Molecular Recognition *via* Iodo···Nitro and Iodo···Cyano Interactions: Crystal Structures of the 1 : 1 Complexes of 1,4-Diiodobenzene with 1,4-Dinitrobenzene and 7,7,8,8-Tetracyanoquinodimethane (TCNQ)

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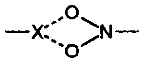
Mutual recognition of iodo and nitro groups through symmetrical iodo–nitro bridging interactions generates symmetrical molecular ribbons in the crystal structure of the 1 : 1 complex of 1,4-diiodobenzene **1** with 1,4-dinitrobenzene **2**; however, in the crystal structure of the 1 : 1 complex of **1** with TCNQ, the mediation of simple, non-bridging $-I\cdots N{\equiv}C$ interactions leads to the formation of skewed ribbons.

The goal of molecular recognition and crystal engineering is to establish rigorous connections between molecular and supramolecular structure *via* intermolecular interactions.[1–3] Ideally one would like to identify robust structural motifs which are transferable from one crystal structure to another, somewhat like a synthon in molecular chemistry. These substructural motifs are of crucial importance in systematic crystal engineering and many of these predesigned building blocks are based on strong ($O–H\cdots O$, $N–H\cdots O$)[4–6] and weak ($C–H\cdots O$)[7,8] hydrogen bonding. Recently we have observed that halogen atoms, presumably due to their $\delta+$ polarizabilities, may form symmetrical (**P**) and unsymmetrical (**Q**,**R**) recognition motifs with nitro groups. Such patterns have been analysed[9] using the Cambridge Structural Database (CSD).[10] In this communication, we describe how such information may be used in the design of supramolecular structures.

To try to engineer a structure that is governed by iodo···nitro interactions, we chose to co-crystallise an equimolar mixture of 1,4-diiodobenzene **1** and 1,4-dinitrobenzene **2**. It was believed that this system has very few crystallisation options other than the formation of molecular ribbons based on the symmetrical motif **P** or, perhaps, on the unsymmetrical motif **Q**. Of course, one might have examined the crystal structure of 4-iodonitrobenzene, so far undetermined, for the occurrence of a similar pattern but it is always more satisfying to construct such supramolecular assemblies from dissimilar molecules because the very formation of a molecular complex strengthens the notion that one is dealing with specific intermolecular interactions. With interactions as weak as $I\cdots O_2N$ or $C–H\cdots O$ one might tend to ascribe self-assembly of a one-component crystal, though very often erroneously, to 'space-filling', 'packing factors', 'volume factors' and so on. Clearly this is not a serious problem when self-assembly is based on strong hydrogen bonding.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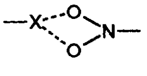
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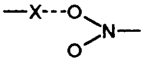
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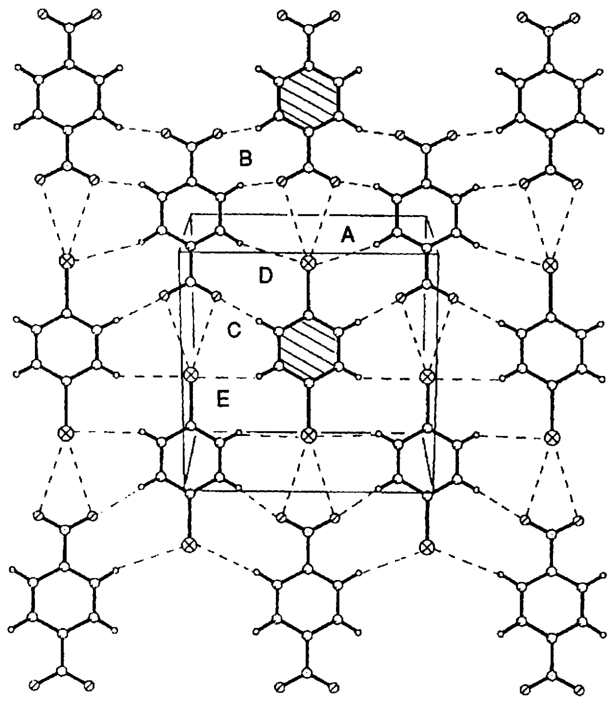

Fig. 1 Structure of complex **3** along [001] to show symmetrical iodo–nitro bridging ribbons and sheet structure. The $I\cdots O$ (A), $C–H\cdots O$ (B,C) and $C–H\cdots I$ (D,E) interactions are indicated.

Dark-yellow crystals of the 1 : 1 complex **3** (mp 156 °C) were obtained exclusively when **1** (m.p. 124 °C) and **2** (mp 168 °C) were co-crystallised from EtOH. A view of the crystal structure† is shown in Fig. 1. Molecules of **1** and **2** are linked by symmetrical $I\cdots O$ interactions (A, Fig. 1) of 3.45 Å and $C–I\cdots O$, 161.3° ($O\cdots I$ van der Waals distance, 3.50 Å) to form ribbons as predicted. IR evidence (KBr) for these interactions is provided by a shift upon complexation from 1566 to 1543 cm^{-1} and from 1344 to 1334 cm^{-1} for the $-NO_2$ stretching frequencies. The ribbons are constrained by crystallographic symmetry to be perfectly straight and flat ($2/m$) and the *P*-designation of their $[I\cdots O]$ interactions is exact. The $[I\cdots O]$ interactions found here are shorter than any of the nine examples located in 32 crystal structures in our earlier CSD study.[9]

The $[I\cdots O]$ mediated ribbons are laterally connected along [021] by two discrete sets of $C–H\cdots O$ hydrogen bonds. Self-recognition of molecules of **2** occurs *via* a centrosymmetric 10-membered ring motif (B, Fig. 1) having $C\cdots O$, 3.31 Å and $C–H\cdots O$, 122°, while molecules **1** and **2** associate (C, Fig. 1) *via* the second $C–H\cdots O$ interaction ($C\cdots O$, 3.44 Å, $C–H\cdots O$, 145°). The lateral interactions between ribbons are further strengthened by two independent $C–H\cdots I$ hydrogen bonds (D and E, Fig. 1). Bond D ($C\cdots I$, 4.31 Å, $C–H\cdots I$, 149°) connects molecules **1** and **2** while bond E ($C\cdots I$, 4.14 Å, $C–H\cdots I$, 136°) involves self-recognition of **1**. The overall result is a corrugated molecular sheet and the three-dimensional structure is obtained by stacking these sheets so that molecules of **1** and **2** overlap. The interplanar stacking distance is 3.50 Å while the centroid-centroid stacking distance is 3.76 Å indicating only moderate $\pi\cdots\pi$ interactions. Fig. 3(*a*) shows the offset plane–plane overlap in the complex. Strong $\pi\cdots\pi$ overlaps are characterised typically by stacking distances less than 3.40 Å.[11] Even so, the yellow colour of the complex indicates that there is some charge transfer.

It is also well known that halogen atoms form short polarisation-induced contacts with cyano groups[12] and we tested our ideas for supramolecular construction by co-crystallising an equimolar mixture of **1** and TCNQ (m.p. 287 °C). Red crystals of complex **4** (m.p. 220 °C, decomp.) were obtained from 1 : 1 MeCN-EtOH and the crystal structure‡ is shown in Fig. 2. This structure is closely related to that of complex **3**. In **4**, however, the I atoms form simple, non-bridged interactions (U, Fig. 2) with only one cyano group of each geminal pair in TCNQ, with I···N, 3.37 Å; C–I···N, 178.0°; I···N≡C 96.3° (N···I van der Waals distance 3.53 Å). This asymmetry of I with respect to the terminal cyano groups gives rise to a zig-zag molecular ribbon in **4**, in contrast to the linear ribbon in **3** that arises from the symmetrical I···O interations. The asymmetry in **4** arises because the separation of the N-termini of TCNQ is too wide to permit an iodo-bridge that would be analogous to the **P**-motif (see Scheme 1) observed in **3**. In complex **4** the 'non-coordinating' I···N distance of 4.29 Å generates an analogue of the I···O **R**-motif.

As in complex **3**, C–H···N and C–H···I interactions are responsible for organising the zig-zag [I···N] mediated ribbons, this time into puckered, rather than planar molecular sheets. Self-recognition of molecules of **1** is achieved through C–H···I hydrogen bonds (X, Fig. 2: C···I 4.04 Å, C–H···I, 153°) that are shorter and more linear than those in **3** and which give rise to centrosymmetric dimers of **1**. Self-recognition of TCNQ molecules is achieved through the formation of two different types of centrosymmetric dimers (Y, Z, Fig. 2). Bond Y has C···N, 3.42 Å, C–H···N, 134° and bond Z has C···N, 3.21 Å, C–H···N, 99°. Analysis of data in the CSD indicates that both of these TCNQ self-recognition motifs are commonly observed and with almost equal frequency. Mutual recognition of **1** and TCNQ occurs through the bridging interaction of the I-coordinated N atom of TCNQ and adjacent C–H atoms of **1** (V, W, Fig. 2). Here, C···N, 3.47, 3.64 Å and C–H···N, 128, 117° in V, W respectively. Intersheet π···π overlap is again only moderately strong here (plane–plane 3.50 Å, centroid–centroid 3.76 Å) but the plane–plane overlap [Fig. 3(*b*)] is characteristic.

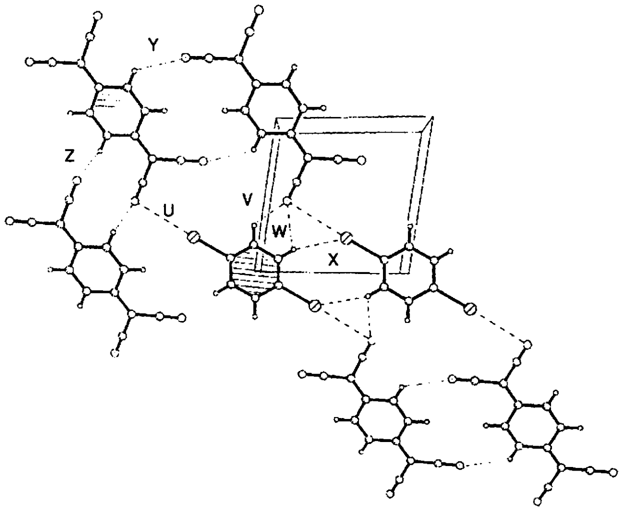

Fig. 2 Structure of complex **4** along [010] to show zig-zag I···N≡C ribbons. The I···N (U), C–H···N mutual recognition (V,W), C–H···I self-recognition (X) and C–H···N TCNQ self-recognition (Y,Z) interactions are indicated.

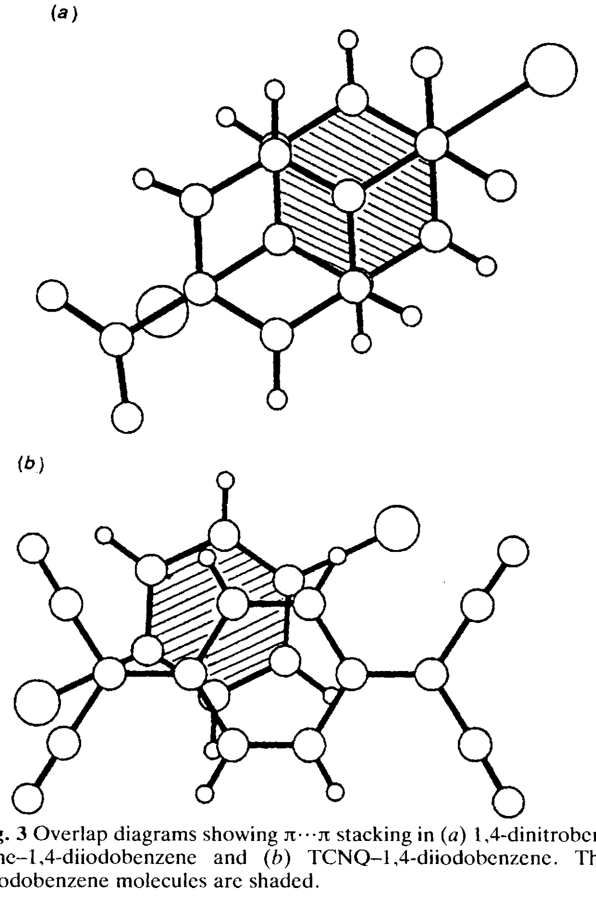

Fig. 3 Overlap diagrams showing π···π stacking in (*a*) 1,4-dinitrobenzene–1,4-diiodobenzene and (*b*) TCNQ–1,4-diiodobenzene. The diiodobenzene molecules are shaded.

Earlier work on I···O_2N and I···N≡C interactions have shown that these interactions are clearly of the 'structure-determining' type, perhaps on account of the high polarisability of the I-atom.[9-12] The present study demonstrates that despite their so-called weakness, intermolecular interactions involving iodine may be used for systematic supramolecular construction and that interactions of the type I···O_2N and I···N≡C seem to have much of the directional specificity that is required for such geometry-based design.

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Footnotes

† Rigaku AFC6S, Mo-Kα, Monoclinic, *C2/m*, $Z = 2$, $a = 9.662(2)$, $b = 9.780(2)$, $c = 7.550(2)$ Å, $\beta = 93.43(3)°$, $T = 123$ K, 665 independent reflections out of 1411 (measured with $5 < 2\theta < 50°$, SHELXL 93,[13] $R = 0.0164$, $wR = 0.0445$, C, N, O, I anisotropic, H isotropic.

‡ Rigaku AFC6S, Mo-Kα, Triclinic, $P\bar{1}$, $Z = 2$, $a = 7.658(2)$, $b = 7.782(1)$, $c = 7.8326(1)$ Å, $\alpha = 75.65(1)$, $\beta = 96.47(1)$, $\gamma = 99.38(1)°$, $T = 123$ K, 1485 independent reflections of 1694 measured with $5 < 2\theta < 50°$, SHELXTL,[13] $R = 0.0152$, $wR = 0.0216$, C, N, I anisotropic, H isotropic.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

References

1 J.-M. Lehn, *Angew. Chem., Int. Ed. Engl.*, 1990, **29**, 1304.
2 J. Rebek Jr., *Chem. Brit.*, 1994, **30**, 286.
3 G. R. Desiraju, *Crystal Engineering: The Design of Organic Solids*. Elsevier, Amsterdam, 1989.
4 J. Yang, E. Fan, S. J. Geib and A. D. Hamilton, *J. Am. Chem. Soc.*, 1993, **115**, 5314.
5 S. B. Copp, S. Subramanian and M. J. Zaworotko, *J. Am. Chem. Soc.*, 1992, **114**, 8719.
6 J. A. Zerkowski, C. T. Seto, D. A. Wierda and G. M. Whitesides, *J. Am. Chem. Soc.*, 1990, **112**, 9025.
7 C. V. K. Sharma, K. Panneerselvam, T. Pilati and G. R. Desiraju, *J. Chem. Soc., Chem. Commun.*, 1991, 832.
8 K. Biradha, C. V. K. Sharma, K. Panneerselvam, L. Shimoni, H. L. Carrell, D. E. Zacharias and G. R. Desiraju, *J. Chem. Soc., Chem. Commun.*, 1993, 1473.
9 G. R. Desiraju, V. R. Pedireddi, J. A. R. P. Sarma and D. E. Zacharias, *Acta Chim. Hung.*, 1993, **130**, 451.
10 F. H. Allen, O. Kennard and R. Taylor, *Acc. Chem. Res.*, 1983, **16**, 146.
11 C. V. K. Sharma, K. Panneerselvam, T. Pilati and G. R. Desiraju *J. Chem. Soc., Perkin Trans. 2*, 2209, 1993.
12 G. R. Desiraju and R. L. Harlow, *J. Am. Chem. Soc.*, 1989, **111**, 6757.
13 G. M. Sheldrick, SHELXTL and SHELXL93: *Programs for Crystal Structure Determination, Refinement and Display*, University of Göttingen, Germany, 1990 and 1993.