C–H ··· O Hydrogen Bond Patterns in Crystalline Nitro Compounds: Studies in Solid-state Molecular Recognition

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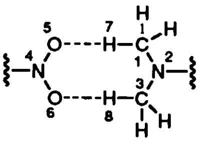
Several C–H ··· O hydrogen bond patterns (I–V) have been studied in the crystal structures of organic nitro compounds. It is shown that NO_2 and NMe_2 groups have complementary functionalities in C–H ··· O mediated molecular recognition in the solid state (pattern I). The role of co-operativity in stabilising these weakly hydrogen bonded networks has been studied computationally by examining aggregates of the prototype molecule *N,N*-dimethylnitroamine. Other geometrically characteristic C–H ··· O patterns (II–V) are found commonly in these crystal structures especially among nitroalkenes and nitroaromatics and such patterns are expected to be of utility in supramolecular assembly.

The emergence of supramolecular chemistry as a major area of research has been accompanied by the corresponding study of the intermolecular forces which must be implicated in the self-assembly of molecular components into supramolecular species with pre-desired architectural and functional features.[1] Most of these efforts have concentrated on strong or conventionally hydrogen bonded O–H ··· O or N–H ··· O building blocks (carboxylic acid, pyrimidine, aminopyridine, acylaminopyridine) and are necessarily limited to a small number of substances.[2] Yet, the scope of supramolecular assembly can be enhanced considerably if one considers, in addition, weak intermolecular interactions.[3] The C–H ··· O hydrogen bond is one such weak interaction with potential for solid state supramolecular assembly.[4,5] C–H ··· O based supramolecular design is interesting because most organic compounds do not contain functional groups capable of strong hydrogen bonding and in such instances one ought to be able to consider C–H ··· O interactions for the design of new supramolecular structures. Additionally, consideration of these interactions is useful even in strongly hydrogen bonded materials because it can reveal secondary and tertiary structural features which are often crucial to the optimisation of specific properties of these materials. The coexistence of these weak and strong hydrogen bonds may at times offer suitable explanations for anomalies in the patterns of strong hydrogen bonds[6,7] and rationalise the structural features of biological molecules.[8]

Cooperativity of intermolecular interactions is a distinctive property associated with supramolecular assembly, which permits additional stabilisation of the molecular aggregates to overcome entropic barriers.[9] Cooperativity is essential for supramolecular assembly. A dimer must be more stable than a monomer, a tetramer more stable than a pair of dimers and so on; otherwise the molecular (or oligomeric) species would be preferred to the supramolecular species. The energy of cooperativity is a crucial resource for self-assembly *via* weak intermolecular interactions. In this paper we have for the first time made an attempt to visualise the role of cooperativity for C–H ··· O hydrogen bonds.



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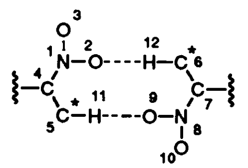
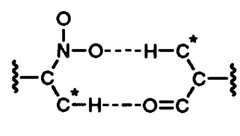


II (* sp^2/sp^3)



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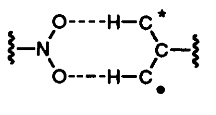
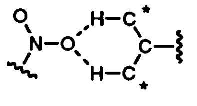
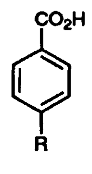


IV(* sp^2/sp^3)



V(* sp^2/sp^3)



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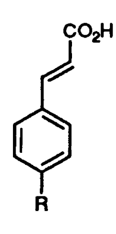

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1a, 2a R = NO_2
1b, 2b R = NMe_2
3 1a : 1b; 4 1a : 2b; 5 2a : 2b

We have described previously that NO_2 and NMe_2 groups are complementary functionalities for C–H ··· O hydrogen bonded molecular recognition (pattern I)[5a] and that nitro compounds bind preferably through certain characteristic C–H ··· O interactions (patterns II–V wherein starred atoms can be either sp^2 or sp^3 hybridised).[6,10] In this paper, we discuss the crystal structures of the 1 : 1 donor–acceptor complexes **3** and **4** which display the NO_2–NMe_2 recognition pattern I and analyse the nature of this binding pattern in detail. Complexes **5** and **6** which may also exhibit this pattern have been prepared. We have used the AM1 approximation method to evaluate the energetics, geometry, cooperativity and charge transfer in motif I using a prototype molecule *N,N*-dimethylnitroamine, **7**, for which good neutron structural data is available. A detailed account of possible recognition patterns of the NO_2 group is presented based on exhaustive searches of the Cambridge Structural Database (CSD)[11] and we have attempted to formulate some guidelines for the effective practice of nitro group crystal engineering with C–H ··· O interactions.

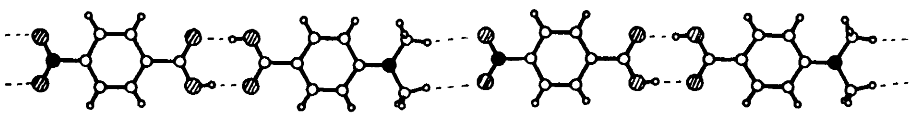

Fig. 1 O–H ··· O and C–H ··· O hydrogen bonds in the crystal structure of complex **3**. Notice the dimer rings formed in each case; N = ●, O = ◍.

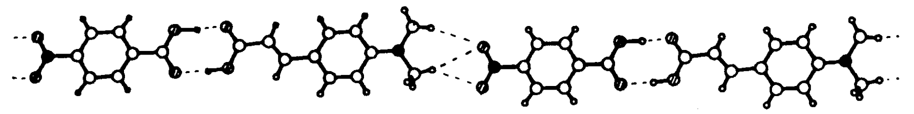

Fig. 2 O–H ··· O and C–H ··· O hydrogen bonds in the crystal structure of complex **4**. The **1a** and **2b** molecules form a linear chain. Notice that pattern I is comprised of bifurcated C–H ··· O bonds unlike in complex **3**; N = ●; O = ◍.

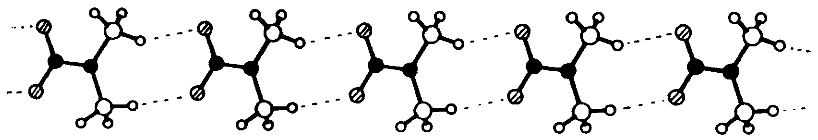

Fig. 3 C–H ··· O Hydrogen bonds (pattern I) formed in the crystal structure of **7**; N = ●, O = ◍.

Experimental

Violet-coloured single crystals of the 1 : 1 donor–acceptor charge transfer complex **4** (m.p. 181–183 °C) were obtained from an equimolar solution of 4-nitrobenzoic acid, **1a**, and *N*,*N*-(dimethylamino)cinnamic acid, **2b**, in 1 : 1 toluene–MeOH. Violet crystals of complex **5** (m.p. 245 °C) were obtained similarly from a solution of 4-nitrocinnamic acid, **2a**, and **2b** but these were too thin for X-ray work. Black–violet crystals of the 1 : 1 complex **6** (m.p. 148 °C) were obtained from a mixed solution of 1,4-dinitrobenzene and *N*,*N*,*N*′,*N*′-tetramethyl-*p*-phenylenediamine in CCl_4–hexane. All these complexes can also be prepared by thorough grinding of the respective compounds. The complexation is very vigorous in the case of complex **6** where even mild rubbing of the starting materials leads to a quantitative solid-state reaction. The preparation of crystals of complex **3** has been described by us previously.

X-Ray Crystallography.—Complex **4**, $C_{11}H_{13}NO_2{:}C_7H_5NO_4$, M = 358.35, triclinic, space group $P\bar{1}$, a = 7.389(2), b = 9.470(2), c = 13.175(3) Å, α = 86.35(2), β = 88.86(2), γ = 67.84(2)°, V = 852.2(5) Å^3, μ(Mo-Kα) = 0.99 cm^{-1}, Z = 2, D_c = 1.397 g cm^{-3}. Intensity data were collected on a Enraf–Nonius CAD4 diffractometer with a ω–2θ scan. A total of 1905 reflections was considered observed at the 3σ level out of 3921 reflections collected. The structure solution of complex **4** was carried out with SHELXS86[12] and the refinement with SHELX76.[13] All the H atoms were located from difference Fourier maps. All the non-H atoms were refined anisotropically. Importantly, for this is a study of C–H ··· O hydrogen bonding, all the H atoms were refined isotropically in the final stages of the refinement. The R value converged at 0.048 and the weighted R value at 0.048. The final difference electron density map did not reveal any significant density above 0.17 and below −0.27 e Å^{-3}. The atomic coordinates with equivalent thermal parameters, bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre.* The crystal structure of complex **3** has been reported by us previously and is given in Fig. 1. The crystal structure of complex **4** is given in Fig. 2.

Semiempirical Calculations.—The AM1 approximation to molecular orbital theory was used in this study to evaluate the energies of the O–H ··· O and C–H ··· O hydrogen bonds in complex **3**. All the calculations were carried out using the MOPAC program.[14] The geometry of the O–H ··· O and C–H ··· O dimers in the crystal structure of complex **3** was the starting point in the optimisation. The C–H ··· O bond energy of the dimer was evaluated by subtracting the energies of the individual monomers. Cooperative effects in C–H ··· O bonds were evaluated by considering linear aggregates of **7**. Such aggregates are segments of the actual crystal structure which consists of a linear array of molecules (Fig. 3). The neutron structural data of **7** were taken as input for the optimisation of linear C–H ··· O bonded molecular aggregates and up to five monomer units were considered to determine the magnitude of the cooperative effects.

CSD Studies.—Screens −28, 153, 85 and 88 were set to eliminate organometallic entries and structures without coordinates or unmatched chemical and crystallographic connectivities. Entries with R-factors greater than 0.10 were also excluded to create a subsidiary IDX file of 2306 nitro compounds. All further 3D graphical searches for NO_2 recognition patterns I–V were made from this subsidiary file. For determining *bona fide* C–H ··· O interactions, C ··· O distances 3.0 ≤ 4.0 Å and C–H ··· O angles of 90 ≤ 180° were considered. The motifs I–V are characterised by two C ··· O distances d_1 and d_2 and two C–H ··· O angles θ_1 and θ_2. For example, motif II can be defined by d_1 = C(6) ··· O(2), d_2 = C(5) ··· O(9) and θ_1 = C(6)–H(12)–O(2) and θ_2 = C(5)–H(11)–O(9). Using such criteria, patterns such as IV and V may be distinguished.

There are 84 entries that contain both NO_2 and NMe_2 functional groups and of these, 15 are duplicates and were not considered any further. For example, the structure of **7** has been determined as many as eight times by neutron and X-ray methods but we have considered only the best structure here. The coordination of H atoms was specified to be either T3 or T4 to get sp^2 or sp^3 hybridised C atoms for these four patterns. Suffixes a and b are used in motifs II–V to distinguish sp^2 and sp^3 C–H groups, respectively.

Results and Discussion

Pattern I and C–H ··· O Bond Cooperativity.—In complex **3** (Fig. 1), a linear ribbon (pattern I) that comprises O–H ··· O and C–H ··· O dimers is the main structural element. The two acid molecules are linked by O–H ··· O hydrogen bonds of 2.606(3) and 2.632(3) Å to form dimers. More interestingly, these dimers are themselves organised using two C–H ··· O bonds involving NO_2 and NMe_2 groups to form pattern I

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* For details of the CCDC deposition scheme, see 'Instructions for Authors,' *J. Chem. Soc., Perkin Trans. 2*, 1994, issue 1.

[C···O 3.658(4), 3.725(4) Å; H···O 2.71(3), 2.71(3) Å; C–H···O 164(2), 172(2)°]. It is worth noting that the conformations of the two methyl groups are such that the two C–H···O angles within the C–H···O dimer are very close to 180°. The relevant H atoms lie only 0.11(3) and 0.16(3) Å from the mean C–H···O dimer ring plane (atoms NO$_2$ and NC$_2$) and the angle between the NO$_2$ and NC$_2$ planes is only 8.4°.

Complex **4** also forms a similar linear acentric molecular ribbon in the crystal which is characterised by a carboxy O–H···O heterodimer [O···O, 2.570(3), 2.657(3) Å] and the C–H···O dimer I (Fig. 2). The carboxy group of acid **1a** is fully disordered (C–O, 1.26, 1.27 Å) while that of acid **2b** is partially disordered (C–O 1.25, 1.28 Å). Fig. 2 shows that pattern I obtained in complex **4** has bifurcated (three-centred) C–H···O interactions[15] instead of two linear C–H···O hydrogen bonds as obtained in complex **3**. An H atom of the NMe$_2$ group is bifurcated by the two NO$_2$ oxygen atoms while one of the NO$_2$ oxygen atoms forms C–H···O bonds with two H atoms. Hence pattern I in complex **4** is more properly represented by three C–H···O interactions, C···O, 3.618(5), 3.700(5) and 3.803(5) Å, H···O 2.82(4), 2.80(4) and 2.88(4) Å, and with the C–H···O angles being 147(3), 168(3) and 164(3)°. The H atoms of the methyl groups were located from difference Fourier maps and are ordered, with the six C–H bond lengths being in the range 0.91–1.06(4) Å. Notably the two H atoms of motif I lie within the plane of the C–H···O dimer [0.08(5) and 0.10(5) Å]. Also the NO$_2$ and NC$_2$ planes of this complex make an interplanar angle of 8.76°, so the whole arrangement is quite planar.

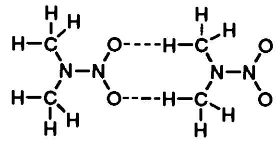
We also tried to prepare single crystals of complex **5** (**2a**:**2b**) to observe the binding characteristics between these two electronically different substituted cinnamic acids but the poor quality of the crystals did not permit any X-ray studies. We also made an effort to build a linear chain exclusively with pattern I (as in the crystal structure of **7**, Fig. 3) and for this purpose a complex **6**[*] of 1,4-dinitrobenzene and *N*,*N*,*N*′,*N*′-tetramethyl-*p*-phenylenediamine was prepared but the diffraction data on this twinned crystal were so poor that although an approximate structure was obtained, it failed to refine.

The change of the donor species from **1b** to **2b** in complexes **3** and **4** does not alter the gross recognition features of the NO$_2$ and NMe$_2$ groups but the relative approach is altered slightly. This example indicates that the exact nature of pattern I is dependent on the molecular geometry and other crystal packing forces present in the solid. Such substitutional changes (like **1b** $\longrightarrow$ **2b**) are of interest and significance because the conjugation (hyperpolarizability) in the chain increases and this property is of relevance in the design of non-linear optical (NLO) materials.

For a supermolecule to be formed, the molecules must form initially a dimer, then a trimer and continue to aggregate till a supramolecular structure is attained. In order for this process to occur, cooperativity should play an important role in the addition of individual units to the growing aggregate. The cooperative effects in C–H···O hydrogen bond formation are now discussed briefly.

The energies of O–H···O and C–H···O hydrogen bonds in complex **3** were evaluated computationally with the semi-empirical AM1 approximation. This method has been used previously to compute O–H···O energies in 1,3-diketone and carboxylic aggregates.[9a,16] It has also been shown to reproduce C–H···O interaction energies and geometries well.[17] The hydrogen bonding energy for the O–H···O dimer of complex **3** was found to be −6.7 kcal mol^{-1} [†] and that of the C–H···O dimer −2.45 kcal mol^{-1}. It should be noted that while the O–H···O geometry and energy are poorly calculated in SCF methods because of an overestimation of the H···H repulsions in the carboxy dimer ring and the neglect of electron correlation effects,[18] there are no similar sources of error in the calculation of C–H···O bond energies. The hydrogen bonds in the optimised structure of **3** are as follows: O–H···O dimer O···O 3.04, 3.10 Å, H···O 2.07, 2.12 Å, O–H···O 174.6, 175.0°; C–H···O dimer C···O 3.49, 3.45 Å, H···O 2.42, 2.33 Å and C–H···O 157.0, 174.7°. It is difficult to compute the cooperative effects of C–H···O bonds in complexes **3** and **4**, as the size of the linear molecular aggregates impede calculations before the cooperativity limit can be reached.

The archetypical structure containing pattern I is that of **7** and this is a very good example of C–H···O cooperativity (Fig. 3, VI). The hydrogen atoms of **7** point exactly towards the O atoms of the NO$_2$ group. As these H atoms are obtained from a neutron study (R = 0.036) there is little ambiguity regarding their position. The NO$_2$ and NC$_2$ groups of **7** are accurately coplanar.



VI

The optimised C–H···O hydrogen bond energies and averaged partial charges of the O and H atoms of pattern I in the linear molecular aggregates of **7** are given in Table 1. The stabilisation per dimer unit *via* C–H···O hydrogen bonding increases with an increase in the number of molecules in the linear chain. A linear molecular assembly is preferred because of the additional cooperativity energy and this extra energy may discriminate against other possible molecular arrangements which do not have this cooperative advantage. The enhancement of charges on the H and O atoms from monomer to *n*-mers indicates mutual induction and charge transfer through C–H···O hydrogen bonds. Table 1 shows that the cooperativity effect begins to level off at the pentamer stage.

Table 1 C–H···O Incremental interaction energies (kcal mol^{-1}) in linear molecular aggregates of **7** and the averaged partial charges of the H and O atoms

	Total energy	Total C–H···O bond energy	Average C–H···O bond energy (per dimer unit)	Atom charge	
				H	O
Monomer	21.7	—	–	0.0764	−0.3588
Dimer	40.2	3.2	3.2	0.1320	−0.3709
Trimer	58.0	7.1	3.6	0.1365	−0.3770
Tetramer	75.4	11.4	3.8	0.1384	−0.3799
Pentamer	93.1	15.4	3.9	0.1395	−0.3817

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[*] Complex **6** is monoclinic with a = 11.36(2), b = 10.93(2) and c = 11.14(1) Å; β = 92.32(5)°.

[†] 1 kcal = 4.184 kJ.

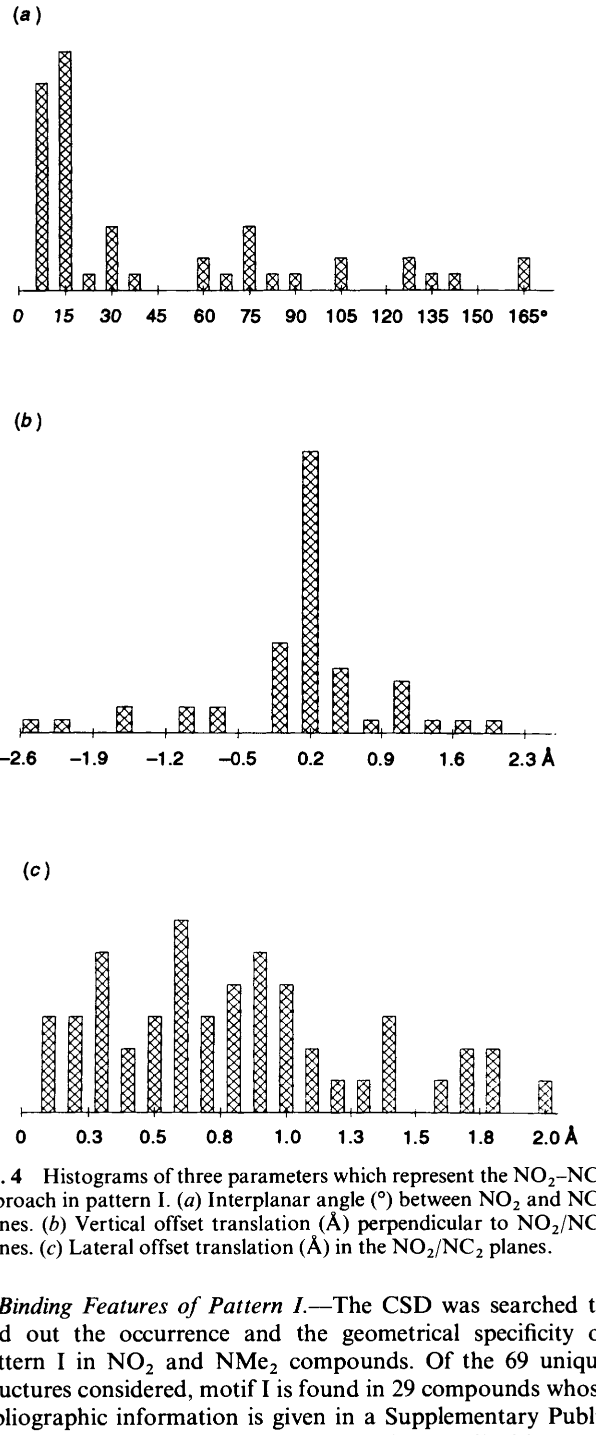


Fig. 4 Histograms of three parameters which represent the NO_2–NC_2 approach in pattern I. (*a*) Interplanar angle (°) between NO_2 and NC_2 planes. (*b*) Vertical offset translation (Å) perpendicular to NO_2/NC_2 planes. (*c*) Lateral offset translation (Å) in the NO_2/NC_2 planes.

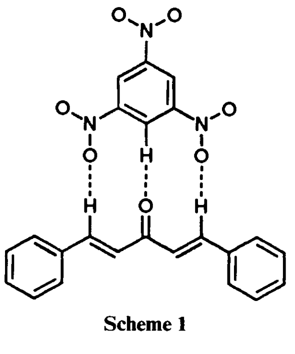
Binding Features of Pattern I.—The CSD was searched to find out the occurrence and the geometrical specificity of pattern I in NO_2 and NMe_2 compounds. Of the 69 unique structures considered, motif I is found in 29 compounds whose bibliographic information is given in a Supplementary Publication.* The NO_2–NMe_2 approach can be described in terms of three parameters. (*i*) The interplanar angle between the NO_2 and NC_2 planes with H atoms ignored. Fig. 4(*a*) represents a histogram of the interplanar angles. (*ii*) The vertical offset or the translation perpendicular to the NO_2/NC_2 plane. To represent this offset we have calculated the average interplanar distances of the NO_2 and NC_2 planes. These distances are shown in Fig. 4(*b*). (*iii*) The lateral offset of NO_2 and NC_2 groups *i.e.* the translation in the mean NO_2/NC_2 plane. This parameter may be described in terms of the difference between the distances of diagonally disposed C and O atoms of pattern I, C(1) ··· O(6) and C(3) ··· O(5). This is shown in Fig. 4(*c*). Small differences in these diagonal distances indicate more symmetrical C–H ··· O dimers with little lateral offset between NO_2 and NC_2 groups while large differences in diagonal distances indicate more unsymmetrical C–H ··· O dimers.

It is clear from Fig. 4(*a*) that the NO_2 and NC_2 groups prefer to be in plane (most of the points lie below 15°). Fig. 4(*b*) indicates that there is hardly any vertical offset between NO_2 and NC_2 groups as most of the points cluster within 0.2 Å of a coplanar arrangement. In contrast, lateral offsets are common and Fig. 4(*c*) shows that many points are scattered with lateral offsets between 0.1 and 1.8 Å. The lateral offset arrangement in pattern I is possibly stabilised by additional bifurcated C–H ··· O interactions as in complex **4**. A superposition stereoplot of pattern I viewed along the plane of the NO_2 group for all the 29 compounds with the NO_2 group being fixed, is shown in Fig. 5. This plot facilitates a visualisation of the relative orientation of the NO_2 and NC_2 groups.

CSD Study of Patterns II–V.—The CSD was searched in a more general analysis of the NO_2 group recognition patterns II–V. These motifs have been observed by us frequently in previous structural studies[6,10] and the present work which is statistical in nature enables us to formulate the most frequent recognition patterns of NO_2 groups, which may be useful in crystal engineering. Patterns II–V are divided according to C–H group hybridisation, *i.e.* sp^2 and sp^3 to visualise the impact of H atom acidity in C–H ··· O bond formation.[19] Table 2 presents some pertinent details.

Fig. 6 shows that the patterns IIa and IIb are largely characterised by symmetrical C–H ··· O interactions, that is those with $d_1 = d_2$ and $\theta_1 = \theta_2$ (see Experimental section for a definition of these terms). This plot indicates that pattern II is preferably centrosymmetric. The number of hits obtained for IIb are reduced significantly compared with IIa because in that case the C–H group is specified to be sp^3 hybridised. Interestingly most of the hits observed for IIb correspond to cyclopropane derivatives (where strictly speaking the H atoms are not really sp^3 hybridised but rather have some sp^2 character) and rigid alicyclic compounds like cubanes and prismanes.

Pattern III is similar to II except that one of the N(O)=O groups is replaced by a C=O group to give a non-centrosymmetric motif. The number of hits obtained for IIIa suggest that this is also a potential building block for molecular recognition and most of the hits observed in this case correspond to esters of nitroaromatic compounds. It may be mentioned here that we have successfully employed such C–H ··· O hydrogen bonds in the solid state supramolecular assembly of molecular complexes of 1,3,5-trinitrobenzene and dibenzylideneacetone (Scheme 1).



Scheme 1

There is a very close relationship between patterns IV and V as both motifs involve similar molecular fragments. Two O atoms of the NO_2 group interact with two H atoms in IV, while

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* For details of the Supplementary Publications Scheme, see 'Instructions for Authors,' *J. Chem. Soc., Perkin Trans. 2*, 1994, issue 1 [Supp. Pub. No 57028 (4 pp.)].

Table 2 Statistical data on patterns I–V in nitro compounds

Pattern	No. of compounds with a potential to form pattern	No. of compounds which actually display pattern	Av. hydrogen-bonded parameters[a]	
			C···O/Å	C–H···O/°
I	69	29	3.65	138.0
IIa	817	280	3.52	127.5
IIb	88	25	3.61	125.8
IIIa	177	50	3.45	128.0
IIIb	33	0	—	—
IVa	136	19	3.59	137.6
IVb	103	10	3.66	135.9
Va	136	68	3.50	135.1
Vb	103	0	—	—

[a] A contact is considered a C–H···O hydrogen bond if $3.0 \leq C\cdots O \leq 4.0$ Å and $100 \leq C–H\cdots O \leq 180°$.

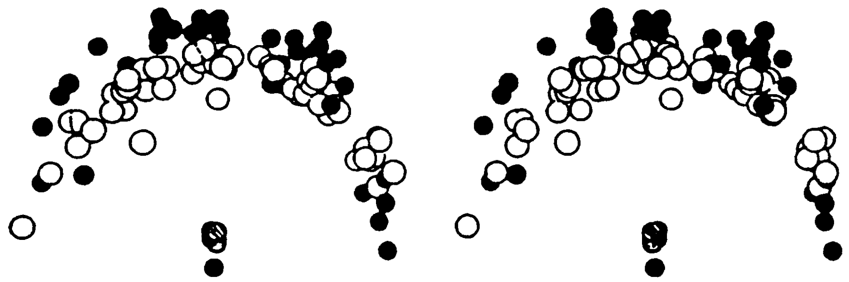
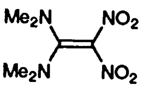


Fig. 5 Stereodiagram of a superposition plot of NO_2 and NC_2 fragments of pattern I in 29 compounds. The plane of the NO_2 group is perpendicular to the plane of the paper and this NO_2 plane is kept fixed from structure to structure; N = ●, O = ⊘, C = ○.



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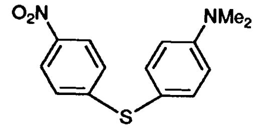

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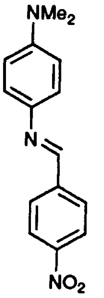

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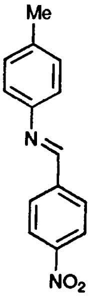

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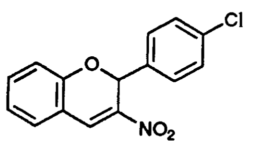

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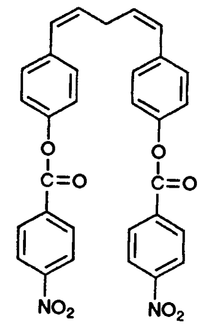

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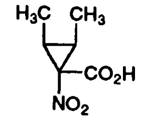

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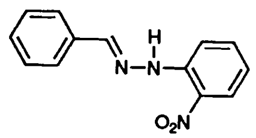

15

only one O atom of the NO_2 group interacts with two H atoms in V (this may be termed an acceptor bifurcated interaction according to the nomenclature of Saenger and Jeffrey).[8] The number of hits obtained for these motifs suggests that pattern V is preferred to IV. It should be recalled that pattern I which is geometrically similar to motif IV also prefers to form bifurcated interactions (Figs. 2 and 4). It seems then that the disposition of H atoms in patterns I and IV or V is conducive to acceptor bifurcation and this is in contrast with the general observation that the H atom (either C–H or O–H) prefers to interact with two O atoms (proton bifurcation).[15] This possibility for bifurcation does not exist for dimer motifs II and III.

Nitro Group Crystal Engineering.—We now discuss a few occurrences of pattern I to highlight different aspects of this motif. The NO_2 and NMe_2 groups in **8** are sterically crowded, the molecular structure is non-planar and hence the I modules in the crystal are three-dimensionally disposed (C···O, C–H···O; 3.73, 3.66 Å, 123.9, 173.6° and 3.68, 3.81 Å, 143.6, 142.3°). This is shown in Fig. 7. The aromatic rings of **9** are mutually perpendicular and the molecule has a bent conformation. The crystal structure of **9** (Fig. 8) has a sinusoidal chain with NO_2 and NC_2 planes being out of plane with an angle of 70.5° between them (C···O, C–H···O 3.60, 3.72 Å and 147, 141°). The planar molecule **10** forms an acentric linear chain with NO_2 and NC_2 groups being in-plane. Interestingly, when the NMe_2 group of **10** is replaced by a Me group (*i.e.*, molecule **11**), motif V is adopted. These examples hint that pattern I can be used to steer the crystal packing reliably if the organic molecules bear only NO_2 and NMe_2 functional groups.

We will now try to address the role of C–H···O hydrogen bonding patterns in nitro group crystal engineering. For this purpose, we have chosen the crystal structures of compounds **12**–**15**. These examples delineate various aspects of patterns II–V and are potential feedbacks in the deliberate design of nitro containing C–H···O mediated supermolecules. Molecule **12**

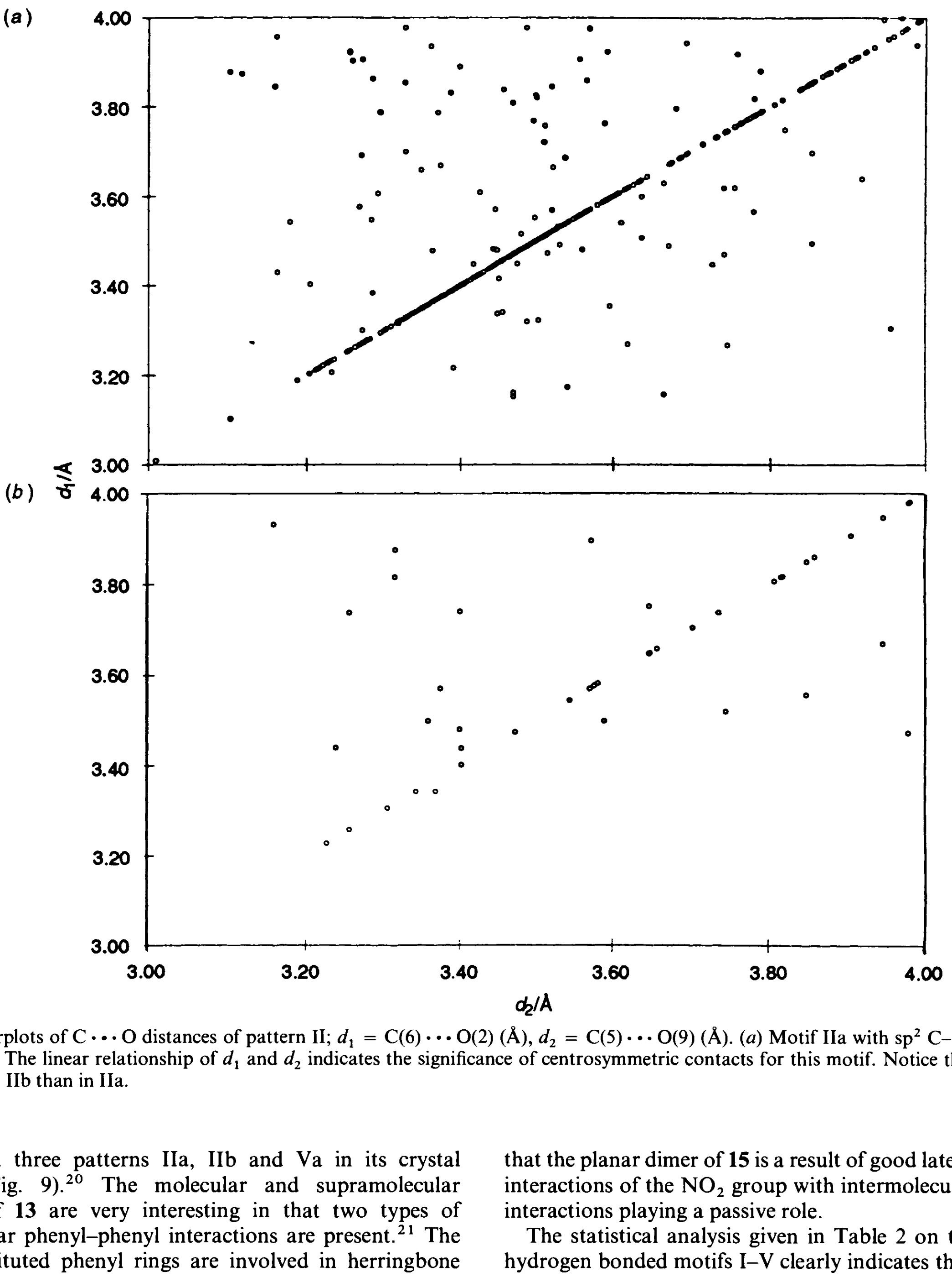

Fig. 6 Scatterplots of C ··· O distances of pattern II; d_1 = C(6) ··· O(2) (Å), d_2 = C(5) ··· O(9) (Å). (*a*) Motif IIa with sp^2 C–H. (*b*) Motif IIb with sp^3 C–H. The linear relationship of d_1 and d_2 indicates the significance of centrosymmetric contacts for this motif. Notice that there are far fewer points in IIb than in IIa.

manifests all three patterns IIa, IIb and Va in its crystal structure (Fig. 9).[20] The molecular and supramolecular structures of **13** are very interesting in that two types of intramolecular phenyl–phenyl interactions are present.[21] The two unsubstituted phenyl rings are involved in herringbone interactions and the nitrophenyl rings are involved in stacking interactions. Curiously, these two stacked nitrophenyl moieties self assemble using motif IIIa as shown in Fig. 10 (one of the O atoms is ethereal). Additionally, the crystal structure also displays pattern IIa (not shown in Fig. 10 for the sake of clarity). The crystal structure of **14** shows a linear chain that has mutually perpendicular O–H ··· O and C–H ··· O dimers (IIb) in the chain (Fig. 11).[22] The reason for this is that both the NO_2 and CO_2H groups are substituted on a single C atom of the cyclopropane ring and have a strong preference for linear and planar O–H ··· O and C–H ··· O dimer formation. The dimer of molecule **15** is shown in Fig. 12 and exhibits patterns IV and/or V with good C–H ··· O interactions in addition to intramolecular N–H ··· O interactions.[23] This example indicates that if the strong proton donors are constrained by intramolecular factors, it is possible that C–H ··· O recognition patterns of the NO_2 group will determine the molecular assembly and in the present case it may be reasonable to assume that the planar dimer of **15** is a result of good lateral C–H ··· O interactions of the NO_2 group with intermolecular N–H ··· O interactions playing a passive role.

The statistical analysis given in Table 2 on the C–H ··· O hydrogen bonded motifs I–V clearly indicates that the H atom acidity and a rigid molecular geometry are crucial for the establishment of C–H ··· O recognition patterns. As Table 2 suggests, there are a small number of hits or no hits at all for fragments with sp^3 hybridised C–H groups. However, the electron-withdrawing nature of the NO_2 group enhances the H atom acidity and may promote the possibility of selective binding in this class of compounds. The larger number of hits obtained for I and IIb despite their low acidity C–H groups indicates the importance of a rigid molecular framework. Many of the hits obtained in this study correspond to simple nitro substituted compounds, with only sp^2 C atoms and it is suggested that such molecules which have the possibility of forming only C–H ··· O interactions (and no other directional interaction) can be used to design supermolecules with high precision (Scheme 1). However C–H ··· O recognition patterns can also be designed with success in the presence of strong interactions if these strong interactions do not interfere with either H or O atoms of patterns I–V. For example,

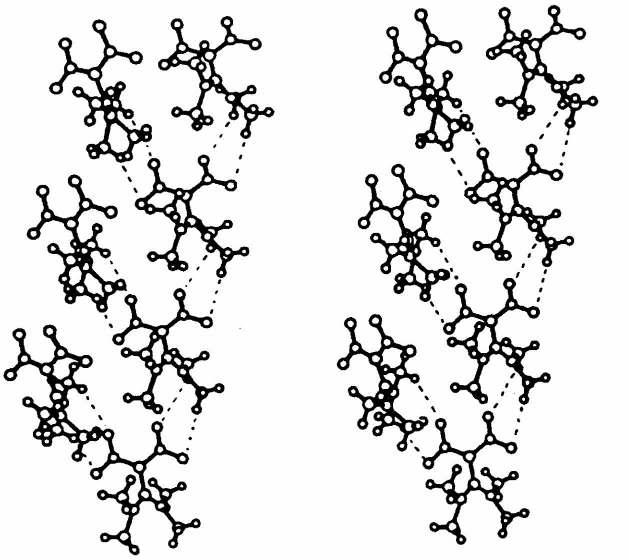

Fig. 7 Stereoview of the crystal structure of alkene **8** to show pattern I. Notice the two-dimensional molecular arrangement.

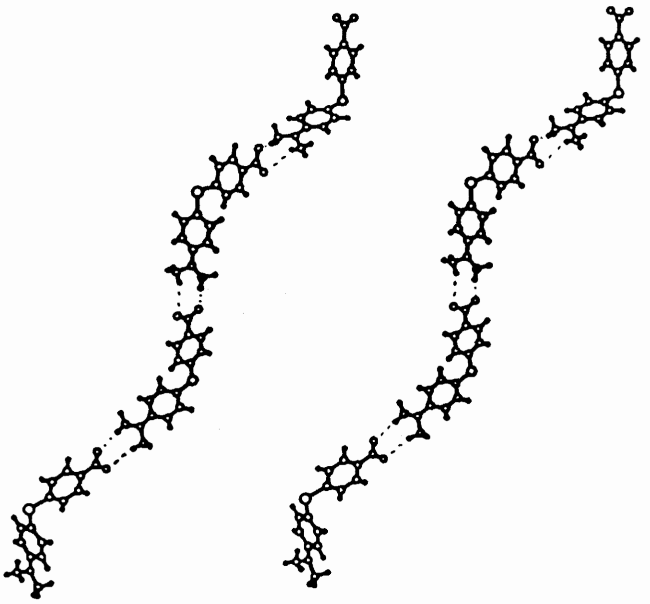

Fig. 8 Stereoview of the crystal structure of thioether **11** to show the sinusoidal chain of molecules linked by pattern I. Note that the NO_2 and NC_2 planes are perpendicular to each other.

complexes **3**, **4** and **14** (Figs. 1, 2 and 11) form carboxy dimers but the C–H···O recognition patterns are intact. Similarly in ester **13**, the major non-bonded interactions (van der Waals and π···π) are optimised in the molecular conformation itself and their role in crystal packing is reduced with the result that the weakly directional C–H···O interactions can form pattern IIIa (Fig. 10). While the crystal structure of **15** has intramolecular N–H···O hydrogen bonds, their role in crystal packing is undermined; consequently, C–H···O interactions play a key role in dimer formation (Fig. 12). These examples suggest that one has to keep track of all the possible interactions of a molecule for efficient solid-state supramolecular design. It is also to be mentioned here that if the recognition patterns I–V are assisted by additional C–H···O hydrogen bonds, that is by a matching of multiple C–H···O interactions in a single recognition pattern, supramolecular design would be very efficient as shown in Scheme 1.

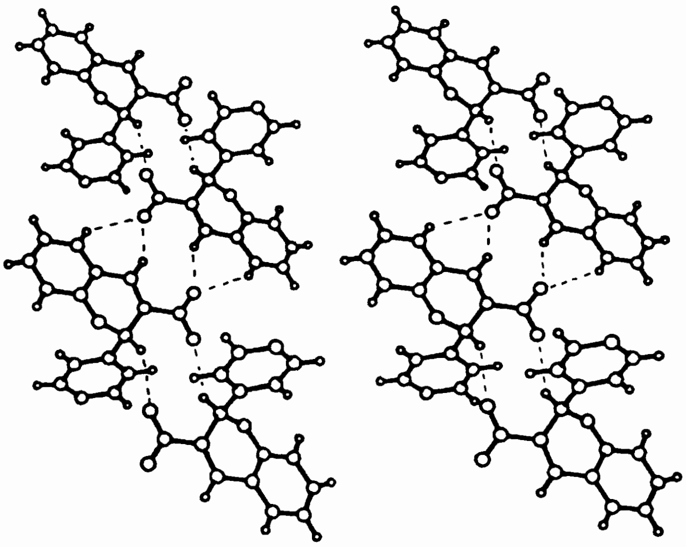

Fig. 9 Stereoview of the crystal structures of **12**. Note that the molecules are stabilised by all three patterns IIa, IIb and V.

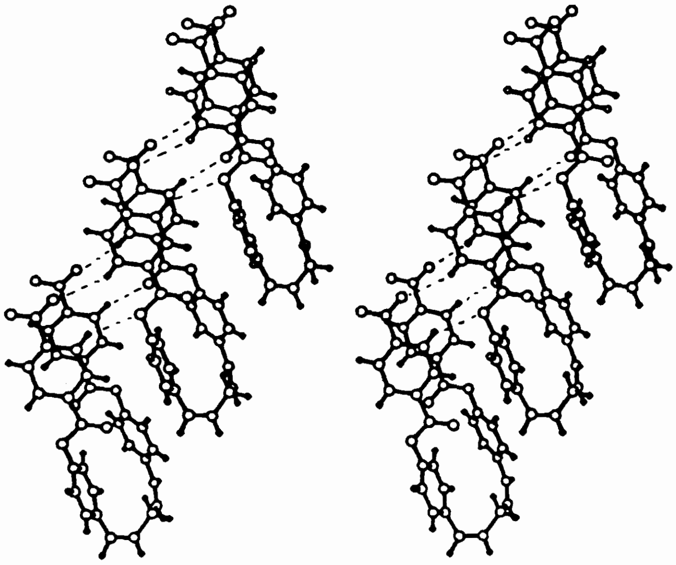

Fig. 10 Stereoview of the crystal structure of diester **13**. Notice the appearance of pattern IIIa.

Conclusions

It is concluded then that weak C–H···O bonds do exhibit cooperativity and charge-transfer-like strong hydrogen bonds and that better computational estimates of these interactions can be obtained only by considering multi-molecular aggregates. Although the patterns suggested in this study involve only O atoms in NO_2 groups, the idea can be extended to explore many new C–H···O building blocks with other types of O atoms. The general observations made on C–H···O recognition patterns in this analysis may facilitate the design of new materials based on these interactions and help in understanding and predicting secondary and tertiary structural features of many organic and bioorganic molecules with more reliability.

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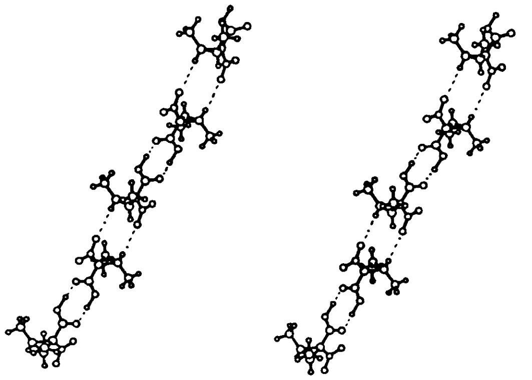

Fig. 11 Stereoview in the crystal structure of cyclopropane **14** to show the linear chain arrangement. The chain is linked by carboxy dimers and IIb dimers; these two dimers are mutually perpendicular.

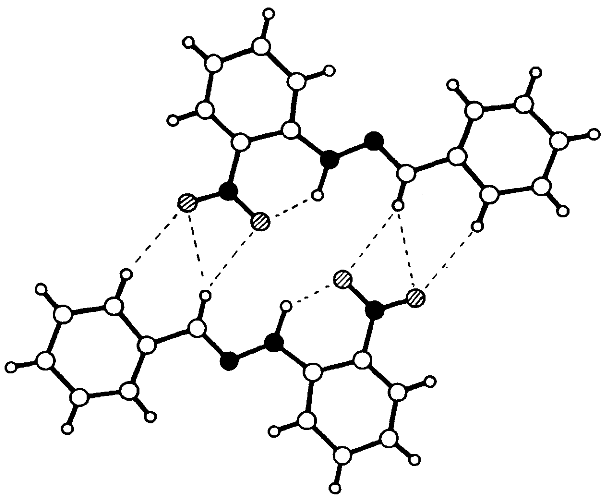

Fig. 12 A dimer of **15** formed by C–H • • • O interactions in the crystal. This dimer reveals motifs IV and/or V which possibly stabilise the planar arrangement. The N–H • • • O bonds are intramolecular; N = ●, O = ▨.

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