The 20 K structure of *p*-amino-*p′*-nitrobiphenyl in the non-constraining environment of its β-cyclodextrin inclusion complex

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Though *p*-amino-*p′*-nitrobiphenyl (PANB) is essentially planar in its crystalline form, it takes on a twisted conformation in its 2 : 2 crystalline inclusion complex with β-cyclodextrin (β-CD); the angles between the two phenyl rings are 40.6(2) and 42.0(1)° for the two molecules respectively, compared with 44.1(1)° for biphenyl in the gas phase, thus indicating the absence of constraints in the β-CD dimer cage.

Cyclodextrins are among the most widely used molecular hosts in the field of supramolecular chemistry.[1] They are used extensively in industry and are also chiral host molecules which can be used as models for studying weak interactions involved in molecular recognition. Room temperature diffraction studies typically show disorder, attributed to the absence of strong host–guest interactions in the inclusion complexes. Such disorder should be reduced at very low temperatures, thus allowing a more precise determination of the molecular parameters of the included species, and analysis of the influence of the geometry on the molecular conformation and electron density.

We report the synthesis and 20 K crystal structure of a *p*-amino-*p′*-nitrobiphenyl (PANB)–β-cyclodextrin (β-CD) complex. To the best of our knowledge this study represents the lowest temperature β-cyclodextrin crystallographic investigation to date. PANB has a long-lived excited triplet state, in which charge is transferred from the amine donor to the nitro acceptor group of the molecule.[2] Accordingly, a large increase in dipole moment of PANB upon excitation occurs.[3] As the diffraction analysis of molecular excited states is now becoming feasible,[4] such effects provide additional motivation for the current study.

Crystals of (β-CD–PANB)₂ pentaicosahydrate were prepared by adding 8 mg of PANB[5] to 20 ml of saturated aqueous β-CD. This solution was heated and stirred in a sealed flask at 85 °C for 2 h, hot filtered to remove any undissolved PANB, and allowed to cool to room temperature over 3–4 days. Small, yellow, wedge-shaped crystals of the complex were obtained.

The crystalline β-CD–PANB inclusion complex (Fig. 1) consists of face-to-face β-CD dimers including two guest PANB molecules in the extended torus.[6] The two PANB molecules pack in the β-CD dimers with overlapping phenyl rings parallel to each other. A difference map ($F_o - F_c$) calculated near the end of refinement revealed an alternate position with much lower occupancy for each of the PANB molecules. The minor component PANB molecules were included in the final cycles with a conformation restrained to be similar to that of the major PANB molecules. The refinement led to a 17% occupancy of the minor sites. Standard deviations in the molecular bond lengths and angles are satisfactory (typically 0.004 Å and 0.4° for non-hydrogen bond distances and angles, respectively). The bond lengths and angles in the

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two independent molecules are identical within the experimental uncertainty. They are also similar to those found in neat PANB crystals[7] (Fig. 2). In *p*-nitroaniline,[8] the nitro N–C bond is much shorter than observed in nitrobenzene,[9] the amine N–C bond is much shorter than in aniline,[10] and the aromatic ring displays alternating long and short bonds, features indicative of a quinonoid resonance form reflecting migration of charge from donor to acceptor. In β-CD–PANB, nitro N–C and amine N–C bond lengths are somewhat shorter than the corresponding bonds in nitrobenzene and aniline. But the difference is not as marked as in *p*-nitroaniline, and no significant distortions of the aromatic rings are found, thus indicating a smaller degree of charge-transfer in PANB.

Even though the bond lengths and angles are very similar in the neat crystals and in the inclusion complex, there are marked differences in overall conformation. Thus, there is a different balance between the requirements of π-conjugation of the phenyl rings and packing forces, and the steric repulsion between the *ortho* hydrogens which is reduced in the non-planar conformer. The PANB molecules in neat crystals are essentially planar [inter-ring twist angle (IRTA) of 2.3(5)° whereas in the β-CD dimer they display a twisted conformation [IRTA =
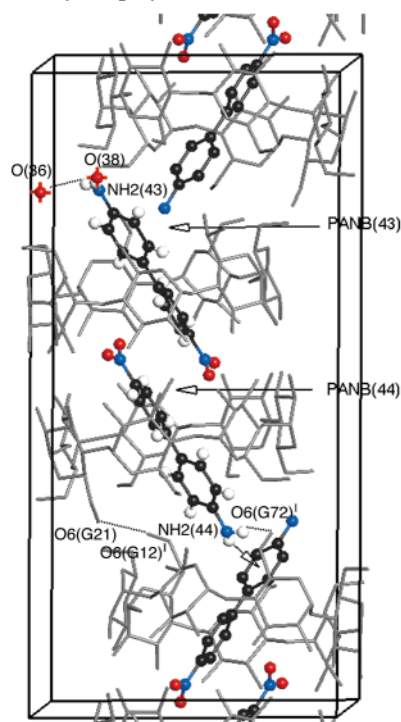
Fig. 1 Structure of the (β-CD–PANB)₂ complex. CDs are in grey while the atoms of the guest PANB molecules are colored as follows: carbon = black; oxygen = red; nitrogen = blue; hydrogen = white. For clarity, only the hydrogens of the PANB molecules in the assymetric unit are shown. Only water oxygen atoms involved in important guest–water interactions are shown. See text for details.
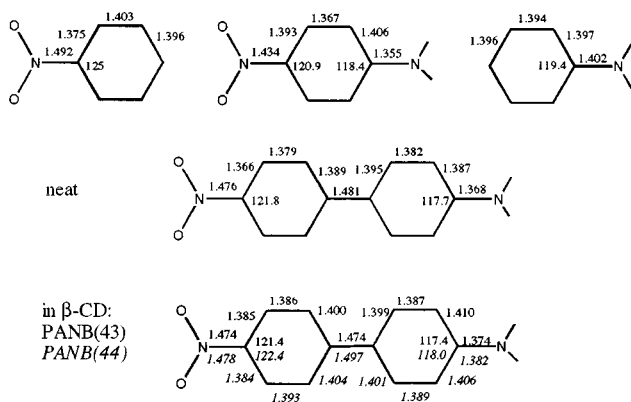
Fig. 2 Comparison of bond lengths and angles in nitrobenzene,[9] *p*-nitroaniline,[8] aniline,[10] neat PANB,[7] and the PANB molecules included in β-CD. Values reported are the average of one or two bond lengths.

40.6(2)° and 42.0(1)° for PANB(43) and PANB(44), respectively]. The difference between the two phases is similar to that observed for biphenyl, which is essentially planar in the solid state,[11] but takes on a twisted conformation in both the gas phase[12] (IRTA = 40–45°) and in its crystalline β-CD inclusion complexes [IRTA = 44.1(1)° as determined by solid state NMR[13]]. Similarly, biphenyl has been observed to take on twisted conformations in other co-crystals[14] (33,[14a] 40.5[14b] and 36.6° [14c]). *Ab initio* geometry optimization of biphenyl and PANB gives twisted conformations for the ground state of both molecules, with twist angles of 45.5 and 41.9°, respectively.[15] Evidently, the β-CD dimer interior provides a 'gas-phase-like' environment, in which the crystal packing forces that produce planar conformations in the neat crystals are no longer operative.

The host dimer entities pack in a 'screw channel' motif.[16] Host–guest interactions include both hydrogen bonding and hydrophobic interactions. The two PANB molecules reside within the β-CD dimer in the same manner, with the nitro ends of the molecules centered in the torus of the dimer. The amine ends of the PANB molecules, which may donate two hydrogen bonds and accept one, protrude from the primary ends of the dimer. One of the PANB molecules, PANB(44), serves as a hydrogen bond donor to a primary hydroxy of an adjacent β-CD dimer [NH2(44)···O6(G72)^I = 3.011(4) Å, ∠C6(44)–NH2(44)···O6(G72)^I = 111.2(3)° ($I = -x, y - 1/2, -z$)]. As a result, this primary hydroxy group (G72) is a +*gauche* conformer[17] with the C6–O6 bond directed towards the host cavity. The other amine hydrogen of PANB(44) is involved in a unique N–H···π face electrostatic interaction with the aniline half of a PANB molecule protruding from the primary face of the adjacent β-CD dimer. The N-to-phenyl ring plane distance is 3.277(6) Å. The two amine hydrogens of PANB(43) are involved in guest–water hydrogen bond interactions [NH2(43)···O(36) = 3.153(7) Å, ∠C6(43)–NH2(43)···O(36) = 110.8(3)°; NH2(43)···O(38)‡ = 3.275(11) Å, ∠C6(43)–NH2(43)···O(38) = 112.8(4)°]. The packing of the PANB molecules within the β-CD dimers leads to quite different intermolecular PANB interactions than exist in neat PANB crystals. The PANB molecules in the latter form an infinite chain of molecules connected by inter-molecular NH2···NO2 hydrogen bonds, while such interactions are absent in the host–guest complex. Nevertheless, the donor–acceptor charge transfer, judged by the C–N bond lengths, is similar in the two crystals.

The structure determination at 20 K reveals a complex in which the guest PANB molecules are sufficiently ordered to allow an accurate and detailed structure determination. Comparison with the theoretically obtained geometry shows the guest molecules to have a conformation close to that calculated for the gas phase. The use of very low temperatures in structural analysis of host–guest complexes has significant advantages, provided, of course, that no first order phase transformations occur on cooling.

Notes and references

‡ Calculated from average positions of disordered water O(38).

1 *Comprehensive Supramolecular Chemistry, Vol. 3, Cyclodextrins*, ed. J. L. Atwood, J. E. D. Davies, D. D. MacNicol and F. Vogtle, Pergamon, Oxford, 1996.
2 P. Piotrowiak, R. Kobetic, T. R. Schatz and G. Strati, *J. Phys. Chem.*, 1995, **99**, 2250.
3 J. Czekalla, W. Liptay and K. O. Meyer, *Ber. Bunsengesselschaft*, 1963, **67**, 465.
4 P. Coppens, D. V. Fomitchev, M. D.Carducci and K. Culp, *J. Chem. Soc., Dalton Trans.*, 1998, 865.
5 PANB was prepared by nitration of 4-nitrobiphenyl with nitric acid (H. C. Gull and E. E. Turner, *J. Chem. Soc.*, 1929, 491). The product was isolated and reduced with sodium hydrogen sulfide to give PANB (J. P. Idoux, *J. Chem. Soc., Sect. C*, 1970, 435).
6 *Crystal data*: for (C$_{42}$H$_{70}$O$_{35}$)$_2$·(C$_{12}$H$_{10}$N$_2$O$_2$)$_2$·25.5H$_2$O, M_r = 3157.81, monoclinic, P2$_1$ (no. 4), a = 15.454, b = 31.693, c = 15.255 Å, $β$ = 102.92°, Z = 2, D_c = 1.440 g cm^{-3}, crystal size 0.094 × 0.063 × 0.063 mm. T = 20.0(1) K. Data were collected by the oscillation method at the X3A1 beamline station at the NSLS at BNL at a wavelength of 0.643 Å. A single 20 × 40 cm Fuji BAS-III imaging plate was used for data collection. The HKL suite (Z. Otwinowski, *Data Collection and Processing*, ed. L. Sawyer, N. Isaacs and S. Bailey, SERC Daresbury Laboratory, Warrington, UK, 1993, p. 56) was used for data processing (R_{merge} = 0.058). In all, 20607 unique reflections were recorded to a resolution of 0.68 Å. The structure was solved by isostructural replacement of the β-CD coordinates from an isomorphous structure. Least-squares refinement on F^2 of 1951 parameters was carried out using SHELXL97 (G. M. Sheldrick, *SHELXL97. Program for the Refinement of Crystal Structures*, University of Göttingen, Germany, 1997) and converged to a final R_1 = 0.0584, wR_2 = 0.1539, and GOF = 1.047 for 18109 reflections with $F_o > 4σ (F_o)$. All non-hydrogen atoms were treated anisotropically except those of the lower occupancy PANB sites which were refined as a rigid body with a single group isotropic displacement parameter. A final difference electron density map showed no distinct features with $ρ_{max}$ = 1.352 and $ρ_{min}$ = −0.828 e Å^{-3}. CCDC 182/1140.
7 E. M. Graham, V. M. Miskowski, J. W. Perry, D. R. Coulter, A. E. Stiegman, W. P. Schaefer and R. E. Marsh, *J. Am. Chem. Soc.*, 1989, **111**, 8771.
8 M. Colapietro, A. Domenicano, C. Marciante and G. Portalone, *Z. Naturforsch., Teil B*, 1982, **37**, 1309.
9 F. Di Rienzo, A. Domenicano and L. R. Di Sanseverino, *Acta Crystallogr., Sect. B*, 1980, **36**, 586.
10 D. G. Lister, J. K. Tyler, J. H. Høg and N. W. Larsen, *J. Mol. Struct.*, 1974, **23**, 253.
11 G. P. Charbonneau and Y. Delugeard, *Acta Crystallogr., Sect. B*, 1977, **33**, 1586.
12 O. Bastiansen, *Acta Chem. Scand.*, 1949, **3**, 408.
13 A. D. Ronemus, PhD Thesis, University of California, San Diego, 1987.
14 (*a*) T. Iwamoto, T. Miyoshi and Y. Susaki, *Acta Crystallogr., Sect. B*, 1974, **30**, 292; (*b*) A. Lipka and D. Mootz, *Z. Anorg. Allg. Chem.*, 1978, **440**, 217; (*c*) K. W. Klinkhammer, *Chemistry*, 1997, **3**, 1418.
15 *Ab initio* geometry optimizations were carried out at the HF/6-31G* level using GAUSSIAN94. Optimizations of planar, perpendicular, and twisted geometries showed the twisted conformation to be of lowest energy.
16 D. Mentzafos, I. M. Mavridis, G. LeBas and G. Tsoucaris, *Acta Crystallogr., Sect. B*, 1991, **47**, 746.
17 W. Saenger, *Inclusion Compounds*, ed. J. L. Atwood, J. E. D. Davies and D. D. MacNicol, Academic Press, London, 1984, vol. 2, 231.

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