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Some 1,3-Dipolar Adducts from Benzodiazepine. II.† Condensation of Nitrilimines with [1,4]Benzodiazepine and [1,4]Benzodiazepin-2-one

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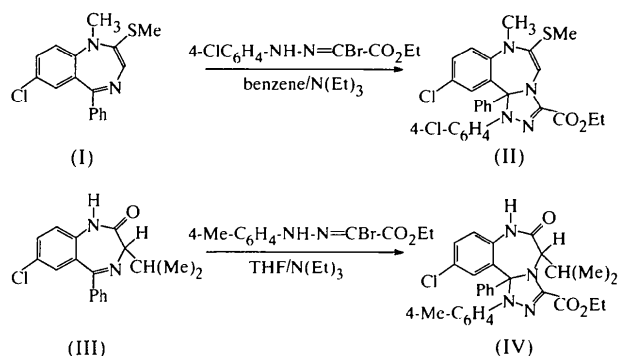
Abstract

The structure of the diadduct ethyl 10-chloro-1-(4-chlorophenyl)-7-methyl-6-methylthio-11b-phenyl-7,11b-dihydro-1*H*-[1,2,4]triazolo[4,3-*d*][1,4]benzodiazepine-3-carboxylate, C₂₇H₂₄Cl₂N₄O₂S, has been established by X-ray crystallographic study. The central seven-membered ring is fused with chlorobenzene and triazolo rings to form the core of the molecule.

† Part I: Essaber *et al.* (1998).

Comment

Several benzodiazepine derivatives containing an additional ring are of pharmacological interest (Sternbach, 1978). In connection with our investigation on possible approaches to the synthesis of novel benzodiazepine derivatives with an additional fused heterocyclic ring (Capozzi *et al.*, 1985), we have condensed 7-chloro-1-methyl-2-methylthio-5-phenyl-1*H*-[1,4]benzodiazepine, (I) (Early *et al.*, 1974), and 7-chloro-3-isopropyl-5-phenyl[1,4]benzodiazepine-2(3*H*)-one, (III) (Sternbach *et al.*, 1962), with nitrilimines (Huisgen & Koch, 1955) generated *in situ* to give compounds (II) and (IV), respectively (see scheme below). The structures of compounds (II) and (IV) have been determined unambiguously from X-ray diffraction studies. However, the poor quality of the structure determination for compound (IV) does not enable us to give a detailed description of its conformation.



In compound (II) (Fig. 1), the seven-membered ring is composed of two planar fragments: N9–C10a–C10b–N11 (r.m.s. deviation 0.030 Å), which includes

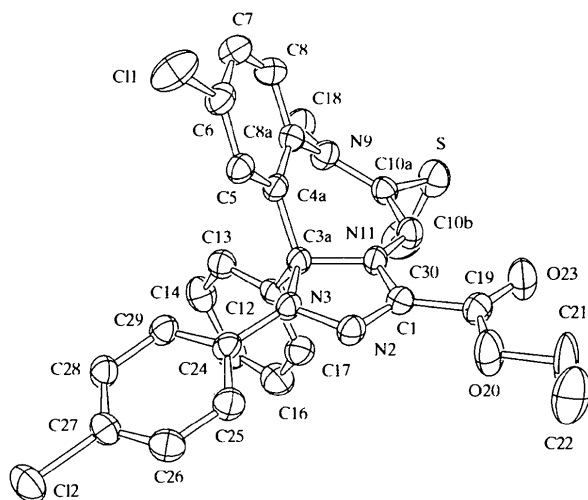


Fig. 1. View of compound (II) with the atom-numbering scheme (C15 partly obscured by C24). Displacement ellipsoids are shown at the 50% probability level.

the double bond C10a=C10b, and C3a-C4a-C8a-N9 (r.m.s. deviation 0.009 Å), which is fused to the benzo ring [r.m.s. deviation 0.012 Å; dihedral angle of 1(2)° with C3a-C4a-C8a-N9]. These two fragments form a dihedral angle of 42.0(2)° and are connected by the C3a-N11 bond of the fused triazolo ring [r.m.s. deviation 0.006 Å; dihedral angle of 23.7(2)° with N9-C10a-C10b-N11]. The triazolo ring has a chlorophenyl ring (r.m.s. deviation 0.024 Å), an ethoxy-carbonyl arm [r.m.s. deviation 0.006 Å; C21 displaced by 0.107(5) and C22 by 0.492(5) Å] and a phenyl ring (r.m.s. deviation 0.005 Å) as substituents.

Experimental

To a solution of benzodiazepine (I) (878 mg, 2.8 mmol) and ethyl arylhydrazono- α -bromoglyoxylate (820 mg, 2.7 mmol) in dry benzene (20 ml) was added triethylamine (5.4 mmol) dissolved in dry benzene (5 ml) (see scheme above). The mixture was stirred for 4 d, then washed with water. The organic layers were concentrated. The crude product was taken up into methanol and the expected compound (II) precipitated in 40% yield (m.p. 481–483 K). Product (II) was then recrystallized from a dichloromethane–heptane (1:1) mixture. Compound (IV), not reported in full here, was prepared analogously. To a solution of benzodiazepine (III) (487 mg, 1.56 mmol) and ethyl arylhydrazono- α -bromoglyoxylate (494 mg, 1.74 mmol) in dry THF (30 ml) was added triethylamine (0.4 ml) dissolved in dry THF (10 ml). The mixture was stirred for 5 d, concentrated and extracted with dichloromethane. The organic layers were concentrated and the crude product was chromatographed on silica gel (Merck 60), with ethyl acetate–hexane (15:85). Product (IV) (43% yield, m.p. 497–499 K) was then recrystallized from an ethyl acetate–hexane (3:7) mixture. Yellow crystals were obtained. [Crystal data for (IV): triclinic $P\bar{1}$; $a = 9.921(1)$, $b = 10.858(2)$, $c = 14.990(3)$ Å, $\alpha = 75.56(1)$, $\beta = 77.25(2)$, $\gamma = 68.53(2)^\circ$; $V = 1440.2(5)$ Å³; $Z = 2$. Of 5651 reflections measured to $\theta_{\max} = 26^\circ$ (Mo $K\alpha$), only 2734 had $I > 2\sigma(I)$. The structure, which was refined to $R = 0.060$, includes a disordered solvent molecule, which could not be clearly identified. The atomic coordinates of (IV) can be obtained from the authors.]

Crystal data

C₂₇H₂₄Cl₂N₄O₂S

$M_r = 539.49$

Monoclinic

$P2_1/n$

$a = 8.110(1)$ Å

$b = 10.045(2)$ Å

$c = 30.670(3)$ Å

$\beta = 90.8(3)^\circ$

$V = 2498(1)$ Å³

$Z = 4$

$D_x = 1.434$ Mg m⁻³

D_m not measured

Data collection

Enraf–Nonius CAD-4 diffractometer

Mo $K\alpha$ radiation

$\lambda = 0.71073$ Å

Cell parameters from 25 reflections

$\theta = 12\text{--}18^\circ$

$\mu = 0.371$ mm⁻¹

$T = 294$ K

Prismatic

$0.80 \times 0.30 \times 0.30$ mm

Orange–yellow

$R_{\text{int}} = 0.017$

$\theta_{\max} = 25^\circ$

$\theta/2\theta$ scans

Absorption correction: none

4765 measured reflections

4395 independent reflections

3183 reflections with

$I > \sigma(I)$

Refinement

Refinement on F^2

$R = 0.047$

$wR = 0.062$

$S = 1.655$

3183 reflections

325 parameters

H atoms not refined

$w = 4F_o^2/[\sigma^2(F_o^2) + 0.0025F_o^4]$

$h = -9 \rightarrow 9$

$k = 0 \rightarrow 11$

$l = 0 \rightarrow 36$

3 standard reflections

frequency: 120 min

intensity decay: 0.3%

$(\Delta/\sigma)_{\max} = 0.008$

$\Delta\rho_{\max} = 0.297$ e Å⁻³

$\Delta\rho_{\min} = -0.294$ e Å⁻³

Extinction correction: none

Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. Selected geometric parameters (Å, °)

N2—N3	1.381 (3)	N11—C3a	1.480 (4)
N2—C1	1.291 (4)	N11—C10b	1.392 (4)
N3—C3a	1.483 (4)	C3a—C4a	1.523 (4)
N9—C8a	1.413 (4)	C4a—C8a	1.410 (4)
N9—C10a	1.406 (4)	C10a—C10b	1.341 (5)
N11—C1	1.374 (4)		
N3—N2—C1	106.0 (2)	N3—C3a—N11	97.9 (2)
N2—N3—C3a	113.1 (2)	N3—C3a—C4a	112.8 (2)
C8a—N9—C10a	122.9 (3)	N11—C3a—C4a	107.3 (2)
C1—N11—C3a	108.8 (2)	C3a—C4a—C8a	119.7 (3)
C1—N11—C10b	129.4 (3)	N9—C8a—C4a	121.9 (3)
C3a—N11—C10b	121.0 (2)	N9—C10a—C10b	127.8 (3)
N2—C1—N11	114.2 (3)	N11—C10b—C10a	125.8 (3)

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *BEGIN in SDP-Plus* (Frenz, 1985). Program(s) used to solve structure: *MULTAN80* (Main *et al.*, 1980). Program(s) used to refine structure: *LSFM in SDP-Plus*. Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *CIF VAX in MolEN* (Fair, 1990).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: CF1198). Services for accessing these data are described at the back of the journal.

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Bis(2,6-dimethylphenyl) Chlorothio- phosphate

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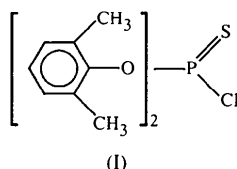
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Abstract

The title compound, C₁₆H₁₈ClO₂PS, displays distorted tetrahedral geometry around the P atom and has twofold axial symmetry, with the S and Cl atoms disordered about the twofold axis. The distance between these partially populated sites is 0.40 (2) Å. The dihedral angle between the two dimethylphenyl rings is 74.54 (8)° and the P—O bond distance is 1.566 (2) Å.

Comment

The use of phosphorus compounds in food manufacture, water treatment, insecticides, detergents, oil additives and resins, and biochemical studies on phosphate metabolism, has attracted many scientists to the study of their spectroscopic and various other properties (Corbridge, 1956; Bellamy & Beecher, 1952; Pastor *et al.*, 1988). The molecular structure of the title compound, (I), has been determined and the results are presented here.



A perspective view of the molecule with the atomic numbering scheme is shown in Fig. 1. The disordered S and Cl atoms are positioned nearly symmetrically on either side of the molecule with respect to the twofold

axis. The partially populated S and Cl atoms are within 0.40 (2) Å of each other; their positions are not as certain as the formal standard uncertainty would suggest. The asymmetric unit corresponds to one half of the molecule, with the P atom sitting on the twofold axis along **b**. The rest of the molecule is generated by the symmetry operation $(1-x, y, \frac{3}{2}-z)$. This disorder is similar to that seen in *N*-[1-(2-benzo[*b*]thienyl)ethyl]-*N'*-carbamoylurea (Henry *et al.*, 1996).

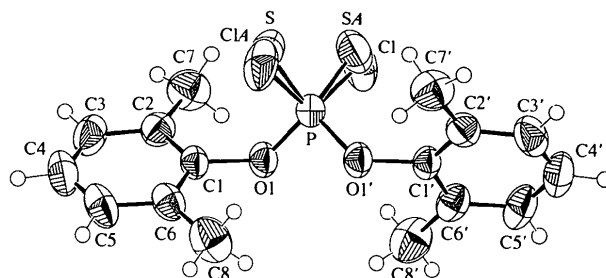


Fig. 1. View of the title molecule drawn using ORTEPII (Johnson, 1976) with 50% probability ellipsoids.

The S, Cl and two O atoms have severely distorted tetrahedral geometry about the P atom [angles 101.3 (1)–113.7 (3)°]. The P=S bond length of 1.914 (9) Å agrees well with the reported value of 1.908 (1) Å for tris(*O*-4-*tert*-butylphenyl)thiophosphate (Büyükgüngör *et al.*, 1995). The P—Cl bond length of 1.976 (7) Å agrees well with the value of 1.981 (1) Å reported for 2-(2,6-di-*tert*-butyl-4-methylphenoxy)-2,4,4,6,6,8,8-heptachlorocyclo-2λ⁵,4λ⁵,6λ⁵,8λ⁵-tetraphosphazetetrane (Hökelek *et al.*, 1996). The mean bond lengths averaged over each type of bond agree well with the values observed in similar compounds (Odabaşoğlu *et al.*, 1992; Krishnaiah *et al.*, 1996).

The angles C1—C2—C3 [116.0 (2)°], C5—C6—C1 [116.4 (2)°] and C2—C1—C6 [124.6 (2)°] within the dimethylphenyl rings appear to be unusual; the diversity of these angles is probably due to the steric effects of the methyl groups. Each dimethylphenyl ring is nearly planar, with a maximum deviation from the plane defined by the six ring atoms of 0.011 (1) Å, while the substituent atoms C7, C8 and O1 deviate by 0.057 (4), 0.047 (5) and 0.045 (3) Å, respectively, from this plane.

Experimental

The synthesis of the title compound and the ¹H NMR, IR and UV spectroscopic characterizations have been described by Odabaşoğlu & Gümrükçüoğlu (1993). IR (KBr) data for the title compound are as follows: 1195–940 (C—O—P), 705 (P=S), 515 cm⁻¹ (P—Cl). Colourless semi-transparent crystals suitable for X-ray diffraction were obtained by slowly cooling a saturated solution in hot *n*-hexane to room temperature.