

The β -polymorph of phenazine

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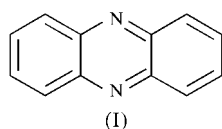
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In β -phenazine, $C_{12}H_9N_2$, the molecules show a sandwich herring-bone type of packing. The experimental crystal structure shows very good agreement with that predicted earlier from systematic searches of potential packing arrangements for the known unit cell [Hammond, Roberts, Smith & Docherty (1999). *J. Phys. Chem. B*, **103**, 7762–7770].

Comment

It is well known that phenazine crystallizes in two polymorphic forms. The structure of the stable phase (α -phenazine, m.p. 449.5 K) was first determined by Herbstein & Schmidt (1955) and later redetermined by Woźniak *et al.* (1991). The existence of a second polymorph was also first recognized by Herbstein & Schmidt (1955), who reported the space group and unit-cell parameters of the β phase and described its morphology. To our knowledge, no other experimental data have been reported on the less stable polymorph to date, and β -phenazine seems to exemplify a disappearing polymorph (Dunitz & Bernstein, 1995). Nevertheless, Hammond *et al.* (1999), using a systematic search of potential packing arrangements, predicted the crystal structure of the β polymorph.

Recently, by chance, we obtained good quality single crystals of β -phenazine, (I), from a crystallization mixture consisting of phenazine, 1,3,5-trihydroxybenzene and ethanol, by slow evaporation of the solution. In the first crop, we isolated several block-like crystals of α -phenazine and two rod-like crystals of dimensions $1.0 \times 0.2 \times 0.2$ mm which, after measuring the unit-cell parameters, turned out to be the β form. The melting point of these crystals (431 K) is 18 K lower than that of the α phase (449 K). The crystal structure of β -phenazine, (I), is presented here.



The bond lengths and angles of the phenazine molecule in both polymorphic forms are very similar. In contrast with α -phenazine, for which a γ arrangement (Desiraju & Gavezzoti, 1989) of the heteroaromatic rings has been

observed, β -phenazine shows a sandwich herring-bone type of packing.

The common structural motif for the two polymorphs is a chain of molecules connected *via* pairs of C–H \cdots N interactions. For the α -form, H \cdots N = 2.89 Å and C–H \cdots N = 146°. For the β -form, H3 \cdots N13ⁱ = 2.71 (2) Å and C3–H3 \cdots N13ⁱ = 156.5 (16)°, and H8 \cdots N14ⁱⁱ = 2.71 (2) Å and C8–H8 \cdots N14ⁱⁱ = 153.9 (16)° [symmetry codes: (i) $x, y, 1 + z$; (ii) $x, y, z - 1$]. The interplanar distance between adjacent phenazine molecules along the chain is 1.26 Å in the α polymorph and 1.088 (3) Å in the β form. In the β polymorph, there is an additional short C–H \cdots N contact between molecules related by an n glide [H5 \cdots N14ⁱⁱⁱ 2.60 (2) Å and C5–H5 \cdots N14ⁱⁱⁱ 145.1 (16)°; symmetry code: (iii) $x - \frac{1}{2}, \frac{1}{2} - y, z - \frac{1}{2}$].

The structure determined from the single crystal of (I) is very close to that predicted by Hammond *et al.* (1999), as can be seen from Fig. 2, which shows the superposition of the postulated and experimentally determined crystal structures. The π – π stack distance in the β -phenazine structure is 3.498 (3) Å (predicted distance 3.53 Å), the centroid–centroid distance within the stack is 3.80 Å (predicted 3.81 Å) and the herring-bone angle is 71.4 (3)° (predicted 72.9°).

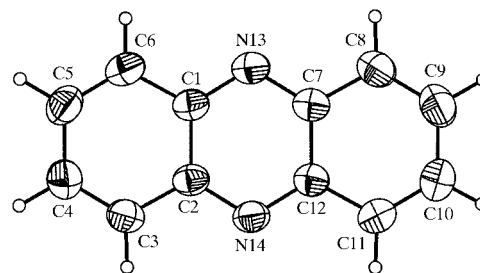


Figure 1

A view of the molecule of β -phenazine with 50% probability displacement ellipsoids. H atoms are shown as small spheres of arbitrary radii.

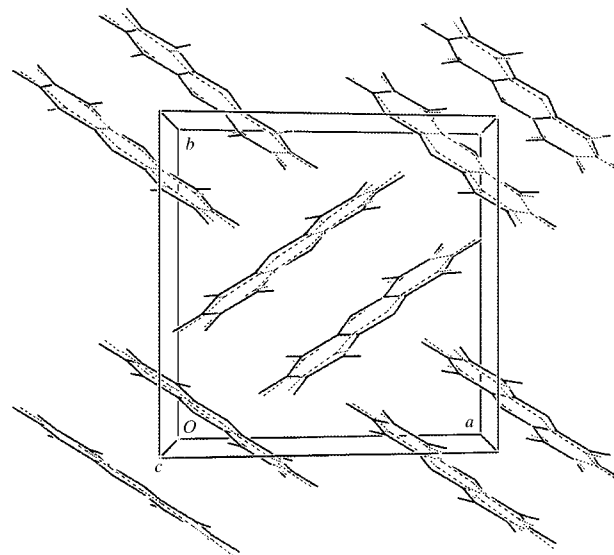


Figure 2

The superposition of the postulated (dashed lines) and experimentally determined (solid lines) crystal structures of β -phenazine.

Experimental

Good quality single crystals of β -phenazine were formed in a crystallization mixture consisting of phenazine (0.694 mmol; Fluka), 1,3,5-trihydroxybenzene (0.395 mmol; Fluka) and ethanol (10 ml) after slow evaporation of the solution.

Crystal data

$C_{12}H_8N_2$	$D_x = 1.309 \text{ Mg m}^{-3}$
$M_r = 180.20$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 2800 reflections
$a = 11.6418 (12) \text{ \AA}$	$\theta = 3.7\text{--}25.0^\circ$
$b = 11.5449 (11) \text{ \AA}$	$\mu = 0.08 \text{ mm}^{-1}$
$c = 6.8981 (7) \text{ \AA}$	$T = 293 (2) \text{ K}$
$\beta = 99.476 (10)^\circ$	Prism, yellow
$V = 914.48 (16) \text{ \AA}^3$	$0.3 \times 0.2 \times 0.2 \text{ mm}$
$Z = 4$	

Data collection

Kuma KM-4 CCD diffractometer	$R_{\text{int}} = 0.031$
ω scans	$\theta_{\text{max}} = 25^\circ$
4500 measured reflections	$h = -13 \rightarrow 13$
1604 independent reflections	$k = -13 \rightarrow 8$
1272 reflections with $I > 2\sigma(I)$	$l = -8 \rightarrow 8$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0716P)^2 + 0.0381P]$
$R[F^2 > 2\sigma(F^2)] = 0.053$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.149$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.23$	$\Delta\rho_{\text{max}} = 0.14 \text{ e \AA}^{-3}$
1604 reflections	$\Delta\rho_{\text{min}} = -0.12 \text{ e \AA}^{-3}$
160 parameters	Extinction correction: <i>SHELXL97</i>
All H-atom parameters refined	(Sheldrick, 1997)
	Extinction coefficient: 0.026 (7)

Refined C—H distances are in the range 0.95 (2)–1.01 (2) Å.

Data collection: *CRYSTALIS* (Oxford Diffraction, 2001); cell refinement: *CRYSTALIS*; data reduction: *CRYSTALIS*; program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *Stereochemical Workstation Operation Manual* (Siemens, 1989); software used to prepare material for publication: *SHELXL97*.

Table 1

Selected geometric parameters (Å, °).

C1—N13	1.341 (2)	C7—N13	1.343 (2)
C1—C6	1.421 (2)	C7—C8	1.419 (3)
C1—C2	1.433 (2)	C7—C12	1.435 (2)
C2—N14	1.344 (2)	C8—C9	1.357 (3)
C2—C3	1.423 (2)	C9—C10	1.419 (3)
C3—C4	1.353 (3)	C10—C11	1.341 (3)
C4—C5	1.415 (3)	C11—C12	1.421 (3)
C5—C6	1.346 (3)	C12—N14	1.341 (2)
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N13—C1—C6	119.88 (16)	N13—C7—C12	121.42 (16)
N13—C1—C2	121.68 (16)	C8—C7—C12	118.81 (17)
C6—C1—C2	118.43 (17)	C9—C8—C7	120.29 (19)
N14—C2—C3	119.68 (15)	C8—C9—C10	120.6 (2)
N14—C2—C1	121.30 (16)	C11—C10—C9	121.0 (2)
C3—C2—C1	119.02 (17)	C10—C11—C12	120.62 (19)
C4—C3—C2	120.04 (18)	N14—C12—C11	119.89 (16)
C3—C4—C5	120.9 (2)	N14—C12—C7	121.45 (16)
C6—C5—C4	120.83 (19)	C11—C12—C7	118.66 (17)
C5—C6—C1	120.73 (18)	C1—N13—C7	116.99 (14)
N13—C7—C8	119.77 (16)	C12—N14—C2	117.14 (14)

Supplementary data for this paper are available from the IUCr electronic archives (Reference: OS1149). Services for accessing these data are described at the back of the journal.

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