320 measured reflections
309 independent reflections
281 observed reflections
  [$I \geq 1.96\sigma(I)$]

2 standard reflections
  monitored every 50
    reflections
  intensity variation: ±0.5%

Refinement

Refinement on F
$R = 0.0319$
$wR = 0.0366$
$S = 1.32$
281 reflections
53 parameters
All H-atom parameters
  refined

$w = 1/\sigma^2(F_o)$
$(\Delta/\sigma)_{\max} = 0.2$
$\Delta\rho_{\max} = 0.18$ e Å^{-3}
$\Delta\rho_{\min} = -0.16$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *SHELX*76 (Sheldrick, 1976)

Table 1. *Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters* (Å^2)

$U_{\rm iso}$ for H atoms; $U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$ for others.

	x	y	z	$U_{\rm iso}/U_{\rm eq}$
N	0.5464 (4)	0	0.0915 (12)	0.0578
O(1)	0.6512 (4)	0	0.1271 (12)	0.0830
O(2)	0.5007 (3)	0.1508 (2)	0.0957 (10)	0.0833
C	0.2000†	0	0.0000†	0.0562
N(1)	0.0971 (6)	0	−0.0235 (18)	0.0850
N(2)	0.2586 (4)	0.1533 (5)	0.0332 (17)	0.0806
H(1)	0.079 (3)	0.093 (5)	−0.005 (8)	0.032 (9)
H(2)	0.299 (5)	0.148 (4)	−0.005 (9)	0.011 (8)
H(3)	0.221 (5)	0.236 (8)	0.060 (15)	0.084 (15)

† Coordinate fixed to define origin.

Table 2. *Selected geometric parameters* (Å, °)

C—N(1)	1.264 (9)	N(2)—H(3)	0.80 (6)
C—N(2)	1.311 (4)	N—O(1)	1.269 (8)
N(1)—H(1)	0.73 (4)	N—O(2)	1.244 (4)
N(2)—H(2)	0.61 (6)		
N(1)—C—N(2)	121.6 (2)	C—N(2)—H(3)	107 (5)
N(2)—C—N(2$^{\rm i}$)	116.6 (4)	O(1)—N—O(2)	117.97 (11)
C—N(1)—H(1)	111 (3)	O(2)—N—O(2$^{\rm i}$)	123.7 (3)
C—N(2)—H(2)	116 (3)		

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

Table 3. *Hydrogen-bonding geometry* (Å, °)

D	H	A	H···A	D···A	D—H···A
N(1)	H(1)	O(2$^{\rm ii}$)	2.23 (4)	2.945 (6)	168 (4)
N(2)	H(2)	O(2)	2.39 (6)	2.962 (8)	160 (4)
N(2)	H(3)	O(1$^{\rm ii}$)	2.18 (6)	2.968 (6)	167 (6)

Symmetry code: (ii) $x - \frac{1}{2}, \frac{1}{2} - y, z$.

Owing to the crystals very high elasticity they could not be cut or shaped and it is possible that the defects in the samples resulted in broadening of the reflection peaks. The crystal diffraction symmetry was determined by precession and Weissenberg methods. The unit cell was chosen in the way corresponding to the crystal morphology and its microstructure. Thus, [100] lies along the sheets of hydrogen-bonded ions, which is not consistent with the Niggli cell parameter a_N = 10.931 Å (*cf. Crystal Data*). As a result of all crystals having reflections broader than normal, presumably because of the low quality of the highly elastic crystals, an appropriately wider scan range of 2.0° was applied. 2θ-θ scan method and a variable scan speed (1.0-20.0° min^{-1}) depending on reflection intensity were applied. The intensities were corrected for Lp effects. The structure was solved by the Patterson method and H atoms were located from difference Fourier maps. The function minimized was $\Sigma w(|F_o|-|F_c|)^2$. Most of the calculations were performed with *SHELX*76 (Sheldrick, 1976); all calculations were performed on an IBM 486DX computer.

This study was supported by the Polish Committee of Scientific Research (project 2-0662-91-01).

Lists of structure factors and anisotropic displacement parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71808 (3 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HU1064]

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Acta Cryst. (1994). C**50**, 1163–1165

N,N′-Bis(2-hydroxypropyl)dithiooxamide

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(*Received* 22 *February* 1993; *accepted* 26 *November* 1993)

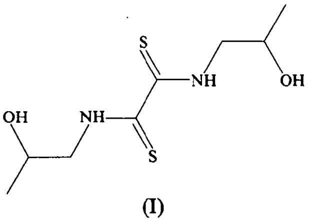
Abstract

The molecular structure of *N,N′*-bis(2-hydroxypropyl)dithiooxamide, $C_8H_{16}N_2O_2S_2$, belongs to the C_i point group, with only half of the molecule in an asymmetric unit. The dithiooxamide part of the molecule is planar with normal bond distances and angles. There are intermolecular hydrogen bonds

between hydroxyl groups of the *n*-glide related molecules with a corresponding O···O distance of 2.758 (2) Å.

Comment

The title compound, (I), is an intermediate product of the total synthesis of 5,5′-dimethyl-2,2′-bi-2-thiazoline (Tomalia & Paige, 1973). It forms a spin-crossover complex with iron(II) together with the thiocyanate ion (Bradley, Mackee & Nelson, 1978).



(I)

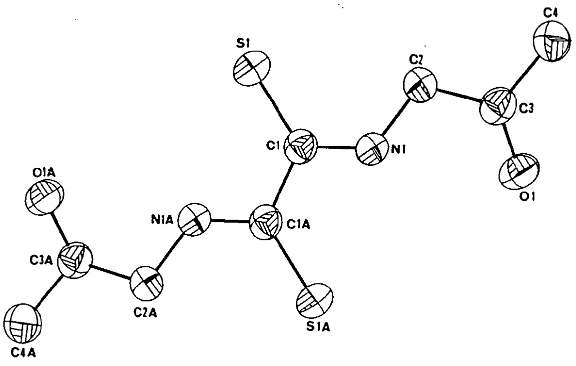


Fig. 1. *ORTEP* (Johnson, 1965) drawing of the molecule with 50% probability displacement ellipsoids.

Experimental

Crystal data

$C_8H_{16}N_2O_2S_2$
$M_r = 236$
Monoclinic
$P2_1/n$
$a = 6.756\ (1)$ Å
$b = 4.823\ (1)$ Å
$c = 18.628\ (3)$ Å
$\beta = 92.48\ (1)°$
$V = 606.4\ (2)$ Å^3
$Z = 2$
$D_x = 1.29$ Mg m^{-3}
$D_m = 1.28$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 16.9\text{–}26.4°$
$\mu = 0.40$ mm^{-1}
$T = 298$ K
Needle
0.6 × 0.2 × 0.2 mm
Colourless

Data collection

Enraf-Nonius CAD-4 diffractometer
2θ scans
Absorption correction: empirical
$T_{min} = 0.959$, $T_{max} = 0.997$
1155 measured reflections
1060 independent reflections
757 observed reflections
$[I \geq 1.5\sigma(I)]$

$R_{int} = 0.032$
$\theta_{max} = 25°$
$h = -8 \rightarrow 8$
$k = 0 \rightarrow 5$
$l = 0 \rightarrow 22$
3 standard reflections
monitored every 120 reflections
intensity variation: <3%

Refinement

Refinement on F
$R = 0.036$
$wR = 0.022$
$S = 1.58$
757 reflections
97 parameters
All H-atom parameters refined
$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{max} < 0.01$

$\Delta\rho_{max} = 0.15$ e Å^{-3}
$\Delta\rho_{min} = -0.16$ e Å^{-3}
Extinction correction: secondary
Extinction coefficient: 0.56 (9)
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters* (Å^2)

B_{iso} for H atoms; $B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$ for others.

	x	y	z	B_{iso}/B_{eq}
S1	0.8163 (1)	0.7627 (2)	0.0633 (1)	4.66 (4)
O1	0.7290 (3)	0.6012 (5)	−0.2150 (1)	4.08 (10)
N1	0.8329 (3)	0.5942 (5)	−0.0706 (1)	3.74 (11)
C1	0.9078 (3)	0.5900 (5)	−0.0045 (1)	3.16 (12)
C2	0.6609 (4)	0.7506 (7)	−0.0958 (1)	3.98 (15)
C3	0.5773 (4)	0.6264 (6)	−0.1649 (1)	3.42 (13)
C4	0.4026 (5)	0.7876 (8)	−0.1950 (2)	4.34 (16)
HO1	0.752 (5)	0.738 (6)	−0.2327 (14)	4.8 (9)

Table 2. *Selected geometric parameters* (Å, °)

S1—C1	1.654 (3)	C3—C4	1.501 (4)
O1—C3	1.427 (3)	C3—C2	1.507 (4)
N1—C1	1.312 (3)	O1···O1^{ii}	2.758 (2)
N1—C2	1.447 (4)	HO1···O1^{ii}	2.00 (3)
C1—C1^{i}	1.522 (4)		
S1—C1—N1	124.5 (2)	N1—C1—C1^{i}	113.1 (2)
S1—C1—C1^{i}	122.4 (2)	C2—C3—O1	110.1 (3)
C1—N1—C2	125.8 (2)	C2—C3—C4	112.0 (3)
N1—C2—C3	109.7 (3)	O1—C3—C4	112.1 (2)
O1—H···O1^{ii}	171 (3)		

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

The structure was solved by direct methods and all analyses were performed using the *NRCVAX* program package (Gabe, Le Page, White & Lee, 1987). H atoms were found in the difference Fourier map after isotropic refinement and refined.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71844 (10 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HL1034]

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Acta Cryst. (1994). C**50**, 1165–1169

Methyl (2-Methoxycarbonylbenzoyl)triphenylphosphoranylideneacetate and its Ethanolate Complex

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(*Received* 29 *March* 1993; *accepted* 6 *December* 1993)

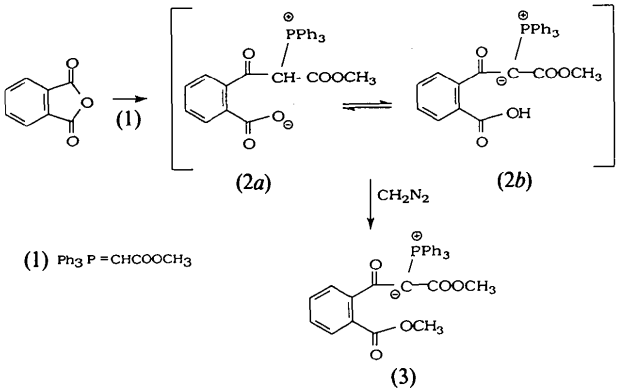
Abstract

Two different crystals of the compound methyl (2-methoxycarbonylbenzoyl)triphenylphosphoranylideneacetate, $C_{30}H_{25}O_5P$ (I) and $C_{30}H_{25}O_5P.0.5C_2H_6O$ (II), were studied by X-ray diffraction. The second crystal contains a molecule of ethanol close to an inversion centre. The solvent molecule is disordered on two positions and is involved in hydrogen bonding with the O atom of a carbonyl group. In crystal (I), the P—C(phenyl) distances vary from 1.808 (6) to 1.819 (5) Å, while the fourth P—C bond is shorter, at 1.759 (4) Å. In crystal (II), the P—C(phenyl) distances are 1.811 (6)–1.817 (6) Å and the fourth P—C bond is also shorter, at 1.763 (6) Å. These values suggest a multiple nature for the P—C bond. A high-field methoxy signal observed in the NMR spectrum was attributed to the shielding magnetic anisotropic effect of the phenyl rings of the PPh_3 group.

Comment

Enol lactones are found in many marine and terrestrial organisms and a large number of natural and synthetic compounds bearing this functionality exhibit interesting and useful biological properties (Pattenden, 1978). The most direct approach to the synthesis of enol lactones is through a Wittig condensation of suitably substituted cyclic anhydrides with stabilized phosphoranes. Although a number of such reactions have been reported (Chopard, Hudson & Searle, 1965; Doyle & Massy-Westropp, 1982, and references therein; Knight & Pattenden, 1975, 1979; Kayser & Breau, 1988, 1989; Breau & Kayser, 1989), the mechanism and the factors controlling the regio- and stereoselectivity have not been systematically investigated until recently (Kayser, Hatt & Hooper, 1991, 1992, Kayser, Hatt, Yu & Hooper, 1993).

During low-temperature NMR studies of the condensations between phthalic anhydride and the stabilized phosphorane methyl triphenylphosphoranylideneacetate (1), a high-field methoxy signal at 2.982 p.p.m. was observed. Trapping with CH_2N_2 gave the product (3), which confirmed the existence of an unstable addition product (2*a*), apparently in equilibrium with (2*b*). The trapped compound (3) showed two methoxy signals: the new methoxy ester signal at 3.826 p.p.m. and the previously noted high-field signal at 3.016 p.p.m. (Kayser *et al.* 1991).



To understand the reason for the high-field methoxy ester signal, the crystal structure of compound (3) was determined.

The results of the two crystal structure determinations have shown that both crystals correspond to the same compound. Crystal (II) contains a molecule of solvent (ethanol), while no solvent was detected in crystal (I). The NMR spectra of the mixture have shown that the crystals containing ethanol are present in a smaller quantity (~25%). Labeled diagrams of the two crystals are shown in Figs. 1 and 2. The two structures are very similar except for the conformation in the crystalline state around C(8). This is evident from Figs. 1 and 2. This difference is caused by the presence of hydrogen bonds in crystal (II), involving O(1) and the ethanol molecule.

The P—C(phenyl) distances are normal and vary from 1.808 (6) to 1.819 (5) Å for (I) and from 1.811 (6) to 1.817 (6) for (II), while the fourth bond P—C(8) is shorter: 1.759 (4) for (I) and 1.763 (6) Å