

# Donor–Acceptor Interactions in Crystal Engineering

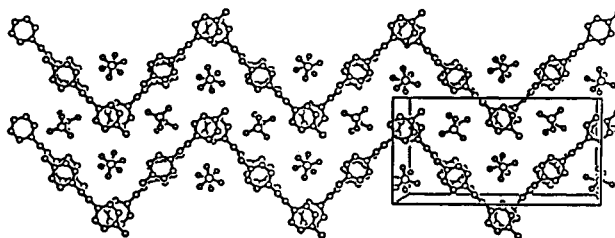
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Received January 3, 2001

## ABSTRACT



The molecular complex formed between 4-methyltolane and bis(4-*N*-methylpyridinium)ethyne ditriflate is reported. The X-ray crystal structure indicates that the crystalline superstructure consists of infinite zigzag ribbons of interlocked donor–acceptor complexes separated by triflate counterions.

The rational design of supramolecular structure can be realized through crystal engineering based on relatively weak intermolecular forces.<sup>1</sup> Among these forces, hydrogen bonding<sup>2</sup> is the most common; however, other interactions including halogen–halogen<sup>3</sup> and halogen–nitrogen<sup>4,5</sup> have been used to organize molecules within the crystal. The weak electron donor–acceptor, or charge-transfer, complexation has received limited application,<sup>6–8</sup> and in this Letter

we describe the formation of an infinite bimolecular ribbon held together by electron donor–acceptor (EDA) complexation.

In this study we formed crystalline molecular complexes from donor (electron-rich) and acceptor (electron-poor) molecules with similar rodlike shapes. As donor we chose the electron-rich 4-methyltolane<sup>9</sup> and as acceptor the dication bis(4-*N*-methylpyridinium)ethyne ditriflate. The acceptor was prepared by methylation of bis(4-pyridyl)ethyne<sup>10,11</sup> in dichloromethane (Scheme 1). The crystalline EDA complexes were prepared by first mixing equimolar, colorless, acetonitrile solutions of the donor and acceptor followed by slow evaporation of the solvent.

The EDA interaction between the colorless donor and acceptor molecules was manifest in the yellow coloration of the crystals. <sup>1</sup>H NMR and elemental analysis of the yellow crystals confirmed the formation of a 1:1 molecular complex.<sup>12</sup> The crystals were analyzed by X-ray crystallography,

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(1) For a review see: Desiraju, G. R. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2311.

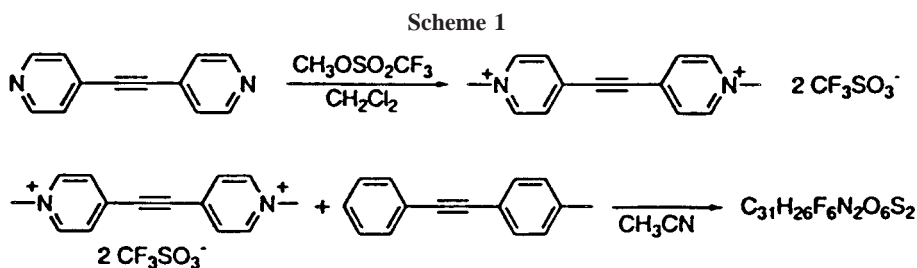
(2) For a review see: Subramanian, S.; Zaworotko, M. J. *Coord. Chem. Rev.* **1994**, *137*, 357.

(3) Schmidt, G. M. J. *Pure Appl. Chem.* **1971**, *27*, 647.

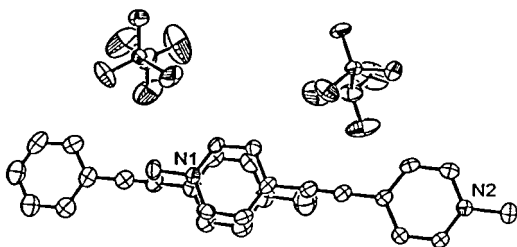
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(5) Xu, K.; Ho, D. M.; Pascal, R. A., Jr. *J. Org. Chem.* **1995**, *60*, 7186 and references therein.

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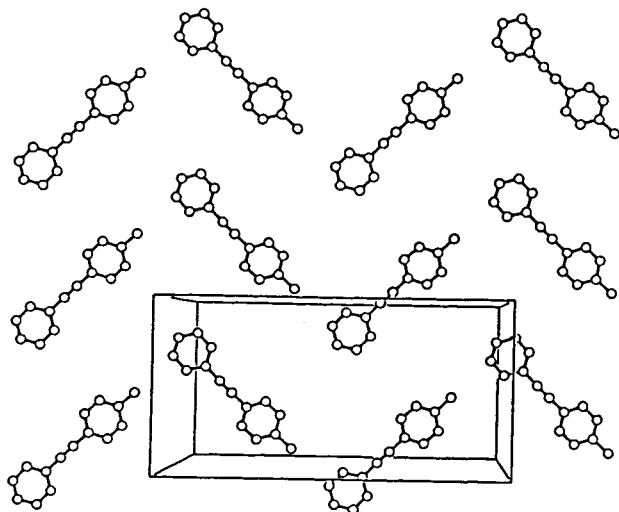


and the partial overlap of adjacent donor and acceptor molecules is shown in Figure 1.<sup>13</sup> The approximate inter-



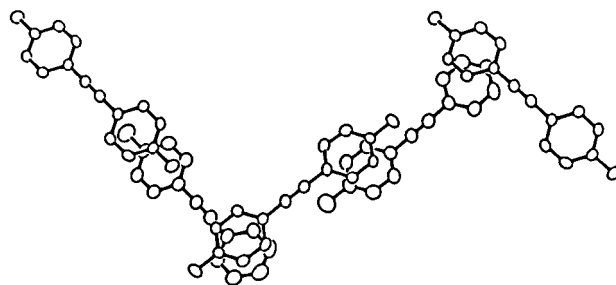
**Figure 1.** Ortep<sup>16</sup> representation of the molecular complex  $\text{C}_{31}\text{H}_{26}\text{F}_6\text{N}_2\text{O}_6\text{S}_2$  drawn with hydrogen atoms omitted for clarity.

planar spacing between donor and acceptor molecules is 3.6 Å, typical of  $\pi$ -stacked donor and acceptor pairs.<sup>8</sup> This simple arrangement, however, belies the elegant lattice packing and superstructure. Indeed, the view normal to the (001) face reveals that the donor molecules form sheets with the head-to-tail orientation shown in Figure 2.



**Figure 2.** View showing a sheet of donor (4-methyltolane) molecules.

The acceptor pyridinium molecules lie in an adjacent parallel sheet with a complementary motif. The partial overlap shown in Figure 1 enables bridging complexation between adjacent donor–acceptor pairs as shown in Figure 3.<sup>14</sup> This bridging,



**Figure 3.** Oblique view showing the bridging complexation of two adjacent pairs of donor and acceptor molecules.

facilitated by the complementary shape and size of the donor and acceptor molecules, then results in the formation of infinite ribbons of interlocked donor–acceptor complexes separated by the triflate counterions as shown in Figure 4. The triflate counterions span the acceptor and donor layers with the sulfonate headgroups penetrating the acceptor layer

(7) For the application of charge-transfer complexation as a tool in crystal engineering directed toward solid-state reactions, see: (a) Bosch, E.; Hubig, S. M.; Lindeman, S. V.; Kochi, J. K. *J. Org. Chem.* **1998**, *63*, 592. (b) Coates, G. W.; Dunn, A. R.; Henling, L. M.; Ziller, J. W.; Lobkovsky, E. B.; Grubbs, R. H. *J. Am. Chem. Soc.* **1998**, *120*, 3641.

(8) For an approach to molecular recognition using EDA complexation, see: Rathore, R.; Lindeman, S. V.; Kochi, J. K. *J. Am. Chem. Soc.* **1997**, *119*, 9393.

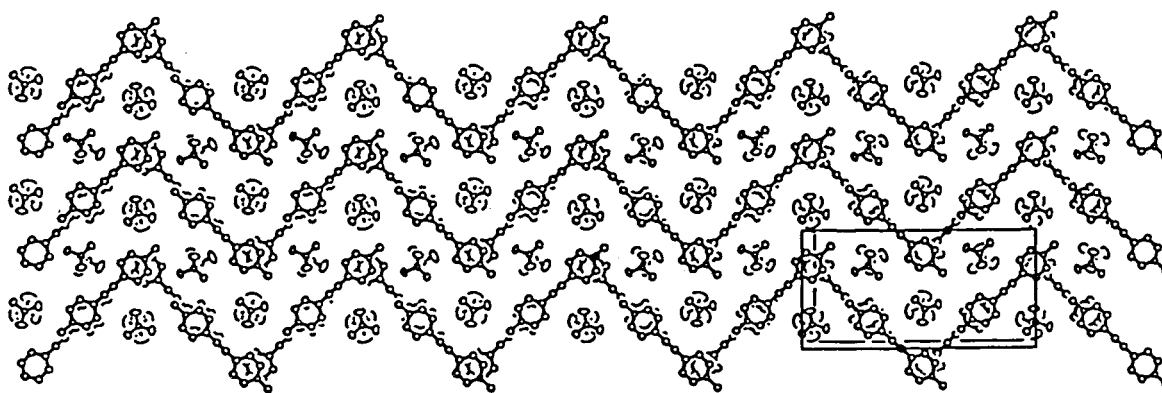
(9) Bosch, E.; Hubig, S. M.; Kochi, J. K. *J. Am. Chem. Soc.* **1998**, *120*, 386.

(10) Bis(4-pyridyl)ethyne was prepared as described in Tanner, M.; Ludi, A. *Chimia* **1980**, *34*, 23.

(11) The crude bis pyridinium salt was recrystallized from ethyl acetate as clear cubic crystals. Anal. Calcd for  $\text{C}_{16}\text{H}_{14}\text{F}_6\text{N}_2\text{O}_6\text{S}_2$ : C, 37.80; H, 2.78. Found: C, 37.95; H, 2.79. <sup>1</sup>H NMR ( $\text{CD}_3\text{CN}$ )  $\delta$  4.01 (s, 6H), 7.85 (d,  $J$  = 6.6 Hz, 4H), 8.44 (d,  $J$  = 6.6 Hz, 4H); <sup>13</sup>C NMR ( $\text{CD}_3\text{CN}$ )  $\delta$  49.57, 95.13, 131.17, 138.12, 146.94.

(12) <sup>1</sup>H NMR ( $\text{CD}_3\text{CN}$ )  $\delta$  2.37 (s, 3H), 4.34 (s, 6H), 7.23 (d,  $J$  = 8.4 Hz, 2H), 7.38–7.52 (m, 7H), 8.17 (d,  $J$  = 6.6 Hz, 4H), 8.73 (d,  $J$  = 6.6 Hz, 4H);  $\lambda_{\text{max}}$  ( $\text{CH}_3\text{CN}$ ) 385 nm. Anal. Calcd for  $\text{C}_{31}\text{H}_{26}\text{F}_6\text{N}_2\text{O}_6\text{S}_2$ : C, 53.14; H, 3.74. Found: C, 53.24; H, 3.71.

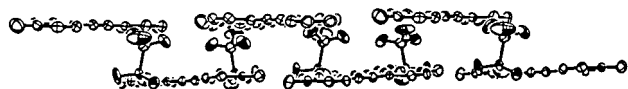
(13) Crystal data:  $\text{C}_{31}\text{H}_{26}\text{F}_6\text{N}_2\text{O}_6\text{S}_2$ ,  $M$  = 700.66, orthorhombic, space group *Pbca*,  $a$  = 11.367(9),  $b$  = 22.1802(18), and  $c$  = 25.876(2) Å,  $\alpha$  = 90,  $\beta$  = 90, and  $\gamma$  = 90°,  $V$  = 6524.0(9) Å<sup>3</sup>,  $Z$  = 8,  $D_c$  = 1.427 Mg/m<sup>3</sup>,  $\lambda$  = 0.71070 Å,  $T$  = 173(2) K.



**Figure 4.** View showing the overlap between adjacent donor and acceptor layers. The infinite ribbons of interlocked donor–acceptor complexes are separated by triflate anions.

as shown in Figure 5. Clearly the size and shape of the triflate anion is vital, ensuring the formation of an interlocked ribbon structure.

It is interesting to note the similarities between the superstructure shown here and the superstructures formed by coordination polymerization.<sup>15</sup> We speculate that many-diverse superstructures may also be engineered using donor–acceptor complexation.



**Figure 5.** View of an adjacent pair of donor and acceptor layers with triflate anions spanning both layers.

**Acknowledgment.** E.B. acknowledges receipt of a Faculty Research Grant and a Summer Faculty Fellowship from the Graduate College of Southwest Missouri State University.

**Supporting Information Available:** Tables of crystal data and structure refinement, atomic coordinates, bond lengths and angles, anisotropic displacement parameters and hydrogen coordinates for  $C_{31}H_{26}F_6N_2O_6S_2$ . This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(14) The related partial overlap between adjacent stilbene derivatives has been reported in the preparation of organic salts with nonlinear optical properties. See: Marder, S. R.; Perry, J. W.; Yakymyshyn, C. P. *Chem. Mater.* **1994**, *6*, 1137.

(15) See, for example: Carlucci, L.; Ciani, G.; Proserpio, D. M. *Chem. Commun.* **1999**, 449.

(16) Drawn using Ortep3: Farrugia, L. J. *J. Appl. Crystallogr.* **1997**, *30*, 565.