toluene, hexane, acetone, ether and tetrahydrofuran were exposed to air and diffused daylight for one week. During the time of examination no decomposition could be observed.



There are only a few applications for (I) in chemistry and industry, but it offers very attractive properties as an intermediate or starting material in chemical synthesis because it provides an easy access to other cyclohexene-1,2-dicarboxylic anhydrides and their analogues (Bailey & Amstutz, 1956). Furthermore, it is easily obtainable from maleic anhydride and butadiene. Also, in contrast to many other [4+2]-cycloaddition adducts, its formation is thermally irreversible which provides an explanation for the very good yields in the synthesis described below. (I) was first described by Diels & Alder (1928). They obtained it in theoretical yield by dissolving butadiene and maleic anhydride in a small amount of benzene and leaving this mixture for 12 h in an autoclave at room temperature. Finally, they heated it for 5 h to 373 K. The reported yield could not be reproduced by other authors, but yields better than 90% of the theoretical value have been reported (Kohler & Jansen, 1938; Jenkins & Costello, 1946; Fieser & Novello, 1942). As expected, no *trans* adduct is formed during the synthesis. Another application of (I) was reported by Fieser & Novello (1942), using it as a starting material for the synthesis of a benzanthracene compound.

(I) crystallizes with two nearly identical molecules in the asymmetric unit. A least-squares fit between all non-H atoms gives an r.m.s. deviation of 0.021 Å. Each molecule has approximate mirror symmetry. Additional symmetry elements between the similar moieties could not be detected. Bond lengths and angles do not show any extraordinary values. The molecules have a boat conformation with a central plane (C4, C5, C8, C9 and C4A, C5A, C8A, C9A, respectively), a bow plane (C9, C1, O2, C3, C4 and C9A, C1A, O2A, C3A, C4A, respectively) and a stern plane (C5, C6, C7, C8 and C5A, C6A, C7A, C8A, respectively). The dihedral angles are 61.02(6) and 61.17(6)° between the central plane and the bow plane, and 47.28(6) and 48.08(6)° between the central plane and the stern plane. A search of the Cambridge Structural Database (Allen & Kennard, 1993; Version 5.15, April 1998) revealed that (I) appears as a moiety of six structures. In five of them (Lee, Peng, Lush, Mu & Liu, 1988; Lee, Peng,