INTER STACK AND INTRA STACK FORCES IN MOLECULAR SOLIDS: A NEW LOOK AT DONOR–ACCEPTOR COMPLEXES AND ORGANIC METALS

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ABSTRACT

While *intra*stack interactions are undoubtedly important in the crystal stabilization of donor–acceptor complexes, the weaker *inter*stack forces may also be structurally significant in that they are a prerequisite to optimal stacking. This is illustrated for a cinnamic acid molecular complex and for TTF-TCNQ.

INTRODUCTION

DONOR–ACCEPTOR or charge transfer complexes are well-known substances made up of two types of molecules, an electron donor (D) and an electron acceptor (A)[1]. Very often D and A are planar and DA complexes are constructed by interleaving the two types of molecules along the stack directions (figure 1). Charge transfer is then conventionally understood as involving π-electrons on D and A molecules adjacent in the stack. Some typical
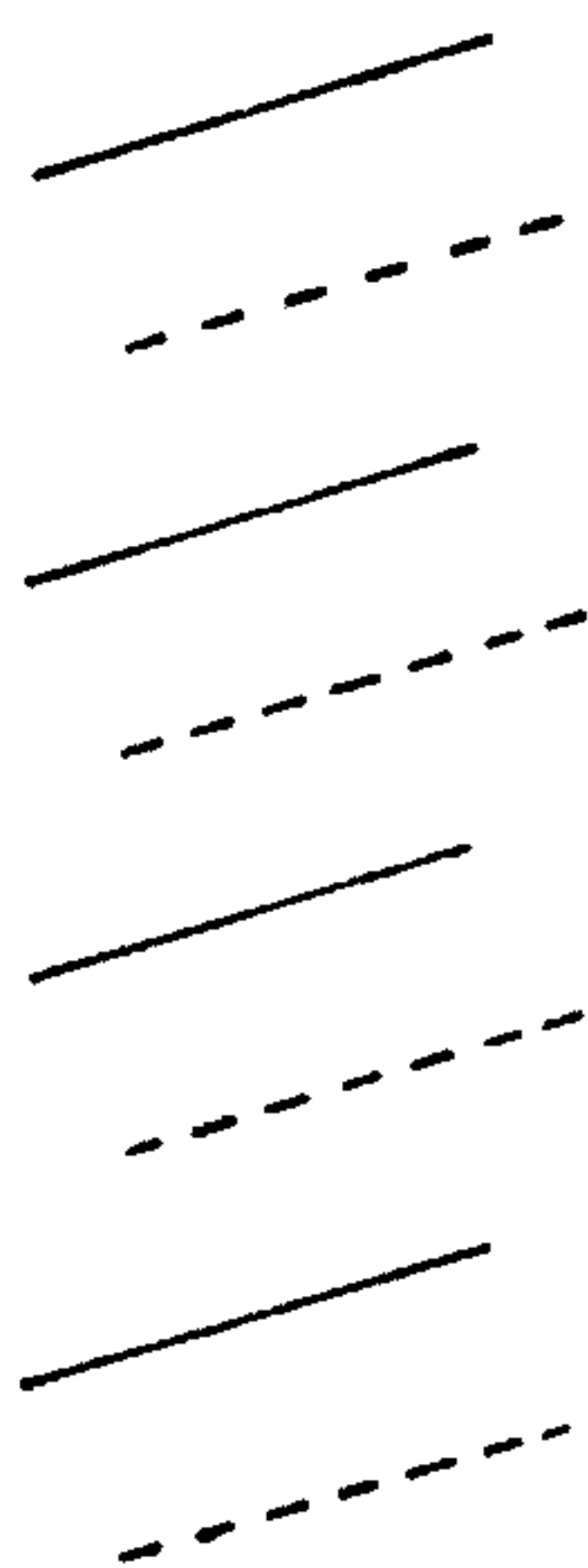

**Figure 1.** Schematic view of a mixed-stack DA complex with a π-donor and acceptor.

aromatic π-donors are anisole, hexamethylbenzene and perylene while representative π-acceptors are chloranil, pyromellitic dianhydride and sym-trinitrobenzene. All these compounds form the so-called 'mixed-stack' DADADA.... type complexes.

While *intra*stack $\pi\pi$ interactions are undoubtedly very important in the stabilization of such DA complexes, an analysis of the coordination geometry of D and A molecules in these crystals reveals that *inter*stack forces may also be significant. Figure 2 shows the stack structure of the 1 : 1 DA complex between 3,4-dimethoxycinnamic acid (D) and 2,4-dinitrocinnamic acid (A). The stack is mixed in character and consists of alternating D and A molecules at unequal spacings so that molecules are in effect grouped as diads[2,3]. Figure 3, on the other hand, depicts the structure of the same complex looking down the stack axis. It may be observed that in this view, D and A molecules constitute a compact sheet-like arrangement. Each D molecule is surrounded by two D and three A molecules, while each A is surrounded by two A and three D molecules. The intermolecular interactions which hold the molecules in a sheet are directionally rather specific. For instance, there are strong O–H ..... O bonds (O .... O, 2.58, 2.61 Å) as shown in the figure.

Calculations of intermolecular energies using the atom–atom potential method[4] reveal that these *inter*stack interactions, though not
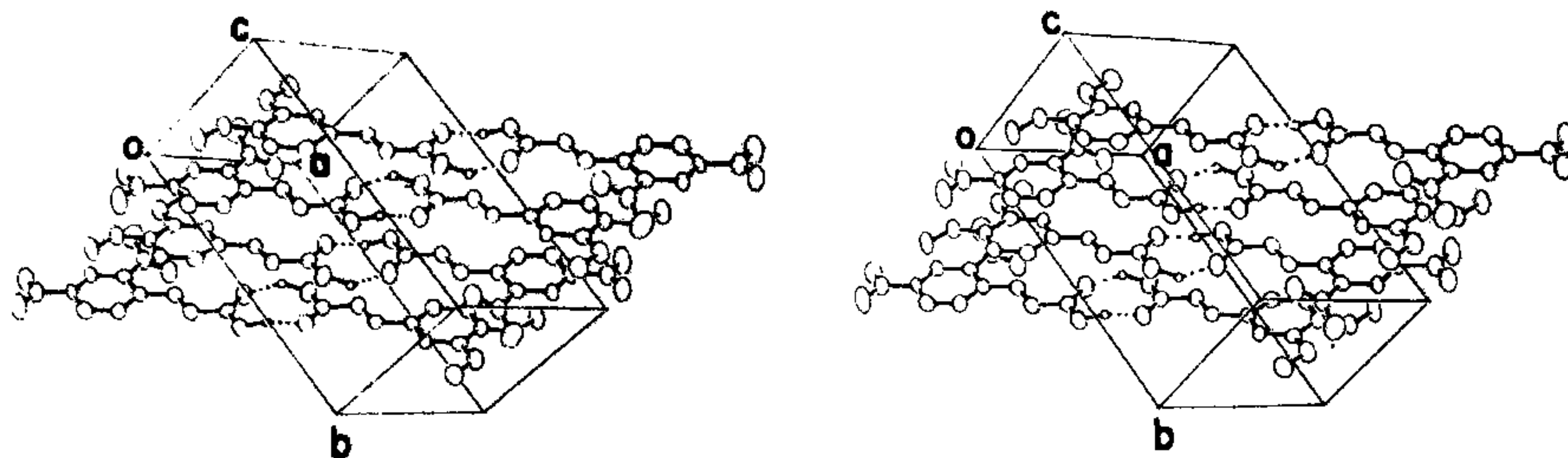
Figure 2. Stereoview of the crystal structure of the 1:1 complex, 3,4-dimethoxycinnamic acid 2,4-dinitrocinnamic acid, to show the unequal stack spacings.
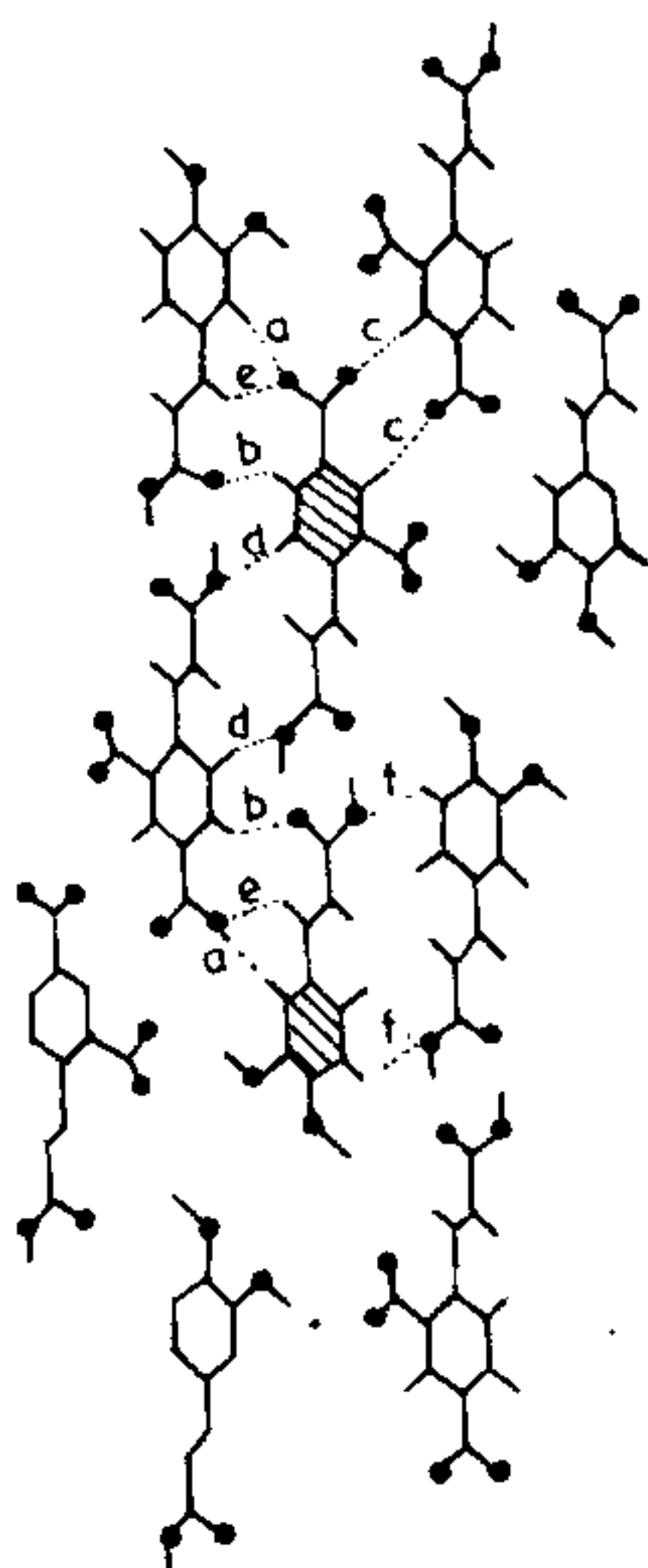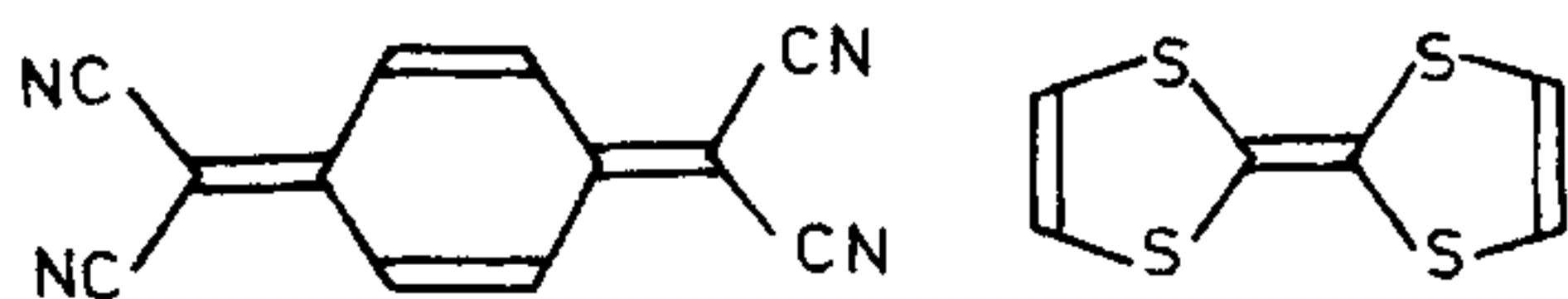

Figure 3. Crystal structure of the 1:1 complex shown in figure 2, looking down the stack direction. C–H ... O bonds (< 2.60 Å) are shown as dotted lines and indicated a–f. Notice the formation of the molecular sheet.

always as large as the *intra*stack C .... C and DA interactions, make a distinctive contribution to the crystal stabilization. In general it is unreasonable to expect only one type of intermolecular interaction to completely define an organic crystal structure. Rather, the simultaneous interplay of different sets of weak interactions uniquely fixes the three-dimensional arrangement of all molecular solids and

DA complexes are no exception. Conversely, DA solids like naphthazarin (5,8-dihydroxy-1,4-naphthoquinone) which are intramolecularly hydrogen-bonded and so not as likely to employ strong *inter*stack forces, are prone to disorder and polymorphism[5]. Most discussions on the crystal chemistry of DA complexes have centred on the $\pi\pi$ or DA interactions only. It should be emphasized that these interactions define the structure only in the stack direction and that a consideration of *inter*stack forces is necessary for a fuller understanding of these solids.

In fact, if these *inter*stack forces are ignored, it becomes very difficult to understand why D and A molecules may sometimes crystallize not in mixed stacks DADADA .... but in a segregated stack fashion, DDDD .... AAAA .... The most celebrated example in the latter category is the highly conducting 1:1 molecular complex between tetracyanoquinodimethane (TCNQ, figure 4) and tetrathiafulvalene (TTF, figure 5). Such a solid is termed as an 'organic metal'. While the acceptor TCNQ forms normal mixed-stack complexes with donors such as anthracene and hexamethylbenzene, D and A molecules are arranged in distinct stacks in the organic metals.

This seemingly unlikely organization of all negatively charged ions in one set of stacks and the positively charged ions into another set of stacks is generally agreed to be an essential prerequisite for high electrical conductivity[6,7]. Yet TTF-TCNQ and other segregated stack
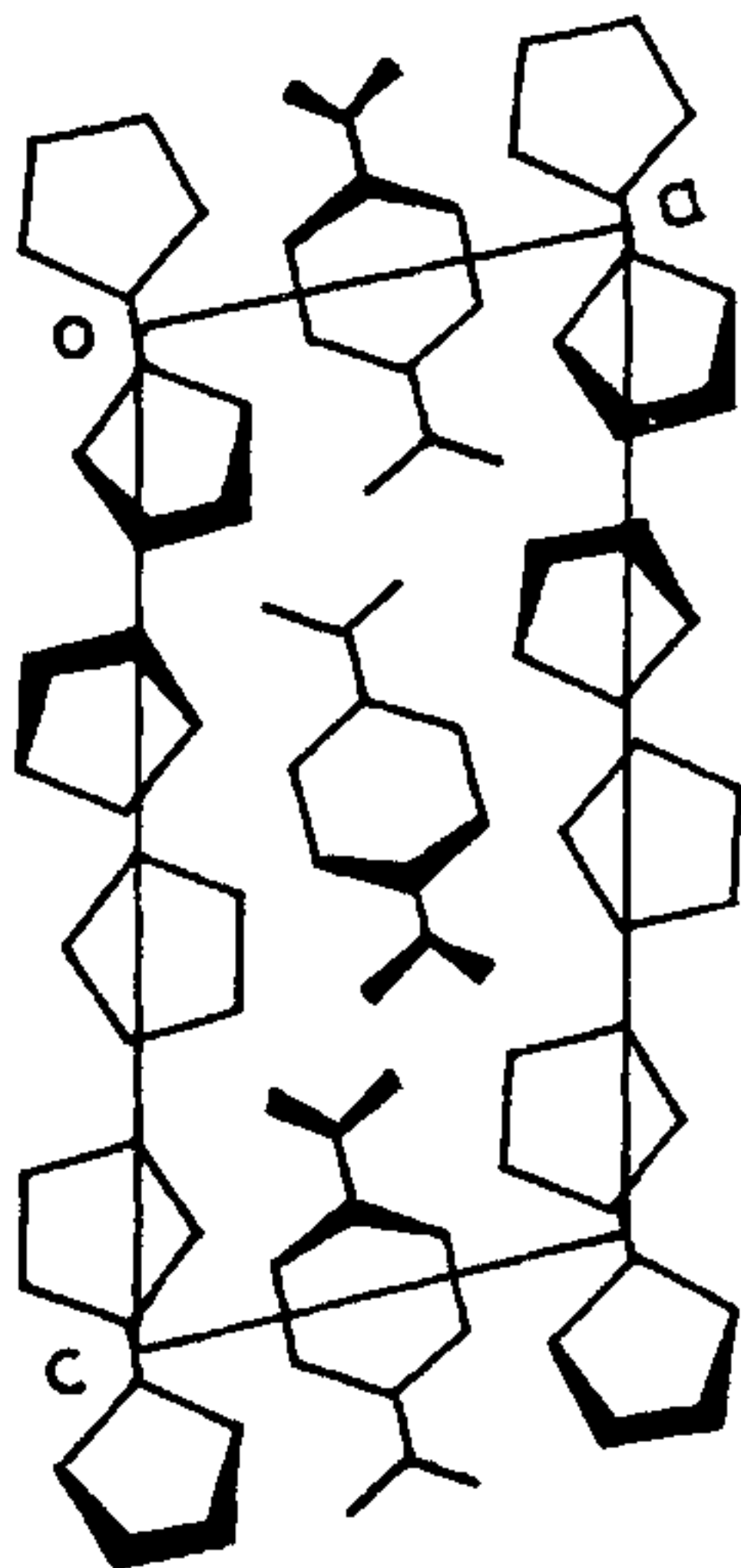
Figures 4, 5. 4. TCNQ. 5. TTF.

Figure 6. Projection of the crystal structure of TTF–TCNQ down the short axis (b).

materials have all the conventional attributes of DA complexes such as well-defined stoichiometry and pronounced optical and electrical anisotropy. An examination of the crystal structure of TTF-TCNQ perpendicular to the stack direction (010) reveals that D and A molecules are arranged in corrugated ribbons along (001) and that a 'parallel' alignment of these ribbons results in the formation of a two-dimensional corrugated sheet as shown in figure 6. Any ribbon contains either D or A. The A ribbons are formed through dipolar N ... C contacts of 3.28 and 3.29 Å while the D ribbons seem to be held by weaker C ... H interactions. However, adjacent ribbons are held by fairly short contacts of 3.20 and 3.25 Å (S ... N), 2.99 and 3.02 Å (C–H ... S) and 2.59 and 2.62 Å (C–H ... N). To summarize,

both these types of *inter*stack contacts (that is, ribbon-forming and ribbon-linking) stabilize the two-dimensional motif. Further, any *inter*stack contact involving both D and A molecules may also be responsible for charge transfer.

Conceptually, it is even more valuable to consider sheet (or ribbon) formation as a prerequisite to stack formation. In other words, a two-dimensional motif, once formed, may only be extended into the third dimension by stacking. The formation of mixed and segregated stack complexes may then be viewed as two slightly different types of stacking. When sheets and ribbons are stacked such that D and A molecules alternate (to optimize D ... A interactions), a mixed stack arises. When sheets are translated by a crystallographic short axis of *ca* 4 Å, a segregated stack is the result.

The twin operations of forming a layer and forming a stack enable a very fine control on the number of D molecules surrounding an A molecule and vice versa. In the limit, an A molecule in a mixed stack complex may be surrounded completely by D in the sheet and by two additional D in the stack. For segregated stack complexes, any A may be surrounded by A and/or D in the sheet but only by two A molecules in the stack. Clearly, a segregated stacking is more likely when the residual electron density on D and A is low. Such a degree of charge-transfer is perhaps possible exclusively via the *inter*stack contacts and this interpretation is consistent with the experimental observation that many segregated stack structures are usually associated with only a limited degree of charge-transfer. It also becomes easier to appreciate why TCNQ never forms segregated stack complexes with benzenoid π-donors but requires, for such purposes, heterocyclic donors such as TTF, HMTTF (figure 7) and TMTSF, (figure 8) where presumably *inter*stack charge transfer is possible through the chalcogen atoms.

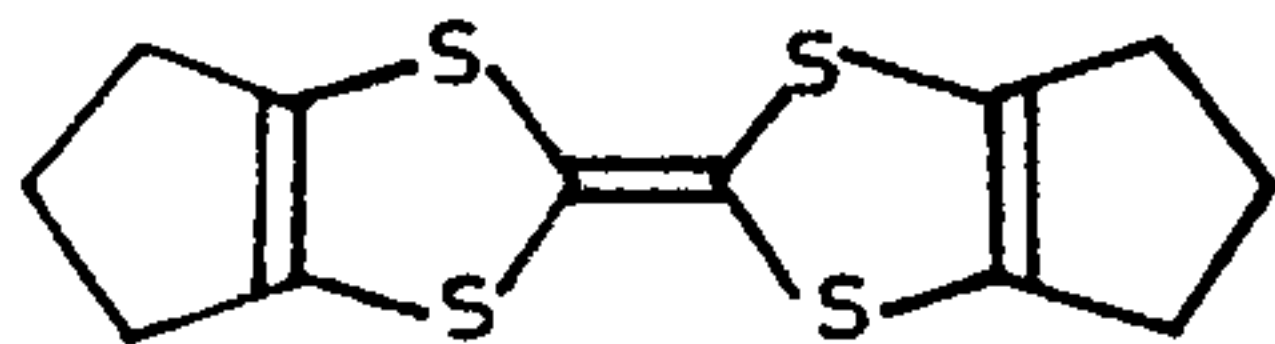An extreme case where *intra*stack interactions are negligible when compared to the
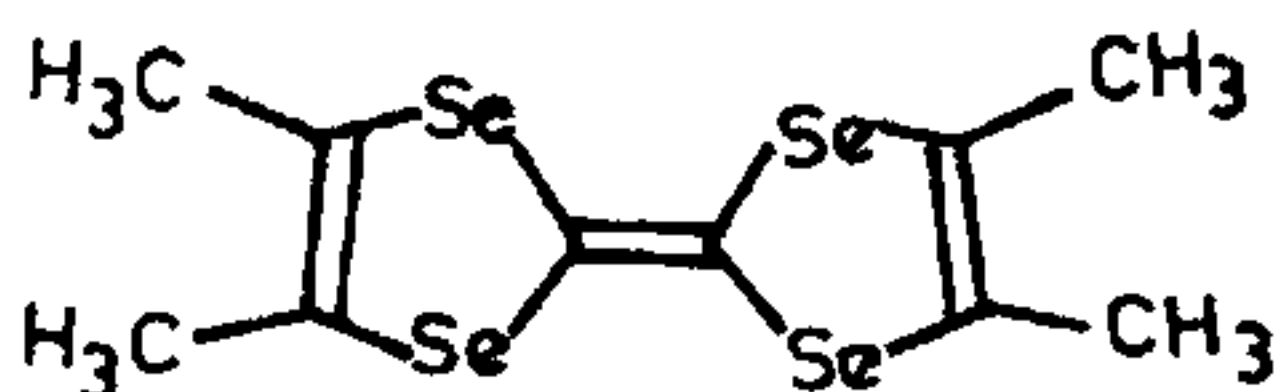
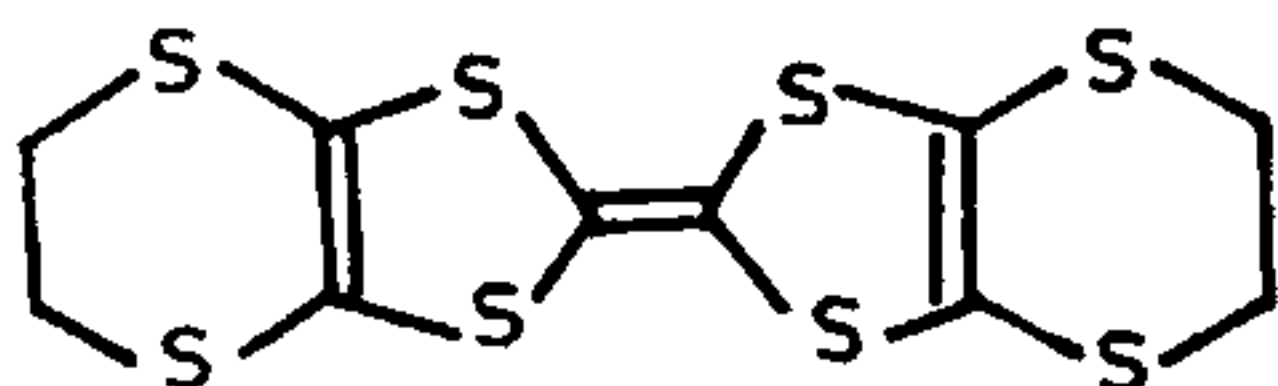**Figure 7.** HMTTF

Figure 8. TMTSF

Figure 9. BEDT-TTF

*inter*stack ones is provided by compounds like (BEDT-TTF)$_2$I$_3$ (figure 9). The ambient pressure superconducting behaviour of this material has evoked intense interest and has been linked to this structural peculiarity[8,9].

In conclusion, it is suggested that in any attempt to 'engineer' or systematically 'steer' towards a specific or desired crystal structure of a DA complex, the *inter*stack interactions, though small energetically, are the crucial ones since they are directionally specific. Once these

are suitably 'locked-in', stacking to obtain mixed or segregated arrangements could depend on coulombic and other factors.

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Erratum