The change in the X-ray dipole moment as a quantitative measure of the polarizing effect of the molecular environment: application to a complex of *p*-amino-*p'*-nitrobiphenyl with triphenylphosphine oxide

Yuegang Zhang and Philip Coppens*

Department of Chemistry, State University of New York at Buffalo, Buffalo, New York, 14260-3000, USA.
E-mail: coppens@acsu.buffalo.edu

The X-ray determined dipole moment has been used to assess the strength of the electrostatic interactions in a new complex of *p*-amino-*p'*-nitrobiphenyl, which is a suitable candidate for photo-crystallographic studies of transient species.

Prior to photo-crystallographic studies of light-induced excited molecular states, suitable candidates for such time-resolved studies must be identified.[1,2] A relatively long-lived triplet excited state of *p*-amino-*p'*-nitrobiphenyl (PANB) has been reported to exist at room temperature in solution.[3] PANB is a typical donor–acceptor molecule; upon excitation an intra-molecular charge transfer occurs from the amine donor to the nitro acceptor group.[4] Correspondingly, fluorescence and time-resolved microwave measurements indicate a large increase in dipole moment (by more than 20 D) when the molecule is excited.[5] In order to increase the conversion percentage of excited state molecules upon irradiation, and/or reduce the number of photons to be absorbed by the crystal, it is highly desirable to dilute the photoactive species with photo-inert spacer molecules. In a previous study, the β-cyclodextrin complex of PANB was found to show disorder in the guest molecules, and thus to be less suitable for photo-crystallo-graphic studies.[3]

We report here on the 90 K structure and charge density of a fully-ordered mixed crystal of PANB. We use the molecular dipole moment as determined from the X-ray diffraction data as a measure of the strength of the electrostatic forces acting on the host molecule. This analysis is based on the extensive evidence indicating a pronounced enhancement of the electrostatic moments of polar molecules in crystals.[6–8] The enhancement is directly dependent on the molecular environment, and it thus varies with crystal composition and molecular packing.

Triphenylphosphine oxide (TPPO) is a strong hydrogen acceptor. It has been shown to form high quality crystals with molecules containing donor hydrogen atoms, like the amino hydrogens of PANB.[9] As the TPPO molecule does not absorb above 300 nm,[10] its absorption does not interfere with the charge-transfer absorption of PANB, which peaks at 400 nm,[11] an essential condition for a photo-inert 'spacer' molecule. X-Ray data on a specimen grown by slow evaporation[12] were collected on a Bruker SMART 1K CCD diffractometer at 90(1) K.[13]

Hydrogen bonding between the NH$_2$ groups and the oxygen atoms of TPPO (Fig. 1) leads to a synthon consisting of four molecules (two each of TPPO and PANB), which is the basic unit in the crystal.[14] The square arrangement of hydrogen bonded atoms is similar to that in TPPO tetrachloropyrocatechol monohydrate, in which water molecules of crystallization are the hydrogen donors.[15] A comparable arrangement is found in bis(triphenylphosphine oxide) tris(toluene-*p*-sulfonamide) where the two P=O groups are bridged by three sets of hydrogen bonds, donated by NH$_2$ groups.[16] Unlike in neat PANB, the nitro groups in PANB/TPPO are involved only in weak O···H–C interactions.[17] The crystals are fully ordered and do not contain solvent molecules.
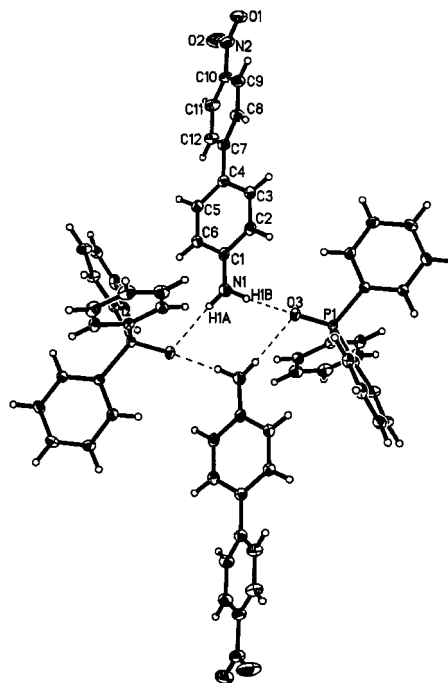

Fig. 1 Illustration of the basic packing motif in the PANB/TPPO crystal.

In the neat crystal the biphenyl group adopts a close to planar conformation (see Fig. 2),[18,19] though calculations[20] indicate the isolated molecule to be twisted by 43.3°, similar to what is found for gas-phase biphenyl.[21,22] In the current structure the inter-ring twist angle is 30.27(3)° (Fig. 2), compared with values of 40.6(2) and 42.0(1)° at 20 K for the two independent molecules in the less constraining environment of β-cyclodex-trin. The concentration of PANB in PANB/TPPO is 2.64 M compared with 6.56 M in the neat crystal.

In general the dipole moment of a molecule in a polar crystal is enhanced relative to that of the isolated molecule in the gas phase. The increase in dipole moment is a quantitative measure of the polarizing field exerted on the molecules by the crystal matrix. While the isolated molecule value is calculated as 9.12 D for the configuration of the PANB molecule as observed in the neat crystal, and as 8.17 D for the twisted optimized geometry,[20] the value derived by topological analysis of the theoretical density for the periodic crystal is 23.0 D.[8] This
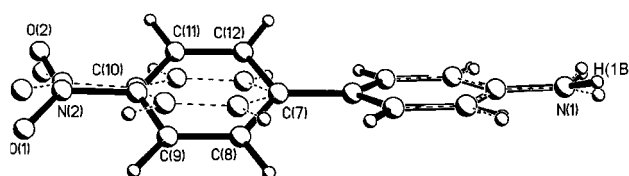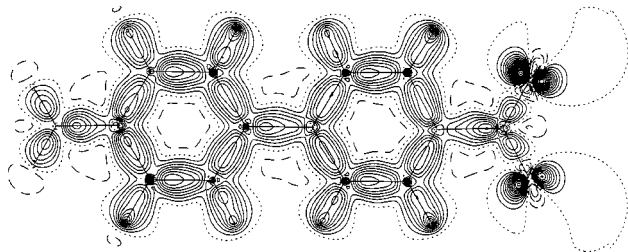

Fig. 2 The molecular structure of PANB in the TPPO complex (twisted), compared with the almost planar conformation in the neat crystal.

Fig. 3 Deformation density map of PANB in the PANB/TPPO crystal as calculated from the aspherical atom multipole refinement results. For illustration purposes, the two phenyl rings of the non-planar molecule have been rotated into the plane of the paper. Contours at 0.1 eÅ^{-3}. Positive contours: full lines; zero contour: dotted; negative contours: broken.

compares with an experimental X-ray result of *ca*. 40 D.[8,19] An aspherical atom refinement[23,24] of the current data shows the molecular dipole moment in the mixed crystal to be 16.8(1.6) D, much in excess of the isolated molecule values, but significantly below that in neat PANB (the static deformation density map in the least square planes of the two phenyl rings is shown in Fig. 3). The neat crystal contains sheets of parallel molecules, leading to parallel and anti-parallel (between sheets) alignment of the dipole moments such as to maximize electrostatic interactions. By comparison, the electrostatic interactions are significantly reduced in PANB/TPPO, in agreement with the relatively weak interactions of the nitro group in the complex. Since the molecular dipole moment can now be routinely obtained from good quality X-ray data, it provides a readily accessible measure of the electrostatic interactions in a crystal.

In summary, the PANB/TPPO mixed crystal is a candidate for excited state diffraction studies, given the absence of disorder and undesirable spectral overlap, and the reduced concentration of the active species. Both the experimental dipole moment and the inter-ring twist angle are intermediate between those of the isolated molecule and the neat PANB crystal. The X-ray dipole moment can be used to characterize related solids, and provides insight into factors relevant to crystal engineering.

Notes and references

1 P. Coppens, D.V. Fomitchev, M. D. Carducci and K. Culp, *J. Chem. Soc., Dalton Trans.*, 1998, 865.
2 Y. Zhang, G. Wu, B. R. Wenner, F. V. Bright and P. Coppens, *Cryst. Eng.*, 1999, **2**, 1.
3 T. J. Brett, S. Liu, P. Coppens and J. J. Stezowski, *Chem. Commun.*, 1999, 551.
4 P. Piotrowiak, R. Kobetic, T. R. Schatz and G. Strati, *J. Phys. Chem.*, 1995, **99**, 2250.
5 J. Czekalla, W. Liptay and K. O. Meyer, *Ber. Bunsen-Ges. Phys. Chem.*, 1963, **67**, 465; M. N. Paddon-Row, A. M. Oliver, J. W. Warman, K. J. Smit, M. P. de Haas, H. Oevering and J. W. Verhoeven, *J. Phys. Chem.*, 1988, **92**, 6958.
6 C. Gatti, V. R. Saunders and C. Roetti, *J. Chem. Phys.*, 1994, **101**, 10 686.
7 S. T. Howard, M. B. Hursthouse, C. W. Lehmann, P. R. Mallinson and C. S. Frampton, *J. Chem. Phys.*, 1992, **97**, 2962.
8 Yu. A. Abramov, A. V. Volkov and P. Coppens, *Chem. Phys. Lett.*, 1999, **311**, 81.
9 M. C. Etter and P. W. Baures, *J. Am. Chem. Soc.*, 1988, **110**, 639.
10 SADTLER standard UV spectrum, 1962, NO. 4852UV.
11 K. A. Al-Hassan and M. A. El-Bayoumi, *Chem. Phys. Lett.*, 1987, **138**, 594.
12 Crystals of PANB/TPPO were grown by slow evaporation (four days) from an acetone solution of PANB (TCI America) and excess TPPO (Aldrich). Large transparent specimens of up to $0.5 \times 1.0 \times 1.0$ cm^3 were obtained, with an orange red color less intense than that of pure PANB. ^{1}H NMR indicated a 1:1 ratio of the two components.
13 *Crystal data* for (C$_{18}$H$_{15}$OP)(C$_{12}$H$_{10}$N$_2$O$_2$): $M = 492.49$, triclinic, $a = 9.2719(8)$, $b = 10.4330(10)$, $c = 14.4569(11)$ Å, $\alpha = 106.122(4)$, $\beta = 107.714(5)$, $\gamma = 94.691(4)°$, $U = 1258.47(19)$ Å^3, $T = 90(1)$ K, space group $P\bar{1}$ (no. 2), $Z = 2$, $D_c = 1.300$ g cm^{-3}, crystal size $0.13 \times 0.25 \times 0.25$ mm^3, μ(Mo-Kα) = 0.144 mm^{-1}, 89125 reflections, 13140 unique reflections ($R_{int} = 0.0421$), $2\theta_{max} = 105.54°$, GOF = 0.865, $R(F) = 0.033$, for 9163 reflections with $F_o > 4\ \sigma(F_o)$, $Rw(F^2) = 0.084$ for all reflections, 426 parameters. Data were collected by the oscillation method on a Bruker SMART 1K CCD diffractometer. Reflections were integrated by the SAINT program and scaled by SORTAV. The structure was solved by direct methods with XS in SHELXTL (SHELXTL NT Version 5.10, G. M. Sheldrick, Program for the Refinement of Crystal Structures, University of Göttingen, Germany, 1997), and refined with XL. All the non-hydrogen atoms were refined anisotropically. Positions of hydrogen atoms were located from the difference Fourier map and refined isotropically, each with its own isotropic temperature parameters. No constraint was applied in the refinement. CCDC 182/1464. See http://www.rsc.org.suppdata/cc/1999/2425/ for crystallographic data in .cif format.
14 N1···O3^I = 3.055(1) Å, ∠N1–H1A···O3^I = 146.6(1.2)°, (I = 1+x, y, 1 + z); N1···O3^{II} = 2.931(1) Å, ∠N1–H1B···O3^{II} = 176.0(1.3)°, (II = 2 − x, −y, 1 − z).
15 M. Y. Antipin, A. I. Akhmedov, Y. T. Struchkov, E. I. Matrosov and M. I. Kabachnik, *Zh. Strukt. Khim.*, 1983, **24**, 86.
16 G. Ferguson and C. Glidewell, *J. Chem. Soc., Perkins Trans. 2*, 1988, 2129.
17 C15···O2^{III} = 3.447(1) Å, ∠C15–H15···O2^{III} = 167.4(1.0)°, (III = 1 + x, y, z).
18 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.
19 A. V. Volkov, G. Wu and P. Coppens, *J. Synchrotron Radiat.*, 1999, **6**, 1007.
20 HF, 6311G** basis set, Jaguar 3.5, Schrödinger, Inc. Portland, OR, 1998.
21 O. Bastiansen, *Acta Chem. Scand.*, 1949, **3**, 408.
22 C. P. Brock and R. P. Minton, *J. Am. Chem. Soc.*. 1989, **111**, 4586.
23 T. Koritsanszky, S. Howard, T. Richter, Z. Su, P. R. Mallinson, N. K. Hansen, *XD-A Computer Program Package for Multipole Refinement and Analysis of Electron Densities from Diffraction Data*, Free University Berlin, Germany, 1995.
24 X–H distances taken from *International Tables for Crystallography, Vol. C*, were used for all C–H and N–H bonds. The κ' restricted multipole model (KRMM)[8] was applied, $R(F) = 0.019$, $Rw(F^2) = 0.041$.

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