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2-(2-Amino-5-bromobenzoyl)pyridine

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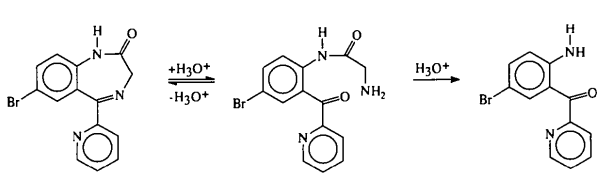
Abstract

Molecules of the title compound, $C_{12}H_9BrN_2O$, are non-planar and are held together in the crystal by both inter- and intramolecular hydrogen bonding.

Comment

The drug bromazepam is a benzodiazepine prescribed for the short-term relief of severe anxiety. It is metabolized mainly by hydroxylation and hydrolysis, and 2-(2-amino-5-bromobenzoyl)pyridine (ABBP) is a minor metabolite excreted in the urine of human patients (de Silva *et al.*, 1974). In acidic media, bromazepam undergoes a two-step sequential hydrolysis reaction *via* a labile ring-opened intermediate to give ABBP and glycine (Inui, Yamamoto, Nakae & Asada, 1982). The kinetics of this reaction have been investigated (Anisuzzaman, 1995) and the crystal structure of bromazepam is known (Butcher, Hamor & Martin, 1983). Crystals of ABBP were obtained by hydrolysing bromazepam with aqueous HCl and allowing the solution to stand for several days at room temperature. The scheme below shows the proposed reaction sequence for the hydrolysis of bromazepam to 2-(2-amino-5-bromobenzoyl)pyridine.



(I) Bromazepam (II) Intermediate (III) ABBP

In ABBP (Fig. 1), an intramolecular N1—H1*A*···O bond is present; N1—H1*A* 0.91 (7), H1*A*···O 1.97 (7), N1···O 2.679 (7) Å and N1—H1*A*···O 135 (5)°. This bond completes a six-membered ring which adopts a sofa conformation, with the H atom slightly displaced [0.17 (6) Å] from the planar portion of the ring. The O atom (coordinates transposed by $\frac{5}{2}-x, -\frac{1}{2}+y, \frac{1}{2}-z$) is also involved in intermolecular hydrogen bonding; N1—H1*B* 0.96 (8), H1*B*···O 2.18 (8), N1···O 3.025 (7) Å and N1—H1*B*···O 146 (6)° (Fig. 2). A similar hydrogen-bonding scheme is present in crystals of 2-aminobenzophenone (Antolini, Vezzosi, Battaglia & Corradi, 1985). The N2···H6 and O···H12 distances in ABBP are 2.404 (6) and 2.638 (6) Å, respectively, the former being shorter than the sum of the van der Waals radii (Glusker, Lewis & Rossi, 1994). The Br···Br intermolecular separation across an inversion centre $(1-x, -y, -z)$ is also short at 3.724 (2) Å and a

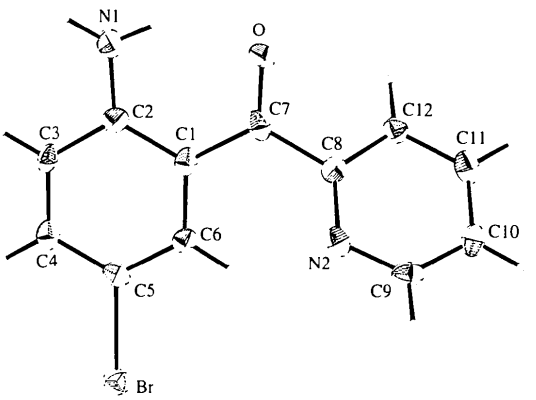


Fig. 1. The atomic arrangement in the title molecule. Displacement ellipsoids are shown at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

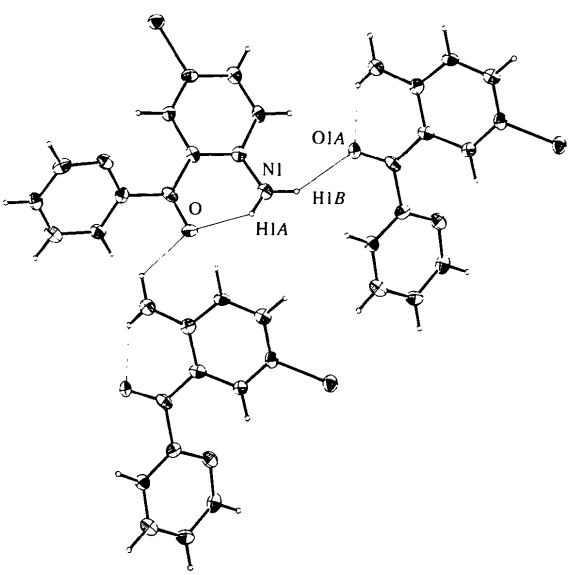


Fig. 2. The hydrogen-bonding network in the title crystal (50% probability ellipsoids). The O1*A* atom is the O atom transposed by $\frac{5}{2}-x, -\frac{1}{2}+y, \frac{1}{2}-z$.

Cambridge Structural Database survey (Allen *et al.*, 1991) of Br···Br intermolecular contacts up to 5 Å, encompassing 2877 compounds, gave a peak (of number of compounds *versus* contact distance) at around 4.1 Å. This agrees well with the predicted potential minimum separation for Br···Br of around 3.95 Å (Pertsin & Kitaigorodsky, 1987).

The aromatic rings are inclined at an angle of 49.9 (1)° to one another and this compares with a value of 56° for benzophenone (Fleischer, Sung & Hawkinson, 1968). The ring formed by intramolecular hydrogen bonding is inclined at an angle of only 1.2 (8)° to the phenyl ring. The amino N atom is displaced by 0.17 (3) Å from the plane defined by its attached atoms, *i.e.* C2, H1*A* and H1*B*.

Experimental

Crystals of ABBP were obtained by hydrolysing bromazepam (see *Comment*).

Crystal data

$C_{12}H_9BrN_2O$
M_r = 277.12
Monoclinic
$P2_1/n$
a = 3.888 (3) Å
b = 9.984 (4) Å
c = 27.537 (8) Å
β = 93.09 (8)°
V = 1067.4 (10) Å^3
Z = 4
D_x = 1.725 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 250 reflections
θ = 2.17–25.06°
μ = 3.828 mm^{-1}
T = 150 (2) K
Needle
0.22 × 0.20 × 0.18 mm
Yellow

Data collection

Delft Instruments FAST diffractometer with an Oxford Cryosystems low-temperature device (Cosier & Glazer, 1986)
Measurement method: area detector
Absorption correction: *XABS2* (Parkin, Moezzi & Hope, 1995)
T_{min} = 0.72, T_{max} = 1.00

4346 measured reflections
1528 independent reflections
1141 observed reflections [$I > 2\sigma(I)$]
θ_{max} = 25.06°
$h = -4 \rightarrow 4$
$k = 0 \rightarrow 11$
$l = 0 \rightarrow 30$

Refinement

Refinement on F^2
$R(F)$ = 0.0427
$wR(F^2)$ = 0.0915
S = 1.010
1528 reflections
154 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0218P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.028

$\Delta\rho_{max}$ = 1.23 e Å^{-3} (at the Br site)
$\Delta\rho_{min}$ = −0.65 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)*

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

	x	y	z	U_{eq}
Br	0.42125 (13)	0.10110 (5)	0.05512 (2)	0.0238 (2)
O	1.1926 (9)	0.5109 (4)	0.20724 (14)	0.0267 (10)
N1	1.0680 (12)	0.2767 (5)	0.2504 (2)	0.0254 (12)
N2	1.1746 (10)	0.5140 (4)	0.0828 (2)	0.0230 (11)
C1	0.9180 (12)	0.3304 (5)	0.1647 (2)	0.0183 (12)
C2	0.9305 (13)	0.2422 (5)	0.2053 (2)	0.0203 (13)
C3	0.7824 (12)	0.1140 (6)	0.1995 (2)	0.0203 (12)
C4	0.6246 (12)	0.0737 (5)	0.1557 (2)	0.0212 (13)
C5	0.6214 (12)	0.1599 (5)	0.1167 (2)	0.0200 (13)
C6	0.7598 (12)	0.2851 (5)	0.1202 (2)	0.0172 (12)
C7	1.0634 (13)	0.4654 (5)	0.1680 (2)	0.0230 (13)
C8	1.0630 (12)	0.5594 (5)	0.1252 (2)	0.0195 (12)
C9	1.1967 (12)	0.6059 (6)	0.0474 (2)	0.0241 (13)
C10	1.1053 (13)	0.7375 (5)	0.0517 (2)	0.0238 (13)
C11	0.9839 (13)	0.7817 (6)	0.0951 (2)	0.0284 (15)
C12	0.9660 (12)	0.6910 (5)	0.1332 (2)	0.0207 (13)

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

Br—C5	1.919 (5)	N2—C8	1.345 (7)
O—C7	1.253 (6)	C1—C6	1.416 (7)
N1—C2	1.370 (7)	C1—C2	1.422 (7)
N1—H1*A*	0.91 (7)	C1—C7	1.463 (8)
N1—H1*B*	0.96 (8)	C7—C8	1.506 (8)
N2—C9	1.346 (7)		
C9—N2—C8	115.8 (5)	O—C7—C1	121.5 (5)
C6—C1—C2	118.6 (5)	O—C7—C8	115.6 (5)
C6—C1—C7	119.7 (5)	C1—C7—C8	122.8 (5)
C2—C1—C7	121.7 (5)	N2—C8—C12	124.0 (5)
N1—C2—C3	117.9 (5)	N2—C9—C10	124.4 (5)
N1—C2—C1	123.5 (5)	H1*A*—N1—H1*B*	113 (6)
C3—C2—C1	118.5 (5)		
O—C7—C8—N2	132.1 (5)	O—C7—C8—C12	−44.0 (6)
C1—C7—C8—N2	−49.0 (7)	C1—C7—C8—C12	134.9 (5)

Absence of crystal decay in the X-ray beam was confirmed by checking equivalent reflections at the beginning and end of data collection, which lasted about 8 h. Data were corrected for Lorentz and polarization effects. The non-H atoms were refined with anisotropic displacement parameters. The amino H atoms were refined freely and all other H atoms were allowed to ride on their attached C atoms with a common isotropic displacement parameter.

Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ZORTEP* (Zsolnai, 1994).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and torsion angles have been deposited with the IUCr (Reference: BM1039). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Bis(diphenylphosphino)methane Disulfide

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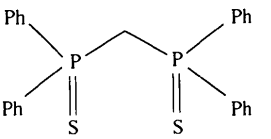
Abstract

The title compound, methylenebis(diphenylphosphine sulfide), $C_{25}H_{22}P_2S_2$, has been structurally characterized and is found to be isostructural with its selenium analog.

Comment

A number of compounds related to the title compound have been characterized previously by X-ray crystallography. Relevant structures include $Ph_2PCH_2PPh_2$ (dppm) [(1); Schmidbaur, Reber, Schier, Wagner & Müller, 1988], $Ph_2P(Se)CH_2P(Se)Ph_2$ (dppmSe$_2$) [(2); Carroll & Titus, 1971] and the related compound $Ph_2PCH_2P(Se)Ph_2$ (dppmSe) [(3); Colton, Hoskins & Panagiotidou, 1987]. The title compound, $Ph_2P(S)CH_2P(S)Ph_2$ (dppmS$_2$), (4), is isostructural with compound (2) and its crystal structure is reported herein.



(4)

The structure of (4) is comprised of discrete monomers with no short intermolecular interactions. A view of the molecular structure of (4) is shown in Fig. 1, with a packing view shown in Fig. 2. The P—S bond lengths [P(1)—S(1) 1.948 (1) and P(2)—S(2) 1.909 (1) Å] in (4) are slightly shorter than the corresponding P—Se bond distances found in compounds (2) [average P—Se 2.100 (4) Å] and (3) [P—Se 2.103 (1) Å]. All other bond lengths are similar to those observed in compounds (1)–(3) and deserve no special comment.

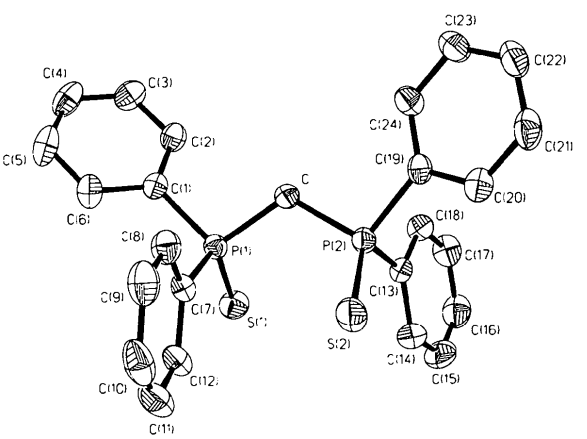


Fig. 1. The structure of compound (4) showing the atom-numbering scheme and 30% probability displacement ellipsoids. H atoms have been omitted for clarity.

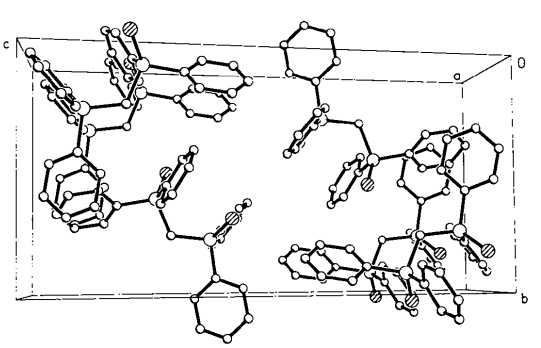


Fig. 2. A view of the packing in compound (4).