Orthorombic
Pbca
$a = 8,5970\ (10)$ Å
$b = 15,420\ (2)$ Å
$c = 22,449\ (3)$ Å
$V = 2976,0\ (7)$ Å^3
$Z = 8$
$D_x = 1,488$ Mg m^{-3}
$D_m = 1,49\ (2)$ Mg m^{-3}
D_m mesurée par flotation

Paramètres de la maille à l'aide de 25 réflexions
$\theta = 2$–$35°$
$\mu = 0,248$ mm^{-1}
$T = 293\ (2)$ K
Parallélépipède
0,4 × 0,4 × 0,2 mm
Jaune

Collection des données

Diffractomètre Nonius CAD-4
Balayage θ
Pas de correction d'absorption
3034 réflexions mesurées
3034 réflexions indépendantes

1788 réflexions avec $I > 2\sigma(I)$
$\theta_{\max} = 34,60°$
$h = 0 \rightarrow 9$
$k = 0 \rightarrow 16$
$l = 0 \rightarrow 23$
3 réflexions de référence fréquence: 60 min variation d'intensité: néant

Affinement

Affinement à partir des F^2
$R[F^2 > 2\sigma(F^2)] = 0,044$
$wR(F^2) = 0,089$
$S = 1,292$
3034 réflexions
241 paramètres
Tous les paramètres des atomes d'hydrogène affinés

$w = 1/[\sigma^2(F_o^2) + (0,0250P)^2]$ où $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0,023$
$\Delta\rho_{\max} = 0,332$ e Å^{-3}
$\Delta\rho_{\min} = -0,281$ e Å^{-3}
Pas de correction d'extinction
Facteurs de diffusion des *International Tables for Crystallography* (Vol. C)

Tableau 1. *Paramètres géométriques (Å, °)*

C1—C2	1,376 (3)	N10—O12	1,221 (3)
C1—C6	1,421 (3)	S13—C14	1,773 (2)
C1—N7	1,452 (3)	C14—C15	1,388 (4)
C2—C3	1,378 (4)	C14—C19	1,417 (3)
C3—C4	1,385 (4)	C15—C16	1,374 (4)
C3—N10	1,464 (3)	C16—C17	1,369 (4)
C4—C5	1,370 (4)	C17—C18	1,386 (4)
C5—C6	1,405 (3)	C18—C19	1,378 (3)
C6—S13	1,771 (3)	C19—N20	1,404 (3)
N7—O9	1,229 (3)	N20—C21	1,370 (3)
N7—O8	1,222 (3)	C21—O23	1,199 (3)
N10—O11	1,230 (3)	C21—C22	1,494 (4)
C2—C1—C6	122,6 (2)	O12—N10—C3	118,0 (3)
C2—C1—N7	116,7 (2)	C6—S13—C14	102,0 (1)
C6—C1—N7	120,7 (2)	C15—C14—C19	119,2 (2)
C3—C2—C1	118,0 (2)	C15—C14—S13	118,6 (2)
C2—C3—C4	122,1 (2)	C19—C14—S13	122,0 (2)
C2—C3—N10	118,9 (2)	C16—C15—C14	121,1 (3)
C4—C3—N10	119,1 (2)	C17—C16—C15	119,7 (3)
C5—C4—C3	119,1 (2)	C16—C17—C18	120,5 (3)
C4—C5—C6	122,0 (2)	C17—C18—C19	120,9 (3)
C5—C6—C1	116,2 (2)	C18—C19—N20	123,8 (2)
C5—C6—S13	122,1 (2)	C18—C19—C14	118,6 (2)
C1—C6—S13	121,7 (2)	N20—C19—C14	117,6 (2)
O9—N7—O8	122,1 (2)	C21—N20—C19	128,4 (2)
O9—N7—C1	118,1 (3)	O23—C21—N20	123,9 (3)
O8—N7—C1	119,8 (2)	O23—C21—C22	122,6 (3)
O11—N10—O12	123,7 (3)	N20—C21—C22	113,5 (2)
O11—N10—C3	118,3 (3)		

Collection des données: *CAD*-4 *Software* (Enraf–Nonius, 1989). Affinement des paramètres de la maille: *CAD*-4 *Software*. Programme(s) pour la solution de la structure: *SHELXS*86 (Sheldrick, 1990). Programme(s) pour l'affinement de la structure: *SHELXL*93 (Sheldrick, 1993). Graphisme moléculaire: *ORTEP*II (Johnson, 1976).

Des documents complémentaires concernant cette structure peuvent être obtenus à partir des archives électroniques de l'UICr (Référence: DU1181). Les processus d'accès à ces archives est donné au dos de la couverture.

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Synthesis and Absolute Structure Determination of Camphanoate Derivatives of Five Bicyclo[3.1.0]hexane Compounds

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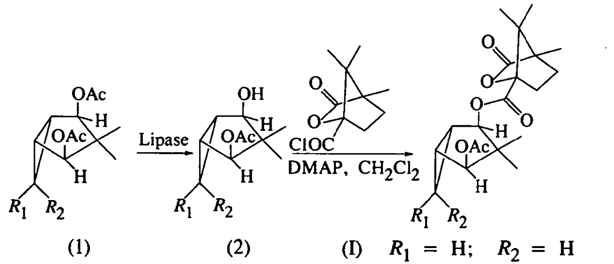
Abstract

The relative and absolute stereochemistry of five compounds, (1*R*,2*S*,4*R*,5*S*)-*exo*-2-acetoxy-3,3-dimethylbicyclo[3.1.0]hexan-*exo*-4-yl camphanoate, $C_{20}H_{28}O_6$, (I), (1*R*,2*S*,4*R*,5*S*,6*R*)-*exo*-2-acetoxy-3,3,*exo*-6-trimethylbicyclo[3.1.0]hexan-*exo*-4-yl camphanoate, $C_{21}H_{30}O_6$, (II), (1*R*,2*S*,4*R*,5*S*,6*S*)-*exo*-2-acetoxy-3,3,*endo*-6-trimethylbicyclo[3.1.0]hexan-*exo*-4-yl camphanoate, $C_{21}H_{30}O_6$, (III), (1*S*,2*S*,4*R*,5*R*,6*S*)-*exo*-2-acetoxy-*endo*-6-(3-butenyl)-3,3,*exo*-6-trimethylbicyclo[3.1.0]hexan-*exo*-4-yl

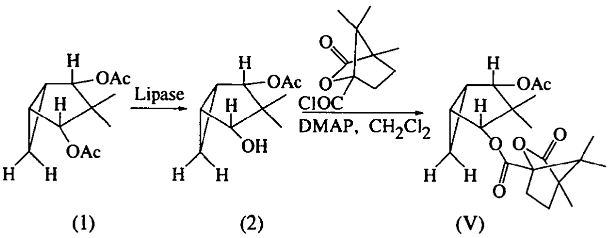
camphanoate, $C_{25}H_{36}O_6$, (IV), and (1*S*,2*S*,4*R*,5*R*,6*S*)-*endo*-2-acetoxy-3,3,*exo*-6-trimethylbicyclo[3.1.0]hexan-*endo*-4-yl camphanoate, $C_{21}H_{30}O_6$, (V), (camphanoate is 4,7,7-trimethyl-3-oxo-2-oxabicyclo[2.2.1]heptane-1-carboxylate) have been determined and the conformation of the five-membered ring of each one is discussed. These compounds were synthesized by an enantioselective esterase-catalysed hydrolysis followed by acylation with camphanoyl chloride.

Comment

Enzymatic hydrolysis of diacetates derived from *meso*-diols can produce hydroxyacetates with high enantiomeric purity (Shoffers *et al.*, 1996). In this context, we have recently disclosed a novel enantioselective synthesis of (1*R*)-*cis*-chrysanthemic acid (Krief *et al.*, 1993), the crucial step of which is the esterase-catalysed hydrolysis of a *meso*-bicyclo[3.1.0]hexane diacetate. Some esters of (1*R*)-*cis*- and (1*R*)-*trans*-chrysanthemic acid are among the most powerful insecticides (Elliott & Janes, 1978) and their synthesis in high yield and with high enantiomeric purity is a major industrial goal. For that reason, we have studied the key reaction (see scheme below) of our synthesis on a series of *meso*-diacetates, (1), possessing the bicyclo[3.1.0]hexane skeleton and bearing two acetoxy groups in 1,3 positions with different orientations (di-*exo* or di-*endo*). The reaction takes place efficiently, especially with di-*exo* derivatives, producing, after 1–3 days, γ-hydroxyacetates, (2), in high yield and with very high enantioselectivity (>95%) (Ollevier, 1997; Swinnen, 1997). The enantiomeric excesses have been determined by ^1H and ^{19}F NMR studies of their Mosher esters (Dale & Mosher, 1973; Dale *et al.*, 1969).



(I) R_1 = H; R_2 = H
(II) R_1 = Me; R_2 = H
(III) R_1 = H; R_2 = Me
(IV) R_1 = Me;
R_2 = $H_2C{=}CH(CH_2)_2$



We wanted to determine the relative and absolute stereochemistry of the five hydrolysis products of (2). The relative stereochemistry of H*b* and H*a* on the five-membered ring can be established by ^1H NMR: the J_{a-b} coupling constant in the *exo* series is between 0 and 2 Hz, and in the *endo* series around 5 Hz. For the absolute stereochemistry determination, we have used the method of Eberle *et al.* (1988). These authors studied camphanoate derivatives of hydroxyacetates by single-crystal X-ray diffraction. Therefore, we reacted the γ-hydroxyacetates, (2), with (−)-(1*S*,4*R*)-camphanoyl chloride in order to produce the camphanoates (I)–(V). This reaction can produce a mixture of two diastereoisomers, but due to the very high enantioselectivity of the enzymatic hydrolysis, the minor diastereoisomer was undetectable.

Compound (I) (Fig. 1) has the absolute configuration 1*R*,2*S*,4*R*,5*S*,12*S*,15*R*. The carbonyl O2 atom [U_{eq} = 0.1058 (8) Å^2] and to a lesser extent O6 [U_{eq} = 0.0834 (6) Å^2] are very agitated. The five-membered ring C1–C5 is in the 'envelope' conformation (C_s symmetry), characterized by the theoretical sequence of torsion angles: $-\omega_1$, ω_2, $-\omega_2$, ω_1 and 0 (Dunitz, 1979). This sequence is fairly well observed in the table of torsion angles (Table 1). In this ring, as shown in Fig. 1, atom C3 is in the lower region of the plane defined by the other four atoms.

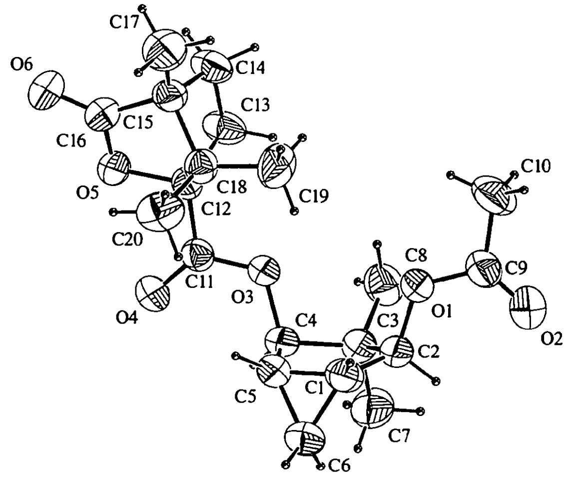


Fig. 1. The molecular structure of compound (I). Displacement ellipsoids are drawn at the 50% probability level.

Compound (II) (Fig. 2) has the absolute configuration 1*R*,2*S*,4*R*,5*S*,6*R*,12*S*,15*R*. Here too, the carbonyl O2 atom is agitated [U_{eq} = 0.0809 (6) Å^2], as well as the terminal C atom (C10) of the acetate group [U_{eq} = 0.0828 (9) Å^2]. The five-membered ring C1–C5 is in the 'envelope' conformation, as can be seen from the characteristic sequence of the torsion-angle values (Table 1), which is also the case for compound (I). In this ring, atom

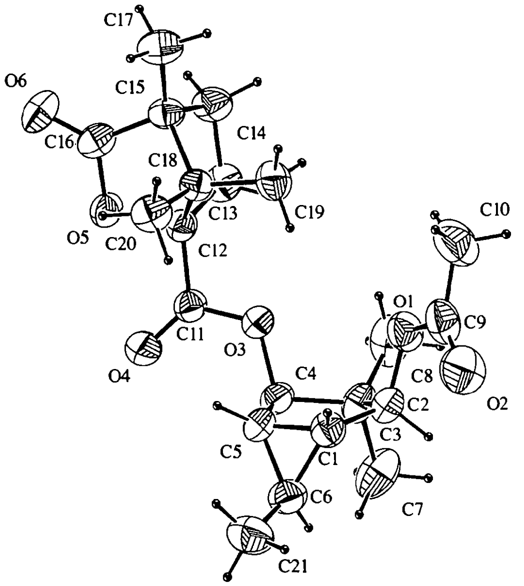


Fig. 2. The molecular structure of compound (II). Displacement ellipsoids are drawn at the 50% probability level.

C3 is in the lower region of the plane defined by the other four atoms.

Compound (III) (Fig. 3) has the absolute configuration 1*R*,2*S*,4*R*,5*S*,6*S*,12*S*,15*R*. In this structure, all atoms are globally more agitated than in the other four compounds presented: the mean U_{eq} for the heavy atoms has a value of 0.0799 Å^2 (the origin of this situation is discussed in the *Experimental*). The carbonyl O2 atom is very agitated [U_{eq} = 0.1527 (19) Å^2], as are a series of terminal C atoms with U_{eq} values greater than 0.10 Å^2 (C7, C10, C17 and C19). The five-membered ring C1–C5 is in the 'envelope' conformation, with a sequence of torsion angles (Table 1) inverted compared with the sequences for the first two compounds (ω_1, $-\omega_2$, ω_2, $-\omega_1$ and 0). In this ring, as shown in Fig. 3, atom C3 is in the upper region of the plane defined by the other four atoms.

Compound (IV) (Fig. 4) has the absolute configuration 1*S*,2*S*,4*R*,5*S*,6*S*,12*S*,15*R*. The two C atoms, C24 and C25, of the terminal double bond of the butenyl substituant are strongly agitated [U_{eq} = 0.133 (2) and 0.172 (3) Å^2], as are the two carbonyl oxygen atoms O2 and O6 [U_{eq} = 0.1073 (10) and 0.1147 (11) Å^2]. The five-membered ring C1–C5 is in the same 'envelope' conformation as compound (III), as can be seen from the characteristic values of the torsion angles (Table 1). Consequently, atom C3 is also in the upper region of the plane defined by the four other atoms.

Compound (V) (Figs. 5 and 6) crystallizes with two molecules in the asymmetric unit. The numbering of the atoms runs from 1 to 21 for the first, and from 31 to 51 for the second. As can be seen in Figs. 5 and 6, these two molecules differ in the relative positions of the camphanoate group and the bicyclo[3.1.0]hexane skeleton. The absolute configuration of compound (V) is 1*S*,2*S*,4*R*,5*R*,6*R*,12*S*,15*R* for the first conformer and 31*S*,32*S*,34*R*,35*R*,36*R*,42*S*,45*R* for the second. In the first conformer, two O atoms (O2 and O4) of the carbonyl functions are strongly agitated [U_{eq} = 0.1330 (15) and 0.212 (3) Å^2]; this situation is discussed in the *Experimental*. To a lesser extent, this is also the case for the carbonyl O6 atom [U_{eq} = 0.0993 (9) Å^2]. The terminal C atoms C8, C17 and C20 are also agitated [U_{eq} = 0.0965 (13),

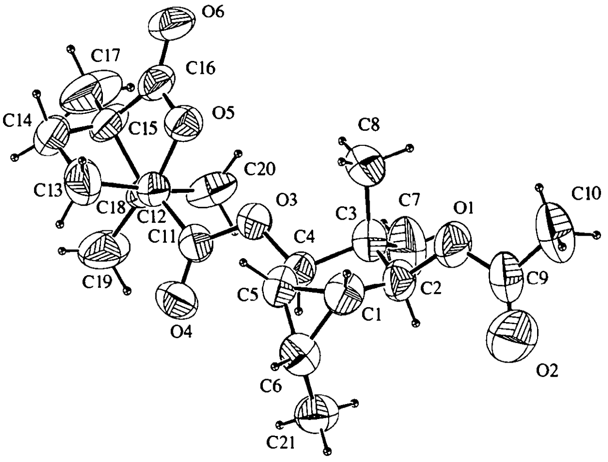


Fig. 3. The molecular structure of compound (III). Displacement ellipsoids are drawn at the 50% probability level.

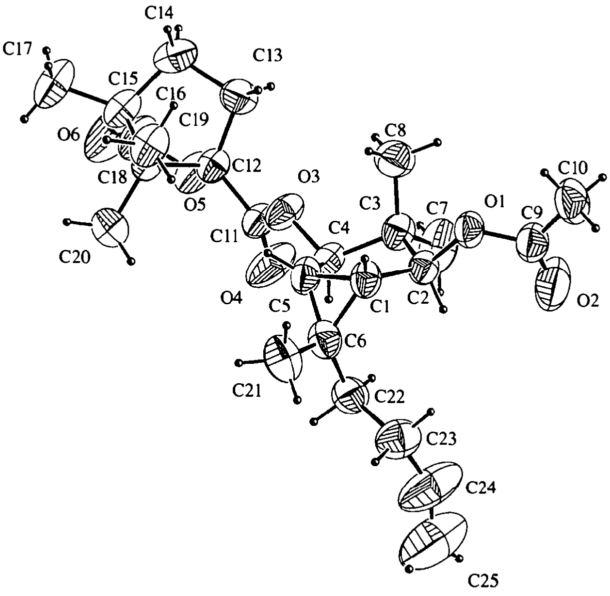


Fig. 4. The molecular structure of compound (IV). Displacement ellipsoids are drawn at the 50% probability level.

0.1057 (15) and 0.0969 (13) Å^2, respectively]. In the second conformer, only the carbonyl O32 atom has high thermal motion [U_{eq} = 0.1236 (14) Å^2], as discussed in the *Experimental*. The five-membered rings C1–C5 and C31–C35 are in the same 'envelope' conformation as compounds (III) and (IV), as can be seen from the characteristic values of the torsion angles (Table 1). Atoms C3 and C33 are thus in the upper region of the planes defined by the other four atoms of their respective rings.

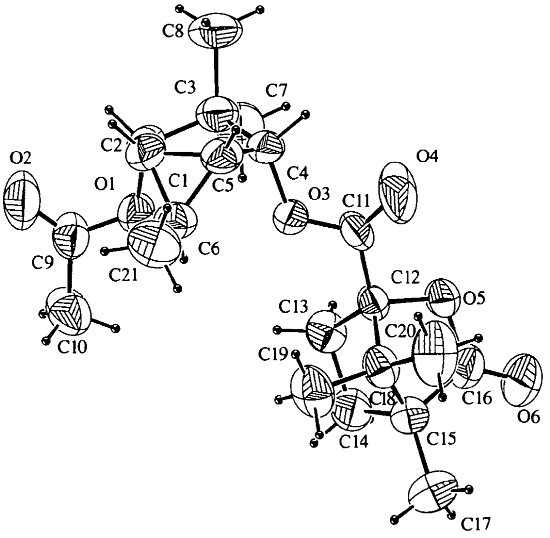


Fig. 5. The molecular structure of the first of the two conformers forming the asymmetric unit of compound (V). Displacement ellipsoids are drawn at the 50% probability level.

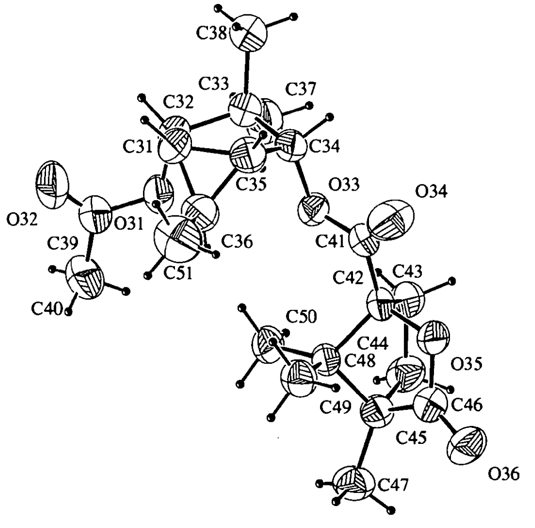


Fig. 6. The molecular structure of the second of the two conformers forming the asymmetric unit of compound (V). Displacement ellipsoids are drawn at the 50% probability level.

In some of the structures presented, the terminal C and O atoms present strong thermal agitation, contrasting with that of other atoms involved in the ring systems. This is particularly true for the terminal C atoms of the butenyl substituent of compound (IV), but also for the carbonyl O atoms (particularly O2 and O32). Here, however, atoms O2 and O32 do not take part in hydrogen bonds, which could have reduced their motion.

The five-membered ring C1–C5 [and C31–C35 for compound (V)] adopts an 'envelope' conformation in all cases, but molecules of (I) and (II) possess inverted torsion angles with respect to those of the other molecules. This conformational inversion reduces the steric interactions due to the presence, for compounds (III), (IV) and (V), of supplementary substituents in the *endo* region of the bicyclo[3.1.0]hexane skeleton.

Experimental

The experimental details of the enzymatic hydrolysis will be published elsewhere. For the preparation of its camphanoate derivatives, the γ-hydroxyacetate (2), dissolved with excess amounts of 4-*N*,*N*-dimethylaminopyridine (DMAP) (3–10 equivalents) in dichloromethane, was heated at reflux of the solvent during 5–10 h with a slight excess of (−)-(1*S*,4*R*)-camphanoyl chloride (Aldrich). The reaction mixture was then hydrolysed with water, extracted with dichloromethane and finally the organic phase was dried over magnesium sulfate. The crude product was purified by chromatography on SiO_2 eluted with a pentane–ether (60/40 *v*/*v*) mixture [m.p. 360–361 for (I), 416 for (II), 403 for (III), 390 for (IV) and 348 K for (V); yields 51% (I), 71% (II), 88% (III), 75% (IV) and 100% (V)]. The crystallization of the five compounds for X-ray diffraction study was conducted in mixtures of ethyl acetate and pentane (80/20 *v*/*v*) for compounds (I) and (V), in ether for compounds (II) and (III), and in a mixture of hexane and diisopropyl ether (25/75 *v*/*v*) for compound (IV). In all cases, the crystals were grown very rapidly, without special care.

Compound (I)

Crystal data

$C_{20}H_{28}O_6$
M_r = 364.42
Monoclinic
$P2_1$
a = 11.5461 (11) Å
b = 12.2484 (7) Å
c = 7.169 (5) Å
β = 102.487 (4)°
V = 989.9 (7) Å^3
Z = 2
D_x = 1.223 Mg m^{-3}
D_m not measured

Cu $K\alpha$ radiation
λ = 1.54178 Å
Cell parameters from 25 reflections
θ = 40–50°
μ = 0.735 mm^{-1}
T = 292 (2) K
Trigonal prism
0.30 × 0.30 × 0.30 mm
Transparent, colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none

θ_{max} = 71.89°
$h = -14 \rightarrow 13$
$k = -13 \rightarrow 15$
$l = 0 \rightarrow 8$

3350 measured reflections
3207 independent reflections
3076 reflections with $I > 2\sigma(I)$
$R_{\text{int}} = 0.026$
3 standard reflections
frequency: 60 min
intensity decay: 4.0%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.043$
$wR(F^2) = 0.109$
$S = 1.084$
3207 reflections
234 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0772P)^2 + 0.0068P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\text{max}} < 0.001$
$\Delta\rho_{\text{max}} = 0.238$ e Å^{-3}
$\Delta\rho_{\text{min}} = -0.336$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute structure: Flack (1983)
Flack parameter = −0.03 (18)

Compound (II)

Crystal data

$C_{21}H_{30}O_6$
$M_r = 378.45$
Orthorhombic
$P2_12_12_1$
$a = 12.806$ (1) Å
$b = 22.332$ (3) Å
$c = 7.2582$ (10) Å
$V = 2075.7$ (4) Å^3
$Z = 4$
$D_x = 1.211$ Mg m^{-3}
D_m not measured
Cu $K\alpha$ radiation
$\lambda = 1.54178$ Å
Cell parameters from 25 reflections
$\theta = 40\text{–}50°$
$\mu = 0.719$ mm^{-1}
$T = 292$ (2) K
Hexagonal prism
0.40 × 0.24 × 0.10 mm
Transparent, colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
3188 measured reflections
2860 independent reflections
2710 reflections with $I > 2\sigma(I)$
$R_{\text{int}} = 0.012$
$\theta_{\text{max}} = 71.75°$
$h = 0 \rightarrow 15$
$k = -27 \rightarrow 20$
$l = 0 \rightarrow 8$
3 standard reflections
frequency: 60 min
intensity decay: 4.0%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.039$
$wR(F^2) = 0.103$
$S = 1.087$
2860 reflections
244 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0647P)^2 + 0.0271P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\text{max}} = 0.001$
$\Delta\rho_{\text{max}} = 0.195$ e Å^{-3}
$\Delta\rho_{\text{min}} = -0.261$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute structure: Flack (1983)
Flack parameter = −0.1 (2)

Compound (III)

Crystal data

$C_{21}H_{30}O_6$
$M_r = 378.45$
Orthorhombic
$P2_12_12_1$
$a = 9.545$ (1) Å
$b = 32.428$ (5) Å
$c = 6.810$ (1) Å
$V = 2107.7$ (5) Å^3
$Z = 4$
$D_x = 1.193$ Mg m^{-3}
D_m not measured
Cu $K\alpha$ radiation
$\lambda = 1.54178$ Å
Cell parameters from 25 reflections
$\theta = 40\text{–}50°$
$\mu = 0.708$ mm^{-1}
$T = 292$ (2) K
Parallelepiped
0.30 × 0.12 × 0.05 mm
Transparent, colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (*NRCVAX*; Gabe *et al.*, 1989)
$T_{\text{min}} = 0.836$, $T_{\text{max}} = 0.997$
3457 measured reflections
3086 independent reflections
1974 reflections with $I > 2\sigma(I)$
$R_{\text{int}} = 0.033$
$\theta_{\text{max}} = 71.97°$
$h = -8 \rightarrow 11$
$k = -29 \rightarrow 40$
$l = -6 \rightarrow 8$
3 standard reflections
frequency: 60 min
intensity decay: 15%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.056$
$wR(F^2) = 0.159$
$S = 0.980$
3086 reflections
244 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.1009P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\text{max}} < 0.001$
$\Delta\rho_{\text{max}} = 0.146$ e Å^{-3}
$\Delta\rho_{\text{min}} = -0.196$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute structure: Flack (1983)
Flack parameter = 0.1 (4)

Compound (IV)

Crystal data

$C_{25}H_{36}O_6$
$M_r = 432.54$
Monoclinic
$P2_1$
$a = 15.580$ (1) Å
$b = 12.889$ (1) Å
$c = 6.2360$ (1) Å
$\beta = 99.051$ (4)°
$V = 1236.63$ (13) Å^3
$Z = 2$
$D_x = 1.162$ Mg m^{-3}
D_m not measured
Cu $K\alpha$ radiation
$\lambda = 1.54178$ Å
Cell parameters from 25 reflections
$\theta = 40\text{–}50°$
$\mu = 0.662$ mm^{-1}
$T = 292$ (2) K
Parallelepiped
0.30 × 0.30 × 0.18 mm
Transparent, colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
3971 measured reflections
3476 independent reflections
3289 reflections with $I > 2\sigma(I)$
$R_{\text{int}} = 0.030$
$\theta_{\text{max}} = 71.90°$
$h = -18 \rightarrow 19$
$k = -15 \rightarrow 11$
$l = -7 \rightarrow 0$
3 standard reflections
frequency: 60 min
intensity decay: 7%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.049$
$wR(F^2) = 0.130$
$S = 1.081$
3476 reflections
280 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0878P)^2 + 0.0639P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.233$ e Å^{-3}
$\Delta\rho_{\min} = -0.336$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute structure: Flack (1983)
Flack parameter = −0.4 (2)

Compound (V)

Crystal data

$C_{21}H_{30}O_6$
$M_r = 756.90$
Monoclinic
$P2_1$
$a = 14.714$ (1) Å
$b = 11.001$ (1) Å
$c = 14.736$ (2) Å
$\beta = 118.527$ (8)°
$V = 2095.7$ (4) Å^3
$Z = 4$
$D_x = 1.199$ Mg m^{-3}
D_m not measured

Cu $K\alpha$ radiation
$\lambda = 1.54178$ Å
Cell parameters from 25 reflections
$\theta = 40$–$50°$
$\mu = 0.712$ mm^{-1}
$T = 292$ (2) K
Irregular shape
0.40 × 0.40 × 0.12 mm
Transparent, colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
6383 measured reflections
5869 independent reflections
5357 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.015$

$\theta_{\max} = 71.83°$
$h = -18 \rightarrow 15$
$k = -10 \rightarrow 13$
$l = 0 \rightarrow 18$
3 standard reflections
frequency: 60 min
intensity decay: 6%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.048$
$wR(F^2) = 0.133$
$S = 1.045$
5869 reflections
486 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0833P)^2 + 0.1229P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.002$
$\Delta\rho_{\max} = 0.431$ e Å^{-3}
$\Delta\rho_{\min} = -0.364$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute structure: Flack (1983)
Flack parameter = 0.0 (2)

Table 1. *Selected torsion angles (°)*

(I)			
C5—C1—C2—C3	−11.7 (2)	C3—C4—C5—C1	15.6 (2)
C1—C2—C3—C4	20.5 (2)	C2—C1—C5—C4	−2.3 (2)
C2—C3—C4—C5	−22.1 (2)		
(II)			
C5—C1—C2—C3	−14.0 (2)	C3—C4—C5—C1	13.1 (2)
C1—C2—C3—C4	21.3 (2)	C2—C1—C5—C4	0.6 (2)
C2—C3—C4—C5	−21.0 (2)		
(III)			
C5—C1—C2—C3	21.8 (4)	C3—C4—C5—C1	−22.1 (4)
C1—C2—C3—C4	−33.8 (4)	C2—C1—C5—C4	0.4 (4)
C2—C3—C4—C5	34.1 (4)		
(IV)			
C5—C1—C2—C3	21.2 (2)	C2—C1—C5—C4	−1.5 (3)
C1—C2—C3—C4	−31.4 (2)	C3—C4—C5—C1	−18.7 (3)
C2—C3—C4—C5	30.6 (2)		
(V)			
C5—C1—C2—C3	−21.5 (3)	C35—C31—C32—C33	−19.6 (3)
C1—C2—C3—C4	32.3 (3)	C31—C32—C33—C34	30.3 (3)
C2—C3—C4—C5	−31.1 (3)	C32—C33—C34—C35	−29.4 (3)
C3—C4—C5—C1	18.4 (3)	C33—C34—C35—C31	17.5 (3)
C2—C1—C5—C4	1.8 (3)	C32—C31—C35—C34	1.3 (3)

During data reduction, corrections for background noise, Lorentz–polarization (Lp) and crystal degradation were applied. The non-H atoms were refined with anisotropic displacement parameters and the H atoms were treated by a mixture of independent and constrained refinement. For compound (III), an absorption correction by ψ scan was applied to the data because the crystal was a needle, causing important variations in transmission lengths of the diffracted rays. For this crystal also, the thermal-agitation factors are globally very high. Due to the data collection strategy, the data at high θ angles were measured last, when crystal degradation was important (15% of decrease in intensity of control reflections). Therefore, the quality of these (generally) low-intensity data is poor and could explain, in part, the high thermal agitation. For compound (V), the thermal-agitation parameters of the carbonyl oxygen atoms O2, O4 and O32 have very important values that could be considered as abnormal. But the carbonyl carbon atoms C9, C11 and C39 directly connected to the O atoms are considerably less agitated. Therefore, these values are the image of a large out-of-plane bending and it is not necessary to introduce supplementary atomic sites with fractional occupancy.

For all compounds, data collection: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1992), cell refinement: *CAD*-4 *EXPRESS*. Data reduction: *NONIUS*93 (Baudoux & Evrard, 1993) for compounds (I), (II), (IV) and (V); *NRCVAX* (Gabe *et al.*, 1989) for (III). For all compounds, structure solution: *SIR*92 (Altomare *et al.*, 1993); structure refinement: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 1990).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1154). Services for accessing these data are described at the back of the journal.

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The First Structural Characterization of a Sulfoximidium Salt

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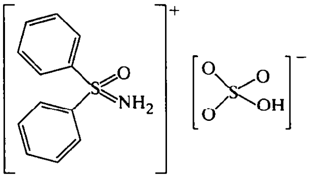
Abstract

The title compound, diphenylsulfoximidium hydrogen sulfate, $C_{12}H_{12}NOS^+.HSO_4^-$, was formed as a hydrolysis product during recrystallization of the product of the reaction of Ph_2SO with $(NSCl)_3$. Hydrogen-bonded networks link the cation and anion, the latter forming a hydrogen-bonded dimer.

Comment

It has been previously reported (Becke-Goehring & Latscha, 1962) that reaction of Me_2SO with $(NSCl)_3$ yielded the compound $[Me_2SNSMe_2][Cl]$. We have been interested in exploring this synthetic methodology to prepare new derivatives, including $[Ph_2SNSPh_2][Cl]$, which has been prepared previously by alternative routes (Furukawa *et al.*, 1973). In the course of our work investigating the reactivity of Ph_2SO with $(NSCl)_3$, we crystallized the title compound, (I), as a hydrolysis product. Hydrolysis probably occurs in the recrystallization for which the acetone solvent was not dried.



(I)

In (I), the cation is composed of a pseudo-tetrahedral S atom bonded to two phenyl groups, an amine group and an O atom (Fig. 1). The hydrogen sulfate counterion exhibits some disorder which has been modelled over three sites with site occupancies in the approximate ratio 0.74:0.17:0.09. Cations and anions are linked together through an N—H···O hydrogen-bonding network [N···O 2.824 (5) Å]. Hydrogen bonding also leads to the hydrogen sulfate anions forming dimers, with an O···O distance of 2.596 (8) Å. In addition, there is a close contact between an *ortho*-phenyl-H atom and a neighbouring O atom of a hydrogen sulfate anion [O5···C12 3.318 (5) Å].

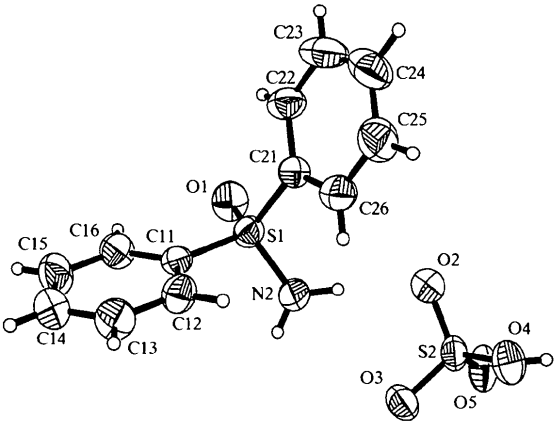


Fig. 1. The asymmetric unit of (I) showing the atom-labelling scheme and 50% probability displacement ellipsoids. Only the major component of the hydrogen sulfate disorder is shown for clarity.

Experimental

The synthesis of (I) was carried out by reaction of Ph_2SO and $(NSCl)_3$ in a 6:1 molar ratio in CCl_4. The solution was refluxed for 18 h and then cooled to room temperature. CCl_4 was removed *in vacuo* and the residue dissolved in acetone. Crystals suitable for X-ray diffraction formed over the course of 3–4 d.

Crystal data

$C_{12}H_{12}NOS^+.HSO_4^-$	Mo $K\alpha$ radiation
$M_r = 315.35$	$\lambda = 0.71069$ Å