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Crystal Structure of Benzene-Solvate of Bis(benzophenone) Azine: A Color Polymorph

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A crystalline complex of bis(benzophenone) azine (BBA), solvated by benzene in a BBA:benzene = 1:1 ratio, was isolated as yellow crystals, and its crystal structure was determined by single-crystal X-ray diffraction analysis at 223 K. The complex crystallizes in the triclinic crystal system in the space group $P\bar{1}$ (#2) with the cell parameters a = 8.646(6)Å, b = 9.096(5)Å, c = 9.217(6)Å, α = 78.01(2)°, β = 64.23(2)°, γ = 67.39(2)°, Z = 1, and V = 601.9(6)Å^3. Benzene is embedded in a channel running along the c-axis. The yellow color of the complex, in contrast to the colorless solvent-free crystals, is attributed to the planar geometry of the C=N–N=C moiety.

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The prediction of the crystal polymorphic behavior of materials is still in its infancy.[1] It is important to try to account for the observed differences in the properties of polymorphs, as much as possible, on the basis of structural findings. Along these lines, the color differences of polymorphic crystals are of considerable interest.[2,3] An extraordinary example is 5-methyl-2-[(2-nitrophenyl)amino]-3-thiophenecarbonitrile, which occurs in several polymorphs including red, orange, and yellow forms.[4] Solvated crystals, known as pseudo-polymorphs,[5] also provide opportunities for studying different crystal and molecular structures of the same compounds. However, color polymorphs in solvated crystals are rarely encountered.[6,7] We have found yellow crystals of bis(benzophenone) azine (BBA) that include benzene as a solvated molecule. Solvent-free crystals of BBA are colorless, and their structure has already been reported.[8] In this paper, we describe the crystal and molecular structures of benzene-solvated BBA and explain the structural and color differences.

The benzene solvate of bis(benzophenone) azine has been isolated as yellow crystals by cooling a benzene solution of BBA from boiling to room temperature over 5 h period. The colors of the BBA-C_6H_5 and BBA crystals are shown in Fig. 3. Benzene solvated crystals are not persistent owing to the easy loss of benzene and become opaque within 10 min. Crystallographic data and experimental details are listed in Table 1. The crystal structure was solved to final values of $R1$ = 0.0372 and $wR2$ = 0.1155 using 9835 reflections.

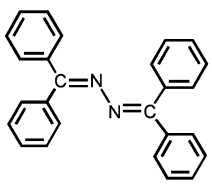

Fig. 1 Chemical structure of BBA.

The BBA molecules in BBA-C_6H_6 crystals are centrosymmetric. Their most characteristic feature is the planar geometry of the C=N–N=C moiety (dihedral angle of C=N–N=C: 180.0(1)°) in contrast to the twisted conformation with a twist angle of 132.5(7)° of solvent-free BBA crystals. Furthermore, the C2–C1=N–N and C8–C1=N–N torsional angles are 178.6(1) and 2.2(2)°, respectively, indicating that the >C=N–N=C< framework is in an almost planar geometry. The C1=N (1.292(2)Å) and =N–N= (1.411(2)Å) distances show no significant differences from those of solvent-free BBA, which

Table 1 Crystal and experimental data

Chemical formula: $C_{32}H_{26}N_2$	
Formula weight = 438.57	
T = 223 K	
Crystal system: triclinic	Space group: $P\bar{1}$ (#2)
a = 8.646(6)Å	α = 78.01(2)°
b = 9.096(5)Å	β = 64.23(2)°
c = 9.217(6)Å	γ = 67.39(2)°
V = 601.9(6)Å^3	Z = 1
D_x = 1.210 g/cm^3	
Radiation: Mo K_α (λ = 0.71075 Å)	
μ(Mo K_α) = 0.703 cm^{-1}	F_{000} = 232.00
Crystal size = 0.60 × 0.30 × 0.10 mm^3	
Crystal color: yellow	
No. of reflections collected = 9835	
No. of independent reflections = 2745	
θ range for data collection: 3.0 to 27.5°	
Data/Restraints/Parameters = 2745/0/167	
Goodness-of-fit on F^2 = 0.961	
R indices [$I > 2.00\sigma(I)$)]: $R1$ = 0.0372, $wR2$ = 0.1155	
R indices (all data): $R1$ = 0.0520, $wR2$ = 0.1225	
$(\Delta/\sigma)_{max}$ = 0.000	
$(\Delta\rho)_{max}$ = 0.21 e$^-$/Å^3	$(\Delta\rho)_{min}$ = –0.14 e$^-$/Å^3
Measurement: Rigaku RAXIS-RAPID	
Program system: Rigaku Crystal Structure 3.8.2	
Structure determination: SHELXS-97	
CCDC deposition number: 847160	

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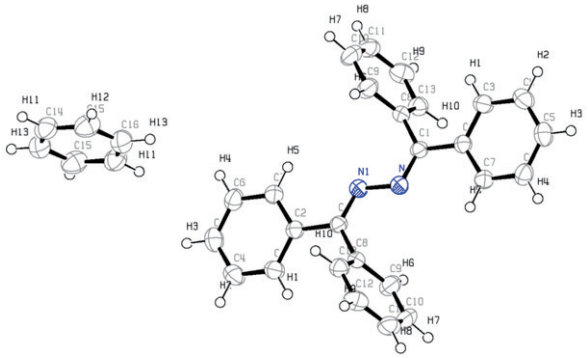

Fig. 2 The molecular structure of BBA-C_6H_6 with the atom labeling scheme. Displacement ellipsoids are drawn at the 50% probability level.

are 1.286(9) and 1.404(8)Å, respectively. One of the benzene rings of benzophenone origin is only slightly twisted from the >C=N–N=C< plane (twist angle: 12.9(2)˚), whereas the other benzene ring is highly twisted (twist angle: 70.6(2)˚). This conformational difference affects C–C_{ipso} bond length. For the close-to-coplanar benzene, the C1–C2 distance is 1.481(2)Å, while for the twisted C1–C8 it is 1.494(2)Å. The extended planar geometry through the C_6H_5–C=N–N=C–C_6H_5 moiety allows more extensive π-electron delocalization in the molecule in contrast to the nonplanar conformation and brings about the yellow coloration of the crystals.

With respect to the crystal structure, a one-dimensional chain of BBA molecules is formed along the *c*-axis owing to the presence of intermolecular face-to-face π-π interaction between the benzene rings of the neighboring molecules. As shown in Fig. 4, this π-π interaction is of the offset type: the C6–C7 bond of the benzene ring is aligned parallel to that of its neighboring molecule to make a parallelogram along with a short C6–C7 contact (3.344(2)Å). Benzene is embedded in a channel running along the *c*-axis without particular intermolecular interactions. Therefore, BBA-C_6H_6 should be regarded as, in terms of the original meaning, a true clathrate crystal.[9] The side view of the molecules, also shown in Fig. 4, indicates that the >C=N–N=C< moiety is planar.

We are further searching for other examples of crystalline molecular complexes of bis(benzophenone) azine to investigate structure-color relations.

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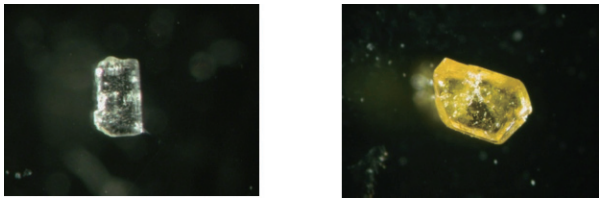

Fig. 3 Colors of (a) BBA and (b) BBA-C_6H_6 crystals.

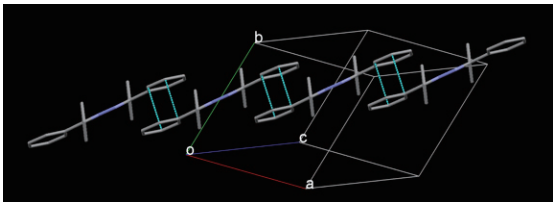

Fig. 4 Crystal structure of BBA-C_6H_6, showing side view of molecular structure in planar >C=N–N=C< framework and intermolecular π-π interactions.

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