C45	−0.3945 (9)	0.7170 (4)	0.2783 (4)	0.062 (2)
C8	−0.1811 (8)	0.5465 (4)	0.2059 (4)	0.060 (2)
C50	−0.4203 (8)	0.9508 (4)	0.0957 (3)	0.056 (2)
C9	−0.2048 (8)	0.5097 (4)	0.1458 (4)	0.065 (2)
C46	−0.2888 (8)	0.7484 (4)	0.3202 (4)	0.060 (2)
C10	−0.1850 (9)	0.5362 (4)	0.0810 (4)	0.067 (2)
C36	0.0752 (7)	1.0058 (3)	0.2488 (3)	0.035 (2)

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

O1—C1	1.234 (8)	C25—C22	1.52 (1)
C1—N2	1.356 (8)	O31—C31	1.215 (8)
C1—C5	1.533 (9)	C31—N32	1.367 (8)
N2—N3	1.397 (7)	C31—C35	1.547 (9)
N2—C6	1.423 (8)	N32—N33	1.395 (8)
N3—C4	1.293 (8)	N32—C36	1.427 (8)
C4—C5	1.534 (8)	N33—C34	1.294 (8)
C4—C12	1.482 (8)	C34—C35	1.535 (9)
C5—C18	1.566 (9)	C34—C42	1.466 (9)
C5—C35	1.571 (9)	C35—C48	1.563 (8)
C18—C19	1.514 (9)	C48—C49	1.505 (9)
O1—C1—C5	127.4 (6)	O31—C31—C35	127.1 (6)
O1—C1—N2	125.7 (6)	O31—C31—N32	126.5 (6)
N2—C1—C5	106.9 (5)	N32—C31—C35	106.4 (5)
C1—N2—C6	129.9 (5)	C31—N32—C36	127.8 (5)
C1—N2—N3	112.7 (5)	C31—N32—N33	113.0 (5)
N3—N2—C6	117.4 (5)	N33—N32—C36	118.4 (5)
N2—N3—C4	108.8 (5)	N32—N33—C34	108.7 (5)
N3—C4—C12	117.8 (6)	N33—C34—C42	117.8 (6)
N3—C4—C5	112.1 (5)	N33—C34—C35	112.6 (5)
C5—C4—C12	130.0 (5)	C35—C34—C42	129.0 (5)
C1—C5—C4	99.4 (5)	C31—C35—C34	99.1 (5)
C4—C5—C35	111.9 (5)	C5—C35—C34	111.3 (5)
C4—C5—C18	114.9 (5)	C5—C35—C31	111.8 (5)
C1—C5—C35	112.5 (5)	C34—C35—C48	113.8 (5)
C1—C5—C18	105.1 (5)	C31—C35—C48	106.2 (5)
C18—C5—C35	112.3 (5)	C5—C35—C48	113.5 (5)
C5—C18—C19	115.4 (5)	C35—C48—C49	114.8 (5)
O1—C1—N2—C6	−0.5 (10)	O31—C31—N32—C36	−10 (1)
N3—N2—C6—C7	38.2 (8)	N33—N32—C36—C41	22.9 (9)
N3—C4—C12—C13	−27.2 (9)	N33—C34—C42—C47	−29.3 (9)
C35—C5—C18—C19	173.7 (5)	C5—C35—C48—C49	178.3 (5)

Reflection intensities were evaluated by profile fitting of a 96-step peak scan among 2θ shells procedure (Diamond, 1969). The model of the structure, completed by a combination of least-squares techniques and difference Fourier synthesis, was refined by full-matrix least-squares methods. Owing to the small observations/parameters ratio, only the non-H atoms of the pyrazolone fragments and the C atoms of the methylene and *p*-methyl groups were refined anisotropically.

Data collection: *P3/V* (Siemens, 1989). Cell refinement: *P3/V*. Data reduction: *SHELXTL-Plus* (Sheldrick, 1992). Program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994). Program(s) used to refine structure: *SHELXTL-Plus*. Molecular graphics: *XP* in *SHELXTL-Plus*. Software used to prepare material for publication: *SHELXTL-Plus* and *PARST*95 (Nardelli, 1995).

Lists of structure factors, hydrogen-bond data, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: NA1248). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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12-(*N*-Benzoylimino)-11,12-dihydrobenzimidazo[2,1-*b*][1,3,5]benzothiadiazepine

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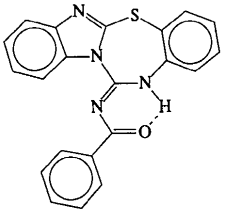
Abstract

The title compound, $C_{21}H_{14}N_4OS$, was prepared from the reaction of *N*-[2-(1*H*-benzimidazol-2-ylthio)phenyl]-*N*′-benzoylthiourea with dicyclohexylcarbodiimide. A puckered seven-membered ring and a short H···H contact between two rings cause the whole molecule to be non-coplanar, even though the delocalized π-bonding system is planar. There is an intramolecular hydrogen bond between the amine H atom and the O atom of the carbonyl group.

Comment

The 1,3,5-thiadiazepines have received a great deal of interest because of their biological activities (Vecchia, Dellureficio, Kisis & Vlattas, 1983). As part of our program to develop new 1,3,5-thiadiazepine derivatives, we previously reported that the reaction of *N*-[2-(1*H*-benzimidazol-2-ylthio)phenyl]thiourea with dicyclohexylcarbodiimide (DCC) produced the unexpected 2-imino-3-(6-methoxybenzimidazol-2-yl)benzothiazoline *via* an intermolecular Smiles-type rearrangement (Song, Jin & Jeong, 1996). In contrast, the *N*-benzoylated compound, *N*′-benzoyl-*N*-[2-(1*H*-benzimidazol-2-ylthio)phenyl]thiourea, was cyclized to give a seven-membered 1,3,5-thiadiazepine compound, (I), in the presence of DCC. It is plausible for the molecule to have a completely delocalized π-bonding system. The structure determination, however, reveals a puckered seven-membered ring and a H···H short contact of *ca* 2.53 Å between the two benzene rings, preventing planarity.



(I)

There is an intramolecular hydrogen bond between the amine H atom and the O atom of the carbonyl group, with a H···O contact distance of 1.99 (6) Å. The puckering of the seven-membered ring is illustrated by the torsion angles in Table 2. The mean plane of the benzimidazole nucleus (atoms N1, N2, C1–C7; r.m.s. Δ = 0.020 Å) forms dihedral angles of 63.6 (1) and 26.0 (2)°, respectively, with those of the benzene (C8–C13; r.m.s. Δ = 0.012 Å) and phenyl (C16–C21; r.m.s. Δ = 0.010 Å) rings, which are inclined at an angle of 49.0 (2)° with respect to one another. To the best of our knowledge, this X-ray structure analysis is the first example of a 1,3,5-thiadiazepine derivative.

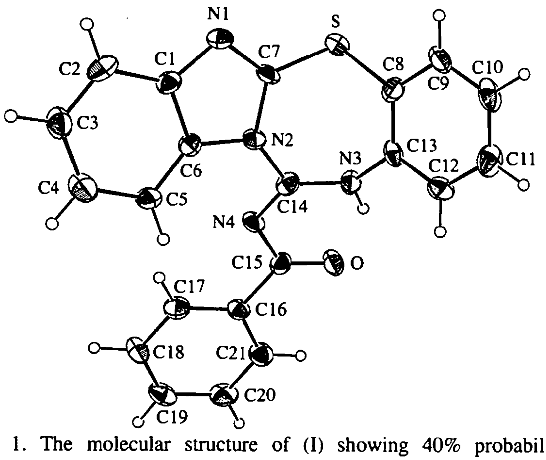


Fig. 1. The molecular structure of (I) showing 40% probability displacement ellipsoids.

Experimental

A solution of *N*′-benzoyl-*N*-[2-(1*H*-benzimidazol-2-ylthio)-phenyl]thiourea (0.81 g, 2 mmol) and DCC (0.62 g, 3 mmol) in 10 ml of acetonitrile was heated under reflux for 3 h. After completion of the reaction, the precipitated dicyclohexylthiourea was filtered off and the filtrate was evaporated *in vacuo*. The product was purified on a silica gel column (eluent 1:1 *n*-hexane:ethyl acetate) and recrystallized from dioxane solution (yield 70%, m.p. 435–436 K).

Crystal data

$C_{21}H_{14}N_4OS$
M_r = 370.42
Monoclinic
$P2_1/c$
a = 12.334 (2) Å
b = 11.742 (3) Å
c = 13.236 (2) Å
β = 116.90 (1)°
V = 1709.5 (6) Å^3
Z = 4
D_x = 1.439 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 9.1–13.8°
μ = 0.209 mm^{-1}
T = 293 (2) K
Tetragonal prism
0.40 × 0.30 × 0.30 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
1384 measured reflections
1323 independent reflections
1172 observed reflections [$I > 2\sigma(I)$]

$R_{\rm int}$ = 0.0292
$\theta_{\rm max}$ = 24.97°
h = 0 → 14
k = 0 → 13
l = −15 → 13
3 standard reflections
frequency: 60 min
intensity decay: none

Refinement

Refinement on F^2
$R(F)$ = 0.0613
$wR(F^2)$ = 0.1126
S = 1.148
1323 reflections
248 parameters
H(C) atoms riding with U(H) = 1.2$U_{\rm eq}$(C); H(N) atoms freely refined

$w = 1/[\sigma^2(F_o^2) + (0.0371P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max}$ = 0.170
$\Delta\rho_{\rm max}$ = 0.229 e Å^{-3}
$\Delta\rho_{\rm min}$ = −0.215 e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

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

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

	x	y	z	$U_{\rm eq}$
S	0.7851 (2)	0.0401 (2)	0.4107 (2)	0.0371 (5)
N1	0.9947 (5)	0.1432 (5)	0.4500 (4)	0.0308 (15)
N2	0.8612 (5)	0.1415 (5)	0.2638 (4)	0.0289 (15)
N3	0.6526 (5)	0.1005 (6)	0.1607 (5)	0.034 (2)
C1	1.0469 (6)	0.1946 (6)	0.3864 (5)	0.028 (2)
C2	1.1598 (6)	0.2467 (7)	0.4269 (6)	0.041 (2)
C3	1.1888 (7)	0.2949 (6)	0.3477 (6)	0.041 (2)
C4	1.1079 (6)	0.2928 (6)	0.2319 (6)	0.041 (2)
C5	0.9960 (6)	0.2430 (6)	0.1916 (6)	0.033 (2)
C6	0.9672 (6)	0.1930 (6)	0.2721 (6)	0.029 (2)
C7	0.8864 (6)	0.1124 (6)	0.3758 (5)	0.029 (2)
C8	0.6605 (6)	0.1343 (6)	0.3453 (6)	0.034 (2)
C9	0.6111 (6)	0.1838 (7)	0.4106 (6)	0.040 (2)
C10	0.5090 (7)	0.2498 (7)	0.3595 (7)	0.047 (2)
C11	0.4575 (7)	0.2725 (7)	0.2451 (7)	0.049 (2)

C12	0.5084 (6)	0.2260 (6)	0.1808 (6)	0.036 (2)
C13	0.6092 (6)	0.1548 (6)	0.2301 (6)	0.029 (2)
C14	0.7637 (6)	0.1026 (6)	0.1633 (6)	0.030 (2)
N4	0.7900 (5)	0.0763 (5)	0.0820 (4)	0.030 (2)
O	0.5999 (4)	0.0007 (4)	−0.0357 (4)	0.0404 (14)
C15	0.7015 (6)	0.0347 (7)	−0.0193 (6)	0.031 (2)
C16	0.7396 (6)	0.0333 (6)	−0.1109 (5)	0.028 (2)
C17	0.8559 (6)	0.0565 (6)	−0.0912 (5)	0.035 (2)
C18	0.8909 (6)	0.0484 (7)	−0.1774 (6)	0.041 (2)
C19	0.8059 (7)	0.0215 (7)	−0.2863 (6)	0.043 (2)
C20	0.6886 (7)	0.0013 (6)	−0.3056 (6)	0.046 (2)
C21	0.6545 (6)	0.0052 (6)	−0.2205 (6)	0.038 (2)

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

S—C7	1.737 (6)	N3—C13	1.408 (8)
S—C8	1.768 (7)	C1—C6	1.382 (8)
N1—C7	1.301 (7)	C8—C13	1.382 (9)
N1—C1	1.406 (8)	C14—N4	1.294 (8)
N2—C6	1.399 (8)	N4—C15	1.380 (8)
N2—C14	1.406 (7)	O—C15	1.237 (7)
N2—C7	1.412 (7)	C15—C16	1.485 (8)
N3—C14	1.356 (8)		
C7—S—C8	97.7 (3)	N2—C7—S	123.6 (5)
C7—N1—C1	105.0 (5)	C13—C8—S	120.8 (5)
C6—N2—C14	125.7 (5)	C8—C13—N3	121.4 (7)
C6—N2—C7	105.6 (5)	N4—C14—N3	127.3 (6)
C14—N2—C7	127.1 (6)	N4—C14—N2	115.8 (6)
C14—N3—C13	130.8 (6)	N3—C14—N2	116.9 (6)
C6—C1—N1	111.0 (6)	C14—N4—C15	120.4 (5)
C1—C6—N2	105.5 (6)	O—C15—N4	125.3 (6)
N1—C7—N2	112.8 (5)	O—C15—C16	121.5 (6)
N1—C7—S	123.5 (5)	N4—C15—C16	113.2 (6)
C14—N2—C7—S	−11.3 (10)	C8—S—C7—N2	−55.4 (6)
C7—S—C8—C13	60.3 (6)	S—C8—C13—N3	1.0 (10)
C14—N3—C13—C8	−60.5 (12)	C13—N3—C14—N2	17.2 (12)
C7—N2—C14—N3	44.1 (10)		

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *SHELXL*93.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: CF1101). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Ethyl {[*N*-(2-Hydroxyethyl)amino](2-hydroxy-1-naphthyl)methyl}phosphonate

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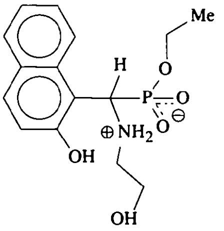
Abstract

The title molecule, $C_{15}H_{20}NO_5P$, has a zwitterionic structure with strong intermolecular N···O and O···O hydrogen bonds. The coordination around phosphorus is distorted tetrahedral, with a maximum bond-angle deviation of 12° from the ideal. The P—C bond length is 1.860 (4) Å and the average P—O value is 1.518 (3) Å.

Comment

Aminophosphonic acids are currently the subject of much interest because of their potential antibacterial (van Assche *et al.*, 1991), antifungal (Cameron, Hudson & Pianka, 1993) and anticancer activities (Lavielle *et al.*, 1991). These compounds may also be of use in metal extraction processes (Aguilar, Miralles & Sastre, 1989). The present structural analysis of the title compound, (I), has been performed in order to determine whether the molecule has distinct acidic -POH and basic -NH- groups or is a zwitterionic structure with $-NH_2^+$ and $-PO^-$ groups.



(I)

As can be seen from Fig. 1, the molecule is a zwitterion. The P1—O3 and P1—O4 bond lengths (Table 2) are almost equal within experimental error and are comparable to reported P—O bond lengths for similar structures (Gibson & Karaman, 1989). They are longer than the P═O double-bond values [1.466 (5) Å] given for some phosphonic acids (Toroš, Prodić & Šljukić 1978; Choi, Failla, Finocchiaro, McPartlin & Scowen, 1994). The P1—O5 and P1—C11 separations are 1.584 (3) and

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