The Origin of Nonlinear Optical Activity of 1,3,5-Triamino-2,4,6-trinitrobenzene in the Solid State: The Crystal Structure of a Non-Centrosymmetric Polymorph as Determined by Electron Diffraction

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Knowledge of the electronic and geometric features of donor−acceptor-substituted π-systems at the molecular and bulk level is crucial to the rational design of materials with nonlinear optical (NLO) properties.[1] Optimization at the molecular level has made great progress, as exemplified by recent work on extended, linear nonaromatic π-systems.[1d] In a different approach, nonbenzenoid structures may also result from the symmetrical attachment of three strong donors and three acceptors to the benzene nucleus. Provided their rings remain planar, these molecules lack permanent dipole moments but may combine high-molecular second-order polarizabilities with increased transparencies in the visible region.[2] In this conjunction, the molecular properties of 1,3,5-triamino-2,4,6-trinitrobenzene (TATB) have been studied extensively by computational methods.[2fg,4a] As determined by X-ray crystallography,[3] TATB adopts a nearly planar conformation and forms a layer structure dictated by six intermolecular O···H contacts. There are two molecules per unit cell. The layers themselves are non-centrosymmetric with approximate trigonal symmetry, but adjacent layers are arranged in a centrosymmetric fashion. This gives rise to the centrosymmetric space group $P\bar{1}$ which is incompatible with the NLO activity observed. Explanations offered to resolve this contradiction have been (a) polymorphism[2c] of TATB—which has not been documented so far—and (b) disorder of the known structure, including (temporary?) defor-
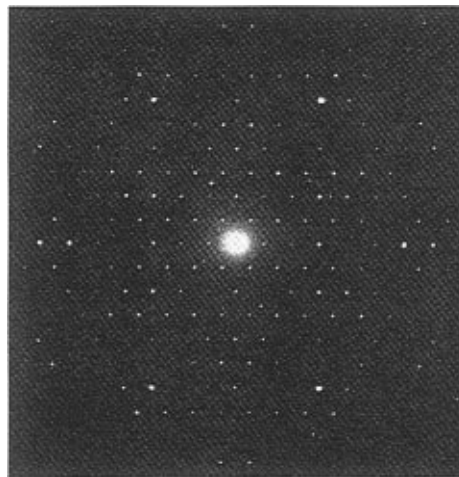
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(1) (a) Prasad, P. N.; Williams, D. J. *Nonlinear Optical Effects in Molecules and Polymers*; Wiley: New York, 1991. (b) Marder, S. R., Sohn, J. E., Stucky, G. D., Eds.; *Materials for Nonlinear Optics*; ACS Symposium Series 455; American Chemical Society: Washington, DC, 1991. (c) Wagnière, G. H. *Linear and Nonlinear Optical Properties of Molecules*; VHCA/VCH: Basel/Weinheim, 1993. (d) Marder, S. R.; Gorman, C. B.; Meyers, F.; Perry, J. W.; Bourhill, G.; Brédas, J.-L.; Pierce, B. M. *Science* **1994**, *265*, 632 and references therein.

(2) (a) Maker, P. D. *Phys. Rev. A: At., Mol., Opt. Phys.* **1970**, *1*, 923. (b) Chemla, D. S.; Oudar, J. L.; Jerphagnon, J. *Phys. Rev. B: Condens. Matter* **1975**, *12*, 4534. (c) Ledoux, I.; Zyss, J.; Siegel, J. S.; Brienne, J.; Lehn, J.-M. *Chem. Phys. Lett.* **1990**, *172*, 440. The term octopolar NLO is used moments in conjunction with NLO-phores without dipole. For example, see: ref 2e, p 77. (d) Joffre, M.; Yaron, D.; Silbey, R. J.; Zyss, J. *J. Chem. Phys.* **1992**, *97*, 5607. Zyss, J. *ibid* **1993**, *98*, 6583. (e) Verbiest, T.; Clays, K.; Samyn, C.; Wolff, J. J.; Reinhoudt, D.; Persoons, A. *J. Am. Chem. Soc.* **1994**, *116*, 9320. (f) Brédas, J.-L.; Meyers, F.; Pierce, B. M.; Zyss, J. *J. Am. Chem. Soc.* **1992**, *114*, 4928. (g) Brédas, J.-L.; Dehu, J.; Meyers, F.; Persoons, A.; Zyss, J. *J. Mol. Cryst. Liq. Cryst. Sci. Technol., Sect. B* **1994**, *6* (3−4), 263. (h) Optical poling with lifetimes of tens of minutes has, however, been demonstrated for ethyl violet: Fiorini, C.; Charra, F.; Nunzi, J.-M.; Samuel, I. D.; Zyss, J. *Optics Lett.* **1995**, *20*, 2469. (i) Cross, G. *Nature* **1995**, *374*, 307.

(3) Cady, H. H.; Larson, A. C. *Acta Crystallogr.* **1965**, *18*, 485. Space group $P\bar{1}$, $Z = 2$; $a = 9.01$, $b = 9.03$, and $c = 6.81$ Å; $\alpha = 108.6°$, $\beta = 91.82°$, $\gamma = 119.97°$; $\rho_{calcd} = 1.94$ g cm^{-3}.

(4) (a) Baldridge, K. K.; Siegel, J. S. *J. Am. Chem. Soc.* **1993**, *115*, 10782. (b) Filippini, G.; Gavezzotti, A. *Chem. Phys. Lett.* **1994**, *231*, 86. (c) Gavezzotti, A. *Acc. Chem. Res.* **1994**, *27*, 309.

Figure 1. Experimental diffraction pattern of [001]zone.

mation of the molecular geometry itself,[4a] displacement of molecules within a layer,[2c] and non-centrosymmetric stacking of layers.[4b,c] Only the latter hypothesis has been supported by packing energy calculations which predict non-centrosymmetric structures of TATB to be of comparable energies without, however, experimental evidence. Since TATB and its alkylated derivatives have aroused considerable interest[2,4,5] as a paradigmatic representative of nondipolar molecules with high second-order polarizabilities, we have been motivated to redetermine its solid-state structure by a combination of a detailed analysis of electron diffraction with an array of computational methods as described previously.[6a,7,8] In this paper we also intend to highlight the power of electron diffraction to elucidate solid-state structures of single crystals.

TATB was crystallized from hot DMSO to give a microcrystalline powder which showed frequency doubling in an SHG microscope.[6b] These crystals were placed on electron microscope grids. It was immediately clear that two different morphologies prevailed: (a) thick crystals with rhombohedral geometry and (b) thin (about 100 Å) hexagonal crystals, only the latter ones being penetrable by the electron beam. The diffraction patterns from the thin crystals in the *ab* projection are shown in Figure 1 and do not correspond to the expected diffraction pattern from the structure given in the literature, but instead a "pseudohexagonal" pattern appeared. In order to solve this apparent discrepancy, different zonal projections of the crystals were obtained by tilting about the *a* and *b* axes. An almost continuous series of zones appeared, indicating a large *c* axis. The result of the tilting experiment can be summarized as follows: (a) Tilting about the (110) direction revealed the [$1\bar{1}1$] and [332] zones at 21° and 30°. Tilting to the right and left gave rise to equivalent diffraction patterns. (b) Tilting about the *a* axis revealed the [032] and [031] zones at 18° and 33°, respectively. Tilting about the *b* axis revealed the [302] and [301] zones at 18° and 33°, respectively. In both cases, the tilting to the right and to the left gave identical results, indicating that the angle between the *ab* plane and the *c* axis is 90°, or close to it. All diffraction patterns have very characteristic and reproducible features: (1) Very strong (300), (320), and (030)

(5) Wolff, J. J.; Limbach, H.-H. *Liebigs Ann. Chem.* **1991**, 691.

(6) (a) Voigt-Martin, I. G.; Schumacher, M.; Garbella, R. *Macromolecules* **1992**, *25*, 961. (b) Loos-Wildenauer, M.; Kunz, S.; Voigt-Martin, I. G.; Yakimanski, A.; Wischerhoff, E.; Zentel, R.; Tschierske, C.; Müller, M. *Adv. Mater.* **1995**, *7*, 170.

(7) Voigt-Martin, I. G.; Yan, D. H.; Yakimanski, A.; Schollmeyer, D.; Gilmore, C. J.; Bricogne, G. *Acta Crystallogr., Sect. A: Fundam. Crystallogr.* **1995**, *51*, 849.

(8) (a) Voigt-Martin, I. G.; Simon, P.; Yan, D. H.; Yakimanski, A.; Baur, S.; Ringsdorf, H. *Macromolecules* **1995**, *28*, 243. (b) Voigt-Martin, I. G.; Yan, D. H.; Wortmann, R.; Elich, K. *Ultramicroscopy* **1995**, *57*, 29.
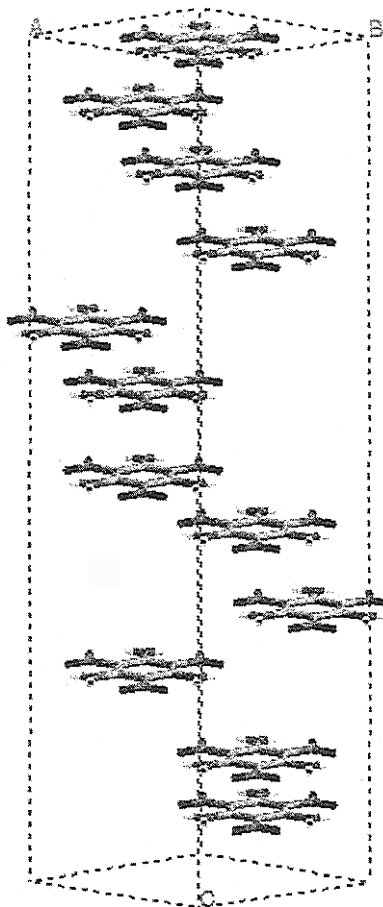
Figure 2. Simulated model with a modulated translatory wave.

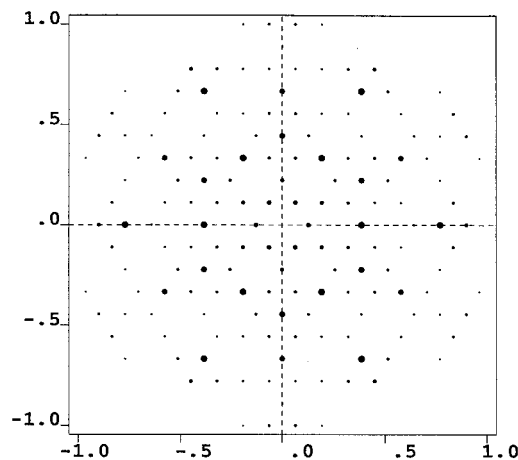**Figure 3.** Simulated diffraction pattern corresponding to the model in Figure 2.

reflections. (2) Very strong (600) and symmetry-related reflections. (3) Characteristic nonhexagnal distribution of intensities around (600) and symmetry related reflections.

These observations indicated a characteristic superstructure with three or six subunits which do not have $P6_1$ symmetry.

In addition, diffraction patterns from fortuitously lying fragments showing the [010] zone, have strong (0012) reflections corresponding to 3.4 Å and streaks parellel to c^* along (100), (200) etc. subdivided into four units. Therefore, there is a shift between layers of molecules separated by 3.4 Å in groups of four. Detailed analysis of these results in the manner described previously[6a,7,8] indicated a trigonal unit cell with the following cell constants: space group $P3_1$, $a = b = 9.00$ Å, $c = 40.90$ Å, $\gamma = 120°$.

The best agreement between the simulated and experimental diffraction patterns is achieved when all TATB molecules in the cell are planar and have D_{3h} symmetry. However, a nonplanar C_{3v} geometry(chairlike conformation) for the TATB molecule was also found to be possible but is very unlikely since chair forms are extremely rare with benzene derivatives.[4e] A detailed discussion of the conformational problem for the TATB molecule in the $P3_1$ crystal will be presented elsewhere.[9]

The diffraction patterns from all zonal projections were simulated first by calculating the conformation of the molecule in the gas phase using the semiempirical quantum mechanical methods (AM1 and PM3) incorporated in MOPAC 6.0. The molecule with optimized geometry was placed in the unit cell as described previously[7,8] using the program package CERIUS 3.2 such that the required density of 1.8 g/cm^3 was achieved using the model shown in Figure 2. Good agreement between calculated and experimental diffraction patterns was achieved in all zones. For space reasons, only the calculated [001] zone is shown in Figure 3 giving an R-factor of 0.29, which is

satisfactory for electron diffraction due to unavoidable inaccuracies from crystal bending and dynamical scattering. The remaining zones and their calculated diffraction patterns will be reported elsewhere.[9] A packing energy of -297 kcal/mol per unit cell was calculated for this model using the force fields discussed previously.[7,8a] While the precise, quantitative value obtained may be open to argument,[4c] the essential criterion, namely a strongly negative packing energy, is fulfilled by the model and supported by experiment. It is clear that the extremely large c axis requires a modulation in the c direction. Good agreement between the experimental and simulated diffraction patterns in all zones was achieved with the model shown in Figure 2 with three independent units, each consisting of four molecules. The stable graphite-like layers are modulated by a translatory wave. The position of the 13th layer agrees with the first one. The absence of an inversion center in these small crystals probably accounts for the SHG activity observed in powder samples of TATB, which has been shown to contain two polymorphs. Detailed calculations of both dipolar and octopolar hyperpolarizability β-components based on equations derived by Zyss[2c,f] will be reported elsewhere.[9]

The simulated electron diffraction patterns from the structure proposed in the literature did not agree with the experimental patterns from the small crystals in any projection. The X-ray powder diffraction pattern showed good agreement with the model structure proposed here but revealed some additional peaks which could not be explained. However, these peaks did correspond to the structure proposed in the literature.[3] It is very likely that these reflections stem from the thick crystals.

It has been proposed[2c,4b,c] that defects in the crystal could be responsible for the second-order NLO effect. However, our high-resolution images have revealed a defect-free crystal lattice,[9] and the analysis of our electron diffraction patterns indicates that the structural modulation on the c axis gives rise to the resultant hyperpolarizability components.

Our results show a possible way of constructing noncentrosymmetric structures of nondipolar NLO-phores: strong hydrogen bonding leads to non-centrosymmetric layers. Frequently, little energy difference, if any, exists between a centrosymmetric and a non-centrosymmetric stacking of layers, making the existence of either polymorph highly possible. We are currently analyzing structures of soluble molecules of a similar type which may also adopt stable layer structures.

Supporting Information Available: Diffraction patterns and calculated models (5 pages). See any current masthead page for ordering and Internet access instructions.

(9) Voigt-Martin, I. G.; Gao, Li.; Yakimanski, A.; Gross, H.; Wolff, J. J. Manuscript in preparation.