

Structures of Two Crystal Forms of the Host–Guest Complex Between *trans*-3,3'-Bis(diphenylhydroxymethyl)azobenzene and Acetone

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Abstract. (I) $\frac{1}{2}\text{C}_{38}\text{H}_{30}\text{N}_2\text{O}_2\cdot\text{C}_3\text{H}_6\text{O}$, $M_r = 331.4$, triclinic, $P\bar{1}$, $a = 10.076$ (2), $b = 12.346$ (3), $c = 9.154$ (2) Å, $\alpha = 98.90$ (2), $\beta = 122.06$ (2), $\gamma = 96.67$ (2)°, $V = 926.3$ (4) Å³, $Z = 2$, $D_m = 1.185$ (1), $D_x = 1.188$ Mg m⁻³, $\lambda(\text{Cu } K\alpha) = 1.5418$ Å, $\mu = 0.565$ mm⁻¹, $F(000) = 352$, $T = 295$ K, $R = 0.055$ for 2459 observed reflections. (II) $\text{C}_{38}\text{H}_{30}\text{N}_2\text{O}_2\cdot\text{C}_3\text{H}_6\text{O}$, $M_r = 604.7$, monoclinic, $C2/c$, $a = 16.782$ (2), $b = 8.744$ (3), $c = 23.386$ (3) Å, $\beta = 107.83$ (2)°, $V = 3267.0$ (12) Å³, $Z = 4$, $D_m = 1.227$ (2), $D_x = 1.229$ Mg m⁻³, $\lambda(\text{Cu } K\alpha) = 1.5418$ Å, $\mu = 0.573$ mm⁻¹, $F(000) = 1280$, $T = 295$ K, $R = 0.050$ for 2342 observed reflections. In both crystals, *trans*-3,3'-bis(diphenylhydroxymethyl)azobenzene is on a centre of symmetry, while acetone is situated at a general position in (I) and on a twofold axis in (II). Molecules in the complex are hydrogen bonded, although the scheme is different in the two crystals.

Introduction. This investigation forms part of studies on compounds which exhibit inclusion phenomena. We found that crystals of *trans*-3,3'-bis(diphenylhydroxymethyl)azobenzene grown from various organic solvents often contain the solvent molecules as the guest of the inclusion complex crystal (e.g. acetone, cyclohexanone, cyclopentanone, γ -lactone, tetrahydrofuran, dioxane, *N,N*-dimethylformamide, dimethyl sulfoxide and pyridine). Of these complex crystals, the host:guest ratio of the title complex is affected by the conditions of crystallization. The crystals with a host:guest ratio of 1:2 were grown by slow evaporation from an acetone solution of the host at room temperature [crystal (I)]. The other crystals with a host:guest ratio of 1:1 were grown by gradual cooling of the crystal (I) melted under 2666 Pa and 353.2 K [crystal (II)]. In order to obtain a definite structural basis for further studies of these inclusion phenomena, the crystal structures of both complexes were determined by single-crystal X-ray analysis.

Experimental. The brownish yellow prismatic crystals of (I) (m.p. 366.2 K), and the brownish-yellow prismatic crystals of (II) (m.p. 390.2 K) were obtained by the procedures mentioned above. The densities of the crystals were measured by flotation in tripotassium citrate aqueous solution. Both crystals were sealed in Lindemann-glass capillaries to prevent efflorescence. Crystal and intensity data were collected on a Rigaku four-circle diffractometer (AFC-5) using graphite-monochromated Cu $K\alpha$ radiation. Three standard reflections were monitored every 100 reflections during data collection, and no intensity variation was observed. Lorentz and polarization corrections were applied but no absorption correction was made. Experimental conditions are given in Table 1.

The structures were solved by the direct method with *MULTAN78* (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) and refined by the block-diagonal least-squares method (*HBLS-V*; Ashida, 1979), minimizing $\sum w(|F_o| - |F_c|)^2$. All H atoms of both crystals were found on the difference Fourier maps and included in the refinement with isotropic thermal parameters. The final R values were 0.059 ($wR = 0.058$) and 0.050 ($wR = 0.072$) for crystal (I) and crystal (II), respectively.

Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV, pp. 71–98). Atomic parameters and equivalent isotropic thermal parameters for non-H atoms are given in Table 2.* All the calculations were performed on an IBM 3081-GX3 at the Information Processing Center of Shimane University.

* Lists of structure factors, anisotropic thermal parameters for non-H atoms and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55208 (28 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AS0561]

Table 1. *Crystal and refinement data*

	Crystal (I)	Crystal (II)
No. of reflections for cell dimensions	25	20
2 θ range (°)	26–40	43–51
Crystal dimensions (mm)	0.50 × 0.40 × 0.25	0.50 × 0.40 × 0.20
Range h	–11 → 11	0 → 19
k	–14 → 14	0 → 10
l	–10 → 0	–25 → 25
Maximum 2 θ (°)	125	125
Method of measuring intensity	2 θ – ω	2 θ – ω
Number of reflections measured	2968	2562
Number of reflections observed [$F_o > 3\sigma(F_o)$]	2458	2342
Number of parameters refined	311	290
R	0.059	0.050
wR	0.058	0.072
w	1.0 for $F_o \leq 17.0$; 1/[1.0 – ($F_o - 18.5$) × 0.002] for $F_o > 17.0$	1.0 for $F_o \leq 25.0$; 1/[1.0 + ($F_o - 25.0$) × 0.222] for $F_o > 25.0$
S	0.38	1.22
Maximum Δ/σ	0.07	0.04
Maximum $\Delta\rho$ (e Å ^{–3})	0.48	0.43
Minimum $\Delta\rho$ (e Å ^{–3})	–0.25	–0.25

Table 2. *Final atomic coordinates (× 10⁴) and equivalent isotropic thermal parameters (Å²)*

$$B_{eq} = (4/3) \sum_i \sum_j \beta_{ij} a_i \cdot a_j$$

Crystal (I)	x	y	z	B_{eq}
N(1)	–4265 (3)	5054 (2)	545 (3)	3.77 (3)
C(2)	–3317 (3)	6174 (2)	1132 (4)	3.43 (3)
C(3)	–1667 (3)	6307 (2)	2361 (4)	3.39 (3)
C(4)	–612 (3)	7358 (2)	3060 (4)	3.53 (3)
C(5)	–1225 (4)	8278 (3)	2508 (4)	4.81 (5)
C(6)	–2873 (4)	8135 (3)	1258 (5)	5.57 (5)
C(7)	–3926 (4)	7093 (3)	569 (4)	4.61 (4)
C(8)	1204 (3)	7521 (2)	4461 (4)	3.66 (3)
O(9)	1990 (2)	8485 (2)	4279 (3)	4.66 (3)
C(10)	1514 (3)	7744 (2)	6326 (4)	3.59 (3)
C(11)	2649 (4)	8684 (3)	7666 (4)	4.42 (4)
C(12)	2950 (4)	8857 (3)	9367 (4)	5.12 (5)
C(13)	2130 (4)	8101 (3)	9741 (4)	5.06 (5)
C(14)	993 (4)	7164 (3)	8419 (4)	5.29 (5)
C(15)	684 (4)	6987 (3)	6717 (4)	4.78 (4)
C(16)	1791 (3)	6501 (3)	4045 (4)	3.85 (4)
C(17)	2565 (4)	5864 (3)	5242 (4)	4.59 (4)
C(18)	3099 (4)	4956 (3)	4765 (5)	5.95 (6)
C(19)	2879 (4)	4699 (3)	3114 (6)	6.54 (6)
C(20)	2122 (4)	5345 (4)	1932 (5)	6.48 (5)
C(21)	1571 (4)	6238 (3)	2380 (4)	5.16 (4)
O(22)	5395 (3)	8950 (3)	6535 (4)	8.75 (5)
C(23)	6421 (4)	8772 (3)	6290 (5)	5.81 (6)
C(24)	8148 (5)	9146 (5)	7765 (7)	9.63 (9)
C(25)	6033 (8)	8227 (6)	4546 (7)	12.80 (12)

Crystal (II)	x	y	z	B_{eq}
N(1)	2246 (1)	2947 (2)	5056 (1)	3.99 (2)
C(2)	2175 (1)	2802 (2)	5650 (1)	3.51 (2)
C(3)	1563 (1)	3714 (2)	5767 (1)	3.51 (2)
C(4)	1419 (1)	3661 (2)	6321 (1)	3.33 (2)
C(5)	1918 (1)	2707 (3)	6761 (1)	3.96 (2)
C(6)	2544 (1)	1829 (3)	6647 (1)	4.59 (2)
C(7)	2671 (1)	1858 (3)	6094 (1)	4.20 (2)
C(8)	719 (1)	4599 (2)	6449 (1)	3.26 (2)
O(9)	964 (1)	4778 (2)	7090 (1)	4.04 (1)
C(10)	–110 (1)	3713 (2)	6231 (1)	3.25 (2)
C(11)	–427 (1)	3205 (3)	5644 (1)	4.71 (3)
C(12)	–1176 (2)	2423 (4)	5453 (1)	5.81 (3)
C(13)	–1629 (2)	2141 (3)	5843 (1)	5.77 (3)
C(14)	–1329 (2)	2663 (4)	6423 (1)	6.15 (3)
C(15)	–575 (1)	3438 (3)	6616 (1)	4.89 (3)
C(16)	654 (1)	6202 (2)	6178 (1)	3.48 (2)
C(17)	–105 (1)	6885 (3)	5885 (1)	4.43 (2)
C(18)	–132 (2)	8413 (3)	5706 (1)	5.79 (3)
C(19)	594 (2)	9242 (3)	5814 (1)	6.31 (4)
C(20)	1350 (2)	8558 (3)	6095 (1)	6.30 (4)
C(21)	1383 (1)	7053 (3)	6283 (1)	4.98 (3)
O(22)	0 (0)	7045 (3)	7500 (0)	6.03 (3)
C(23)	0 (0)	8432 (4)	7500 (0)	5.33 (4)
C(24)	719 (3)	9309 (4)	7431 (2)	9.76 (7)

Table 3. *Selected bond distances (Å) and angles (°)*

	Crystal (I)	Crystal (II)
Host molecule		
N(1)–N(1)	1.245 (4 ^b)	1.243 (3 ^b)
N(1)–C(2)	1.426 (4)	1.435 (3)
C(4)–C(8)	1.542 (5)	1.535 (4)
C(8)–O(9)	1.432 (4)	1.433 (3)
C(8)–C(10)	1.532 (5)	1.528 (3)
C(8)–C(16)	1.532 (5)	1.537 (3)
Guest molecule		
O(22)–C(23)	1.204 (6)	1.213 (5)
C(23)–C(24)	1.480 (8)	1.479 (7)
C(23)–C(25)	1.446 (9)	
Host molecule		
C(2)–N(1)–N(1)	114.2 (2 ^b)	114.5 (2 ^b)
N(1)–C(2)–C(3)	114.7 (3)	115.1 (2)
N(1)–C(2)–C(7)	124.8 (2)	124.6 (2)
C(4)–C(8)–O(9)	105.6 (2)	105.6 (1)
C(4)–C(8)–C(10)	109.0 (3)	109.6 (2)
C(4)–C(8)–C(16)	110.5 (3)	111.8 (1)
O(9)–C(8)–C(10)	110.6 (3)	110.0 (2)
O(9)–C(8)–C(16)	108.2 (2)	107.1 (1)
C(10)–C(8)–C(16)	112.7 (2)	112.5 (1)
Guest molecule		
O(22)–C(23)–C(24)	120.8 (4)	121.1 (4)
O(22)–C(23)–C(25)	121.9 (5)	
C(24)–C(23)–C(25)	117.2 (5)	
C(24)–C(23)–C(24)		117.5 (4 ^{ab})

Symmetry code: (i) $-x - 1, -y + 1, -z$; (ii) $\frac{1}{2} - x, \frac{1}{2} - y, 1 - z$; (iii) $-x, y, \frac{1}{2} - z$.

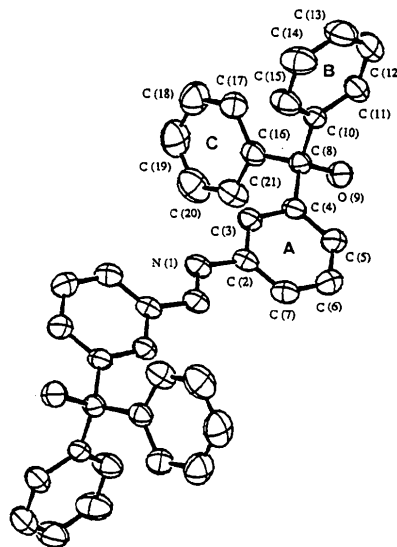


Fig. 1. A perspective view of the host molecule with atomic numbering scheme.

Discussion. A perspective drawing of the host molecule is given in Fig. 1 (ORTEPII; Johnson, 1976). In (I), the host is situated at a centre of symmetry, although the guest is situated in a general position. In (II), the host is also situated at a centre of symmetry and the guest molecule lies on a twofold axis of rotation. The host:guest ratio for each crystal is consistent with that determined by thermogravimetric analysis. Chemically equivalent bond distances and angles in both crystals are similar to each other (Table 3). Torsion angles are not significantly differ-

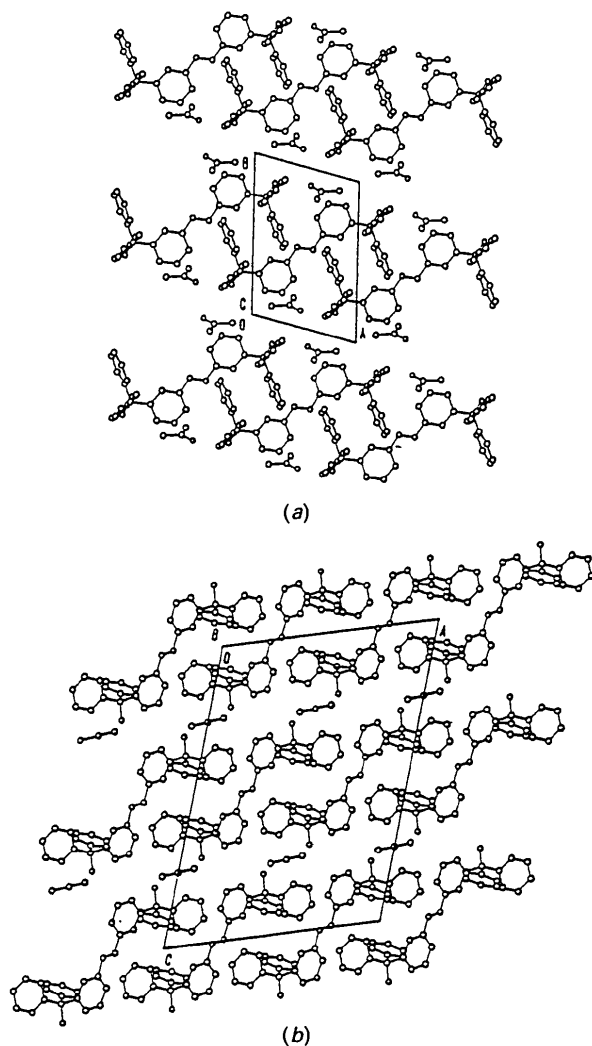


Fig. 2. Crystal structures of (a) crystal (I) and (b) crystal (II).

ent between both crystals. The three dihedral angles formed by three benzene rings are similar in both crystals: 72.5 for (I) and 71.9° for (II) between *A* and *B* rings, 77.4 for (I) and 73.9° for (II) between *A* and *C* rings and 78.3 for (I) and 80.0° for (II) between *B* and *C* rings.

The crystal-packing diagrams for both crystals are given in Fig. 2 (PLUTO; Motherwell & Clegg, 1978). In crystal (I), the carbonyl O atom of an acetone molecule makes a hydrogen bond with the hydroxy O atom of the host molecule [O(9)⋯O(22) = 2.831 (5) Å]. On the other hand, in (II) the carbonyl O atom of the acetone links two host hydroxy O atoms related by a twofold rotation symmetry at (*x*, *y*, *z*) and (−*x*, *y*, ½ − *z*) through two equivalent hydrogen bonds [O(9)⋯O(22) = 2.901 (3) Å]. The difference in the hydrogen-bond scheme between crystals (I) and (II) is reflected in the difference of the melting points of the two crystals.

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Structure of 2,3-Naphthalenedicarboxylic Acid

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Abstract. C₁₂H₈O₄, *M_r* = 216.20, monoclinic, *C*2/*c*, *a* = 5.087 (2), *b* = 19.222 (3), *c* = 9.552 (2) Å, β = 93.81 (3)°, *V* = 932.0 (5) Å³, *Z* = 4, *D_x* =

1.54 g cm^{−3}, λ = 0.71073 Å, μ = 1.09 cm^{−1}, *F*(000) = 488, *T* = 295 K, *R* = 0.037 for 687 unique reflections having *I* > 3σ(*I*). In the structure reported here, a twofold axis lies in the plane of the molecule and bisects the three central ring bonds. The average

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