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Acta Cryst. (1997). **C53**, 1318–1320

Diisopropyl Hydrazocarboxylate–Triphenylphosphine Oxide Adduct†

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(Received 14 June 1996; accepted 1 April 1997)

Abstract

Crystals of the title complex, C₈H₁₆N₂O₄·C₁₈H₁₅OP, belong to the *P2₁/c* space group. The triphenylphosphine oxide and diisopropyl hydrazocarboxylate molecules form a stable centrosymmetric 2:2 complex through a series of hydrogen bonds.

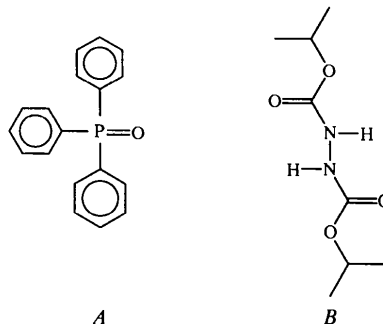
Comment

Etter has undertaken a systematic study of complexes incorporating the triphenylphosphine oxide molecule (see, for example, Etter, Rasmussen, Gleason, Kress, Duerst & Gillard, 1986; Etter & Panunto, 1988; Etter & Reutzel, 1991, 1992; Etter, Urbanczyk-Lipkowska, Zia-Ebrahimi & Panunto, 1990). Since triphenylphosphine oxide is a very strong proton acceptor it often forms highly stable crystalline complexes with other molecules. These crystals are often reasonably large and well developed (Etter & Baures, 1988). Etter has also shown that triphenylphosphine oxide may be used to displace and modify the hydrogen-bonding pattern occurring in some of the organic molecules with which it forms complexes.

The bonds distances and angles in the triphenylphosphine oxide molecule, *A*, are normal; the P=O bond is 1.492 (1) Å, while the P—C bonds average

† Alternative name: isopropyl 3-(isopropoxycarbonyl)carbazate–triphenylphosphine oxide (1/1).

1.797 Å. In the diisopropyl hydrazocarboxylate molecule, *B*, the central N41—N51 bond is 1.381 (2) Å and there is a *gauche* torsion angle, $\tau = 72^\circ$, around this bond. All the C—H distances in molecule *A* are in the range 0.88 (3)–1.04 (3) Å, with U_{iso} values between 0.056 (5) and 0.150 (11) Å². The two N—H distances in molecule *B* are 0.82 (2) and 0.90 (2) Å.



Four molecules (two *A* + two *B*) are connected to each other through hydrogen bonds of the N—H(*B*)···O(*A*) type and form a centrosymmetric ten-membered ring. There is a three-center hydrogen bond involving the phosphoryl O atom, H(*B*)···O(*A*)···H(*B*). This system is not symmetrical since the two N···O bonds are 2.896 (2) and 2.880 (2) Å, while the two N—H···O bond angles are 159 (2) and 172 (2)°. Each phosphoryl O atom is connected to NH groups of two centrosymmetrically related diisopropyl hydrazocarboxylate molecules. Although there is no report of such an arrangement with phosphines, a comparable eight-membered ring system has been observed in a diacetamide–benzamide host–guest assembly (Etter & Reutzel, 1991). The carbonyl O atoms of molecule *B* do not participate in hydrogen bonding. The C=O bond lengths are 1.202 (2) and 1.206 (2) Å.

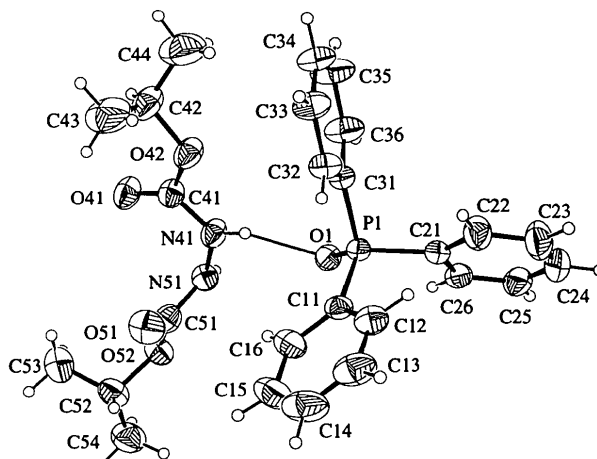


Fig. 1. ORTEP (Johnson, 1976) drawing of the two structural units, C₁₈H₁₅PO and C₈H₁₆N₂O₄, and the atomic numbering schemes. The ellipsoids are drawn at the 40% probability level, while the H atoms are represented as spheres of arbitrary size.

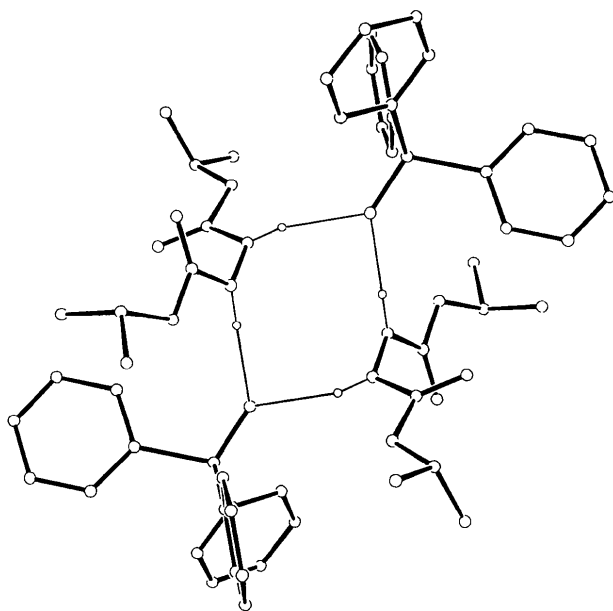


Fig. 2. Drawing showing the hydrogen bonding in the complex.

Experimental

Crystals of the title compound were unexpectedly obtained while trying to purify a diamine, 3-methylcadaverine dihydrochloride, by recrystallization in a 1:1 acetone-ethanol mixture. The procedure, reported by Equi, Brown, Cooper, Ner, Watson & Robins (1991), was followed in order to prepare the above diamine, required for subsequent syntheses. The reaction involved heating 3-methylpentane-1,5-diol in THF with a solution of hydrazoic acid in benzene, diisopropyl hydrazocarboxylate and triphenylphosphine. The last step of the preparation, the purification by recrystallization, yielded excellent crystals which proved to be the title compound rather than the expected diamine.

Crystal data

$C_8H_{16}N_2O_4 \cdot C_{18}H_{15}OP$

$M_r = 482.51$

Monoclinic

$P2_1/c$

$a = 8.903(3) \text{ \AA}$

$b = 14.911(4) \text{ \AA}$

$c = 19.778(4) \text{ \AA}$

$\beta = 98.337(2)^\circ$

$V = 2597.7(12) \text{ \AA}^3$

$Z = 4$

$D_x = 1.234 \text{ Mg m}^{-3}$

D_m not measured

Cu $K\alpha$ radiation

$\lambda = 1.5418 \text{ \AA}$

Cell parameters from 25

reflections

$\theta = 20\text{--}22^\circ$

$\mu = 1.229 \text{ mm}^{-1}$

$T = 293 \text{ K}$

Prism

$0.76 \times 0.36 \times 0.22 \text{ mm}$

Transparent

Data collection

Enraf-Nonius CAD-4

diffractometer

$\theta/2\theta$ scans

Absorption correction: none

18 569 measured reflections

4921 independent reflections

4460 reflections with

$I_{net} > 2\sigma(I_{net})$

$R_{int} = 0.035$

$\theta_{max} = 69.90^\circ$

$h = -10 \rightarrow 10$

$k = -18 \rightarrow 18$

$l = -24 \rightarrow 24$

5 standard reflections

frequency: 30 min

intensity variation: 2.0%

Refinement

Refinement on F

$R = 0.047$

$wR = 0.056$

$S = 4.22$

4460 reflections

384 parameters

H atoms: see below

$w = 1/[\sigma^2(F) + 0.00005F^2]$

$(\Delta/\sigma)_{max} = 0.057$

$\Delta\rho_{max} = 0.31 \text{ e \AA}^{-3}$

$\Delta\rho_{min} = -0.37 \text{ e \AA}^{-3}$

Extinction correction:

Larson (1970)

Extinction coefficient:

0.61 (4)

Scattering factors from *Inter-*

national Tables for X-ray

Crystallography (Vol. IV)

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

P1—O1	1.4916 (13)	C32—C33	1.382 (3)
P1—C11	1.8041 (19)	C33—C34	1.358 (3)
P1—C21	1.7964 (18)	C34—C35	1.366 (3)
P1—C31	1.7929 (18)	C35—C36	1.379 (3)
C11—C12	1.388 (3)	O41—C41	1.202 (2)
C11—C16	1.375 (3)	O42—C41	1.341 (2)
C12—C13	1.368 (3)	O42—C42	1.468 (3)
C13—C14	1.355 (5)	N41—C41	1.348 (3)
C14—C15	1.357 (5)	N41—N51	1.381 (2)
C15—C16	1.403 (3)	C42—C43	1.423 (4)
C21—C22	1.388 (3)	C42—C44	1.479 (4)
C21—C26	1.388 (3)	O51—C51	1.206 (2)
C22—C23	1.383 (3)	O52—C51	1.354 (2)
C23—C24	1.384 (4)	O52—C52	1.457 (3)
C24—C25	1.365 (4)	N51—C51	1.342 (3)
C25—C26	1.378 (3)	C52—C53	1.469 (4)
C31—C32	1.377 (3)	C52—C54	1.493 (4)
C31—C36	1.383 (3)		
O1—P1—C11	111.5 (1)	P1—C31—C36	116.1 (1)
O1—P1—C21	111.9 (1)	C32—C31—C36	118.7 (2)
O1—P1—C31	111.3 (1)	C31—C32—C33	120.3 (2)
C11—P1—C21	106.6 (1)	C32—C33—C34	120.5 (2)
C11—P1—C31	108.8 (1)	C33—C34—C35	120.0 (2)
C21—P1—C31	106.4 (1)	C34—C35—C36	120.2 (2)
P1—C11—C12	123.3 (2)	C31—C36—C35	120.3 (2)
P1—C11—C16	118.0 (2)	C41—O42—C42	116.0 (2)
C12—C11—C16	118.8 (2)	C41—N41—N51	119.1 (2)
C11—C12—C13	121.1 (2)	O41—C41—O42	126.0 (2)
C12—C13—C14	119.6 (3)	O41—C41—N41	125.2 (2)
C13—C14—C15	121.2 (2)	O42—C41—N41	108.8 (2)
C14—C15—C16	119.7 (3)	O42—C42—C43	109.5 (2)
C11—C16—C15	119.6 (2)	O42—C42—C44	107.5 (2)
P1—C21—C22	122.3 (2)	C43—C42—C44	113.2 (3)
P1—C21—C26	118.6 (1)	C51—O52—C52	116.5 (2)
C22—C21—C26	119.1 (2)	N41—N51—C51	118.3 (2)
C21—C22—C23	120.5 (2)	O51—C51—O52	124.8 (2)
C22—C23—C24	119.2 (2)	O51—C51—N51	126.3 (2)
C23—C24—C25	120.8 (2)	O52—C51—N51	108.9 (2)
C24—C25—C26	120.2 (2)	O52—C52—C53	108.9 (2)
C21—C26—C25	120.2 (2)	O52—C52—C54	106.6 (2)
P1—C31—C32	125.2 (1)	C53—C52—C54	114.2 (2)

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

N—H...O	N—H	H...O	N...O	N—H...O
N41—HN41...O1	0.82 (2)	2.12 (2)	2.898 (2)	159 (2)
N51—HN51...O1'	0.90 (2)	1.99 (2)	2.880 (2)	172 (2)

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

The structure refinement was conducted in anisotropic mode for the non-H atoms and isotropic for most H atoms. The atomic coordinates and isotropic displacement parameters of the methyl H atoms at C43, C44, C53 and C54 of molecule *B* were not refined. The C—H distances were kept at 0.95 \AA and the C—C—H angles at 109.5 $^\circ$.

Data collection: *CAD-4 Software* (Enraf-Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *NRCVAX DATRD2* (Gabe, Le Page, Charland, Lee & White, 1989). Program(s) used to solve structure: *SHELXS86* (Sheldrick,

1985). Program(s) used to refine structure: *NRCVAX LSTSQ*. Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *NRCVAX TABLES* (Version of January 1994).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK1276). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1997). **C53**, 1320–1322

4,4'-Bis(acetylamino)-2,2'-di(2-thienyl)biphenyl-Ethanol (1/1)

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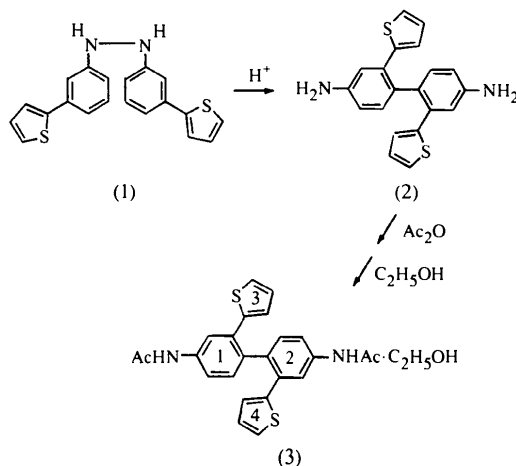
(Received 3 December 1996; accepted 24 April 1997)

Abstract

Dihedral angles between the four aromatic rings in the title compound, C₂₄H₂₀N₂O₂S₂.C₂H₅OH, show that the rings are twisted relative to each other, with H atoms oriented towards shielded phenyl ring regions. Hydrogen bonding between the biphenyl molecule and the solvent ethanol connect these units in infinite layers.

Comment

4,4'-Diamino-2,2'-di(2-thienyl)biphenyl, (2), was isolated from the acid-catalyzed benzidine rearrangement (Subotkowski, K.-Subotkowska & Shine, 1993) of bis-[3-(2-thienyl)phenyl]diazane, (1). Acetylation of compound (2), followed by recrystallization from ethanol gave the title compound, (3). Work-up and characterization details of compounds (1)–(3) will be published elsewhere. The ¹H NMR spectra showed that the chemical shift of H9 and H9' present in the thienyl rings of compound (3) was 6.53 p.p.m., *i.e.* shifted unusually upfield, suggesting that these two H atoms are oriented towards shielded regions of the phenyl rings. The molecular structure of compound (3) has been investigated to clarify the molecular conformation of the ring systems.



Bond lengths and angles for the molecule are as expected. The O1—C11 [1.218(5) Å] and O1'—C11' [1.228(5) Å] bond lengths of the acetylamino groups correspond to double bonds (Table 1). In the thienyl rings, the S—C distances range from 1.633(4) to 1.716(4) Å, with an average value of 1.688(3) Å; the two C—S—C angles are 93.1(3) and 93.1(2)°, with an average value of 93.1(2)°. These values are similar to those found for 2-(2-aminophenylthio)-2-(2-thienyl)ethyl 2-thienyl ketone (Morgant, Labouze, Viossat, Lancelot & Dung, 1996).

Each of the four aromatic rings in the title molecule is planar, with a maximum deviation of 0.017(3) Å for the C1 atom of the C1—C6 phenyl ring. The dihedral angle between the two phenyl rings is 63.7(1)° and those between the phenyl rings and the connected thienyl rings are 37.8(2) and 39.9(1)°.

The distances between H9 and H9' and the C atoms in the primed and unprimed phenyl rings are in the ranges 2.834(6)–3.957(7) and 2.790(5)–3.809(6) Å, respectively, and the distances between H9 and H9' and the centroids of the primed and unprimed phenyl rings are 3.153(5) and 3.052(4) Å. These distances reveal that H9 and H9' are positioned above the primed and