C–H, O Hydrogen bonded multi-point recognition in molecular assemblies of dibenzylidene ketones and 1,3,5-trinitrobenzenes

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Dibenzylideneacetone 1a, 2,5-dibenzylidene cyclopentanone 1b, 2,6-dibenzylidene cyclohexanone 1c and 2,5-dibenzylidene cyclopent-3-enone 1d form crystalline stoichiometric complexes with 1,3,5-trinitrobenzene 2a, picryl chloride 2b and picric acid 2c. The structures of these complexes are mediated by multi-point C–H, O hydrogen bonds. Some of these patterns of molecular recognition also contain stronger O–H, O hydrogen bonds. The C–H, O hydrogen bonds within these multi-point supramolecular synthons are generally shorter and more linear than the other C–H, O hydrogen bonds found in these complexes.

The assembly of molecules into nanosize aggregates has emerged as a major endeavour in modern chemistry. It has been recognised that nanoscale systems represent a meeting point of the chiselling down by technologists of macrosize precursors and of the building up by chemists from molecular size precursors. Supramolecular systems formed by self-organisation principles are good examples of nanostructures. Supramolecular chemistry emphasises the collective properties of molecules and in this regard, the physical and chemical properties of molecular aggregates are often significantly different from those of the constituent molecules.

A crystal is a supramolecule par excellence and the recognition patterns that are formed in crystals may be termed supramolecular synthons if a crystal is viewed as a retrosynthetic target. Crystal engineering, the premeditated assembly of molecules in the solid state, then becomes the supramolecular equivalent of organic synthesis and accordingly, a supramolecular synthon may be defined as a structural unit within a supramolecule which can be formed and/or assembled by known or conservable synthetic operations involving intermolecular interactions. Crystal engineering with conventional (or strong) O–H, O and N–H, O hydrogen bonds may appear sufficiently reliable, but it is in reality incomplete if weak intermolecular interactions are not considered. The advantage of using weak intermolecular interactions in crystal engineering is that the repertoire of compounds that can be used to construct supramolecular motifs and patterns is significantly increased.

Among the weak intermolecular interactions, C–H, O hydrogen bonds have attracted considerable attention. The ability of the C–H group to form various types of hydrogen bonds, such as C–H, O, C–H, N, C–H, F and C–H, M, is well-established and is comparable to that of the N–H and O–H groups. Cambridge Structural Database (CSD) studies on several aspects of C–H, O hydrogen bonds have resulted in a better understanding of the nature of these interactions and this in turn has led to the utilisation of these interactions in the construction of supramolecular synthons through a consideration of the complementarity of functional groups. Recently, we have shown that the C–H group in organometallic cluster compounds also forms C–H, O hydrogen bonds with the CO ligand and that the stability of these interactions depends on the basicity of the CO ligand. These studies also reveal that C–H, O hydrogen bonds are directional with the preferred C–H, O angle being around 140°. All these studies suggest that C–H, O hydrogen bonds show properties similar to those of strong hydrogen bonds. To summarise, C–H, O hydrogen bonds can be used quite efficiently in the design of supramolecular synthons and crystal structures. However, owing to the inherent weakness of these interactions, multi-point recognition rather than single-point recognition is the preferred strategy.

Here we aim to design and analyse the robustness of the three-point C–H, O recognition synthons I which is a mimic of the well-known synthon II that is constructed purely with strong hydrogen bonds. For this purpose, the crystal structures of complexes 3a–g have been solved and analysed. Synthon I is found to occur in complexes 3a–e but not in 3f and 3g. The CSD was used to analyse the patterns observed in these structures and in some other a,b-unsaturated carbonyl compounds.

Experimental

Preparation of materials

1,3,5-Trinitrobenzene 2a was prepared in three steps from 2,4-dinitrotoluene. Nitrization of 2,4-dinitrotoluene gave 2,4,6-
trinitrotoluene, which was oxidised with \(K_2Cr_2O_7\) to provide 2,4,6-trinitrobenzoic acid.\(^{1,4}\) This was decarboxylated in the presence of NaOH to give compound 2a.\(^2\) Picric acid 2c was prepared and picryl chloride 2b was prepared by the reaction of 2c with POCl\(_3\) and N,N-diethylthylamine.\(^2\) The dibenzylideneketones were prepared by the condensation reaction of 2 equiv. of benzaldehyde with 1 equiv. of the corresponding ketones. Compound 1d was prepared by allylic dibromination of 1b with N-homosuccinimide (NBS)-CCI\(_4\) followed by debromination with \(Zn\)-MeOH.\(^3\) Pentacenedione was prepared by the condensation reaction of cyclohexane-1,4-dione and phthalaldehyde.\(^4\)

Preparation of crystals

Yellow crystals of the 2:1 complex 3e were obtained from an equimolar solution of 2a and 1c in 1:1 dichloromethane-hexane. Similarly, yellow crystals of the complexes 3f–q were obtained from an equimolar solution of the molecular components in 1:1 chloroform-hexane. The preparation of complexes 3a and 3b has been described by us previously.\(^5\)

X-Ray crystallographic studies

Data were collected for all the complexes on an Enraf-Nonius FAST area detector with a rotating anode X-ray source. The crystal structures of complexes 3a and 3b have been reported already and only the essential features are given here. The crystal structures of complexes 3c–q are presented here. The solution of the structures for all the complexes were carried out with the SHELXL93 program and the refinements were carried out with the SHELXL93 program.\(^6\)

Complex 3e crystallises in the triclinic space group \(\text{P}\overline{1}\). Most of the sample consisted of twinned crystals and the data were collected on a solitary untwinned sample. The solution for its crystal structure was obtained in the space group \(\text{P}\overline{1}\) since it failed to solve in \(\text{P}\overline{1}\). The structure was then refined in the space group \(\text{P}\overline{1}\). In complexes 3d and 3e, the dibenzylideneketone moiety and one of the nitro groups are disordered. It may be noted that this disorder could not be fully modelled in the refinements and that the attendant lack of precision in the atomic positions is unavoidable. This means that the finer details of the hydrogen bonding cannot be discussed in detail. However, these structures have been included here for the sake of completeness. All the non-H atoms were refined anisotropically. All the H-atoms, except in complex 3h, were located from difference Fourier maps and refined isotropically in the final stages of the refinement because this is a study of the \(C\overline{1}\overline{h}\) O hydrogen bonds. The hydrogen atoms in complex 3h were fixed geometrically and refined with the riding model. Salient crystallographic information for the complexes in this study is given in Table 1.\(^1\)

CSD studies

Data were retrieved from the CSD (ver. 5.08).\(^7\) Screens – 28, 34, 35 and 88 were used to eliminate organometallic entries and unmatched chemical and crystallographic connectivities. Entries with \(R\)-factor greater than 0.10 and disordered structures were also excluded. A \(C\overline{1}\overline{h}\) O geometry was considered a \textit{bona fide} hydrogen bond when the C–O distance is less than 0.4 \AA\ and the O–angle is between 110 and 180.\(^8\) Geometrical calculations were performed using QUEST3D-GSTAT, an automatic graphical non-bonded search program of the CSD.

\(^1\) Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, J. Mater. Chem., 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 1145/32.

Results and Discussion

Synthon I in complexes of 2a

The choice of trinitrotoluene 2a as one of the components to form the supramolecular synthon I is due to the high acidity of its aromatic C–H and the ability of nitro groups to form C–H...O hydrogen bonds. The choice of dibenzylideneketones as the second supramolecular component is made by matching complementary groups. Our earlier observation\(^9\) that 1,2-unsaturated carbonyl compounds form C–H...O hydrogen bonded patterns III and IV further strengthened our idea for the choice of dibenzylideneketones.

Compound 2a forms a 2:1 crystalline complex 3a with dibenzylideneketone 1a. The expected synthon I is observed in 3a and the overall crystal structure is fortified by additional C–H...O hydrogen bonds on the other side of the carbonyl group [Fig. 1(a)]. In order to avoid this alternate C–H...O hydrogen bonded pattern and also to assess the robustness of synthon I, we considered complexes of 2a with 1b and 1c instead of 1a. Compound 2a also forms a 1:1 crystalline complex 3b and 3c with 1b and 1c, respectively [Fig. 1(b) and (c)]. Synthon I is found in both these complexes and the alternative C–H...O hydrogen bonded pattern which involves the hydrocarbon side of the molecule is found in complex 3b but not in 3c. The presence of the alternate motif on the hydrocarbon side in complexes of 1a and 1b is attributed to the higher acidity of vinylc and allylic C–H groups, respectively, which enables them to make the three-centre motif consisting of vinylcallylic C–H...O hydrogen bond pattern. The observation that the occupancies of two orientations of 1b in this complex are constrained by crystallographic symmetry to be 0.5 and 0.5 indicates that synthon I and the alternate C–H...O hydrogen bonded pattern are of comparable significance. The C–H...O hydrogen bond recognition pattern V is found in complexes 3b and 3c but not in 3a. The presence of synthon I and pattern V in the complexes of 3b and 3c are shown in Fig. 1(b) and (c), respectively.

To analyse the C–H...O hydrogen bonds in the complexes of 2a, plots of the C–O distances versus the C–H...O angles were calculated (Fig. 2). Circles, triangles and squares represent the C–H...O hydrogen bonds in complexes 3a, 3b and 3c respectively. The C–H...O hydrogen bonds which are part of synthon I are shown as filled symbols. From this plot, one notes that the C–H...O hydrogen bonds within synthon I are shorter and more linear and that they constitute the essence of these crystal structures. This observation strengthens the idea that the significance of a C–H...O hydrogen bond increases if it is part of a multi-point synthon. The C–H...O hydrogen bonds of synthon I are strongest in complex 3b but somewhat weaker in 3a and 3c.

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complexes with dibenzylideneketones. Synthon I in complexes of 2b allows it to mimic a molecule of pentacenedione, as shown in Fig. 3(e) and (f). The three-dimensional packing of these compounds is shown in Fig. 4(b). These results show that there is a limit to the robustness of synthon I in this family of crystal structures. Picric acid 2c which contains a strongly hydrogen bonding OH group is capable of disrupting the recognition motif of trinitrobenzenes with dibenzylideneketones.

### Table 1. Crystallographic data of complexes 3a–g

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*R values

### Synthon I in complexes of 2b

To test the robustness of synthon I in the presence of other functional groups like Cl and OH, we have prepared complexes of 2b with 1b and 1d and of 2c with 1a and 1b. It is well known that 2c forms stable complexes with various aromatic compounds through π–π interactions and it has been used in crystal engineering experiments to design a three-point bonded synthon, in crystal engineering experiments to design a three-point bonded synthon. From the examination of the crystal structures of pure 2b and 2c, it was found that the three nitro groups are coplanar with the aromatic ring in 2b but not in 2c. In 2b the ortho nitro group which is not involved in intramolecular O-H...O hydrogen bond is out of the aromatic ring plane. Therefore, both 2b and 2c were expected to form complexes with dibenzylideneketones.

### Compound 2b forms 2:1 crystalline complexes 3d and 3f with ketones 1b and 1d, respectively. Even though compounds 1b and 1d are chemically different, they form isostructural complexes with 2b due to the disorder in the dibenzylidene moiety. The presence of C-H...O hydrogen bonded synthon I in complexes 3d and 3e indicates that the Cl group does not interfere in the formation of I. These crystal structures are almost reminiscence of 3a, 3b and 3c except that O, Cl interactions are formed as shown in pattern VII. The nitro group oxygen atoms which participate in VII are disordered. The disorder of molecule 1b in these two complexes allows it to mimic a molecule of pentacenedione, as shown in Scheme I. Therefore, it was anticipated that pentacenedione should cocrystallise with compound 2b to yield 1. However, this could not be realised experimentally because pentacenedione failed to cocrystallise with 2b due to a mismatch of solubilities.

### Absence of synthon I in complexes of 2c

Compound 2c forms 1:1 molecular complexes 3f and 3g with compounds 1b and 1a, respectively. In both complexes, the C-H...O hydrogen bonded synthon I is absent. Interestingly, in complex 3f the O-H group forms an intramolecular hydro- gen bond with the keto group of molecule 1b (O, O, H, O, O-H, O-H, 2.90 and 2.66 Å, 123˚). This also forms two C-H...O hydrogen bonds (C-H, O-O, C-H, 3.18 and 2.98 Å, 164˚ and 3.42 and 2.23 Å, 156˚) to form a supermolecule of 1b and 2c that involves one O-H...O and two C-H...O hydrogen bonds (Fig. 4(b)). The three-dimensional packing of these supermolecules is shown in Fig. 4(b). These results show that there is a limit to the robustness of synthon I in this family of crystal structures. Picric acid 2c which contains a strongly hydrogen bonding OH group is capable of disrupting the recognition motif I of trinitrobenzenes with dibenzylideneketones.

In complex 3g, the situation is entirely different from the other complexes in that there is no intramolecular O-H...O hydrogen bond with a keto group as in complex 3f. Instead, ...
Fig. 1 (a) Crystal structure of complex 3a (1a: 2a in 1:2 ratio) to show synthon I (highlighted) and the alternate C–H, O hydrogen bonded patterns. (b) Crystal structure of complex 3b (1b: 2b in 1:2 ratio) to show synthsos I and V and the alternate C–H, O hydrogen bonded patterns. (c) Crystal structure of complex 3c (1c: 2c in 1:2 ratio) to show synthsos I and V.
The formation of 1, some weaker C–H–O–H containing equimolar amounts of 1 prepared to the sp3
and sp2
actions dominate the packing of the crystal. In complex molecules 2a–e, respectively, have been examined by looking at their NIPMAT plots. A pictorial matrix is formed using the atoms of a molecular skeleton (A
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) and the matrix element A
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 which is defined by the shortest intermolecular contact A
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 and shown in terms of a grey scale. The shorter the contact, the greyer the square which represents that particular contact. This greyness is scaled at the bottom of the figure. The dark line in this scale indicates the sum of the van der Waals radii of any two atoms. If there are two different molecular skeletons (A
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) and (B
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) in the supramolecular structure, then their interactions are shown in four sections. The upper left and lower right rectangles indicate the A
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 interactions while the lower left and upper right squares indicate A
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 interactions. Hence, the plot obtained is a simultaneous visual representation of all the intermolecular interactions. Fig. 6(a) and (b) are the NIPMAT plots of complexes 3f and 3g, respectively. In Fig. 6(b), the overall greyness in the upper left and lower right rectangles, which represent the C–H–O interactions and stacking interactions between molecules 2a and 1a, is more when compared with the corresponding areas of Fig. 6(a) (2e and 1b). This implies that in complex 3g the C–H–O hydrogen bonds and stacking interactions dominate the packing of the crystal. In complex 3f, compound 2b has relatively less acidic sp3
 C–H groups compared to the sp3
 C–H moiety of 1a and so the intermolecular O–H–O hydrogen bonds take the lead with the assistance of some weaker C–H–O bonds.

\(\tau\)–\(\pi\) Stacking interactions

The formation of 1,2 molecular complexes 3a–e from solutions containing equimolar amounts of 1 and 2 can be justified by considering \(\tau\)–\(\pi\) stacking. A molecule of 1 contains two phenyl rings and can accommodate two molecules of 2. It is well known that aryl groups prefer to interact in either an edge-to-face or an offset face-to-face orientations and compound 2a forms charge-transfer complexes with aromatic compounds. Recently, compound 2a has been used as a guest for chiral molecular tweezers through these interactions. All the molecular complexes of 2a and 2b form these interactions with slightly offset stacking. Fig. 7 shows a superposition of these interactions in the above complex. The centroid to centroid distance and plane to plane angles in these complexes range from 3.64 to 4.83 Å and 0.81 to 10.4°. However, the stacking interactions are different in complexes 3f and 3g. Complex 3f is stabilised by \(\tau\)–\(\pi\) and herringbone interactions [Fig. 4(b) and 7(f)] while complex 3g is stabilised by \(\tau\)–\(\pi\) interactions alone [Fig. 7(g)]. The variation in the donor–acceptor ratios of complexes 3f and 3g when compared with that in 3a–e is a consequence of the change in interactions between aromatic rings in these complexes.

CSD studies

The CSD was searched for the C–H–O hydrogen bonded patterns III, IV and VIII and O, Cl interaction VII to understand their nature and to ascertain their frequency of occurrence, which would indicate their robustness. There are

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Fig. 2. Scatter plot of C–H–O interactions in the complexes (I) 3a, (II) 3b and (III) 3c. Filled symbols are the C–H–O hydrogen bonds that contribute to synthon I. Notice that all these filled symbols are in the strong hydrogen bonded region.

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Fig. 3(a) Crystal structure of 1b (2b in 1:2 ratio) to show synths 1, V and VII. (b) Crystal structure of 3e (2e in 1:2 ratio) to show synths I, V and VII. Both disordered positions of the nitro group are shown for molecule 2b.
Scheme 1 Disorder of molecule 1b and 1d in complexes 3d and 3e.

From this plot it can be seen that many of the C–H, O hydrogen bonds are clustered in the strong hydrogen bonds region, i.e. in a C–O range of 3.35 to 3.65 Å and a C–H, O angle of 155–175°.

There are 173 hits in 159 crystal structures for synthon IV. Fig. 9(a) is the scattergram of C(9), O(1) versus C(4), O(6) and indicates the centrosymmetric nature of IV. Fig. 9(b) is the scattergram of C–H, O angles versus C, O distances in IV. Here the C–H, O hydrogen bonds are clustered between the C, O distance of 3.25 to 3.55 Å and C–H, O angle of 140 to 160°.

Halogen to nitro oxygen atom contacts are well known and have been used in the design of target crystal structures. A total of 19 crystal structures is present in the CSD for ortho-substituted chloro–nitro aromatics and if O, Cl distances only in the range 2.8 to 4.0 Å were considered, 17 of these were found to contain VII, indicating robustness of this synthon.

There is a total 82 hits from 17 crystal structures for the alternate O, Cl interaction displayed in synthon IX. That the number of hits per structure is higher than expected is an artefact of the unsymmetrical O, Cl interaction displayed in synthon IX. That the O, Cl interactions exist as symmetrical VII and unsymmetrical IX variations.

189, 159, 44 and 18 crystal structures present for synthons III, IV, VIIIa and VIIIb, respectively.

Synthon III is present 205 times in 189 crystal structures. Fig. 8(a) is the scattergram of C(7), O(1) versus C(3), O(6) distances and it shows the centrosymmetric nature of III. The off-diagonal points are from structures that have two molecules in the asymmetric unit, in other words these interactions occur between symmetry independent molecules. Fig 8(b) is the scattergram of C–H, O angle versus C, O distances for III.
Fig. 6 NIPMAT plots of complexes (a) M and (b) 3g. Note that there are more dark grey squares in the upper left and lower right rectangles in (b) when compared with (a). This indicates stronger and more numerous C–H–O hydrogen bonds and stacking interactions in 3g compared to M.
Motif VIIIa occurs in the molecular complex 3g and was found 47 times in 44 crystal structures, whereas VIIIb was found 18 times in 18 crystal structures. Fig. 11(a) is the scattergram of C(15), O(1) versus C(7), O(9) and shows the centrosymmetric nature of VIIIa. Fig. 11(b) is the scattergram of C–O distances versus C–H–O angles. Open circles represent the C–H–O motifs of VIIIa and filled circles represent the C–H–O motifs of VIIIb. The C–H–O hydrogen bonds and angles of VIIIa are clustered between 3.35 and 3.50 Å and 145 and 155°, and for VIIIb they are clustered in the C–O range of 3.15 and 3.35 Å and C–H–O angle range of 135 and 145°. These distance and angle distributions indicate
that many of the C–H...O motifs involved in synthon VIIIb are shorter but less linear compared to the hydrogen bonds in synthon VIIIa. When Fig. 8(b) and 9(b) are compared with Fig. 11(b) it is clear that the C–H...O bonds involved in synthon VIIIa,b are less linear than the bonds in synths I and III. 

**Supramolecular synthons III, IV, VII and VIII in crystal engineering**

We now discuss a few occurrences of the synthons III, IV, VII and VIII to highlight different structural aspects. For this exercise, we have chosen molecules 4–7. Synthon III is the C–H...O counterpart of the N–H...O hydrogen bonded recognition motif found in cis-amides. The crystal structure of benzoquinone is composed of synthon III which gives it a sheet-like structure. In 4, the two quinonoid halves of the molecule are tetrahedrally disposed because of the spiro ring junction. In the crystal structure of 4 (Fig. 12), there are two symmetry-independent molecules and these form a ribbon pattern constituted with successive synthons III. Only one of the two quinonoid halves of any molecule participates in this pattern and four distinct C–O distances result because two symmetry-independent molecules are involved. The C–H...O dimeric motif and the zig-zag chain arrangement of molecules of 4 resemble the structure found in secondary amides. The crystal structure of 5 (Fig. 13) shows the expected linear chain with synthon IV.

The crystal structure of 6 (Fig. 14) is interesting as it maintains the three-fold symmetry with the three nitro groups nearly perpendicular to the plane of the phenyl rings. This arrangement leads to the formation of a rosette-like structure.

Fig. 8 (a) Scatter plot of C–O distances to show the centrosymmetric nature of synthon III. (b) Scatter plot of C–O distances versus C–H, O angles in synthon III. Notice that the points are clustered in the C–O range 3.4–3.6 Å and C–H, O range 155–175°.

Fig. 9 (a) Scatter plot of C–O distances to show the centrosymmetric nature of synthon IV. (b) Scatter plot of C–O distances versus C–H, O angles in synthon IV. Notice that the points are clustered in the C–O range 3.25–3.55 Å and in the C–H, O range 140–160°.

Fig. 10 Scatter plot of Cl(10), O(1) versus Cl(5), O(6) distances. Notice the centrosymmetric nature of synthons VII and IXb.

Fig. 11 (a) Scatter plot of C(7), O(9) and C(15), O(1) distances to show the centrosymmetric nature of synthon VIIa. (b) Scatter plot of C–O distances versus C–H, O angles in synthon VIIa and VIIb. Open circles represent the C–H, O hydrogen bonds of synthon VIIa and closed circles represent the bonds in VIIb with synthon VII. The crystal structure of 7 (Fig. 15) contains two molecular components and leads to the anticipated chain structure through C–H, O hydrogen bonds as in synthon VIII. These studies suggest that one can utilise III, IV, VII and VIII as supramolecular synthons in crystal engineering experiments.

Conclusions

This work shows that C–H, O hydrogen bonds can be profitably utilised to design robust three-point supramolecular synthons. The C–H, O hydrogen bonds involved in multi-point synthons are stronger than the other isolated C–H, O hydrogen bonds in the same and related structures. The presence of strong hydrogen bonding functional groups usually influences C–H, O bonded recognition, but if the strong hydrogen bonds are optimised, the recognition through the weak interactions would be just as effective. Furthermore, the retroanalysis of a supramolecular synthon leads to complementary molecules which assemble in a predictable fashion and form the target motif. Such an approach to the construction of molecular assemblies is analogous to the synthesis of complex molecules from simpler substrates.

Here we have discussed the formation of the C–H, O hydrogen bonded synthon I where donors and acceptors are arranged in alternate fashion (ADA–DAD). The related AAD–DDA supramolecular synthon made up of stronger N–H, O and O–H, O hydrogen bonds has been identified recently in the crystal structure of 2′-deoxycytidine.

\[ \text{Fig. 12} \text{ Crystal structure of 4 (SPUNDQ20) to show the zig-zag chain of molecules linked by C–H, O hydrogen bonded synthon III} \]

\[ \text{Fig. 13} \text{ Crystal structure of 5 (MIMOSA10) to show the linear chain of molecules linked by synthons IV} \]

\[ \text{Fig. 14} \text{ Crystal structure of 6 (WANMGN) to show the hexagonal network of molecules linked through O, Cl interactions of synthon VII} \]

\[ \text{Fig. 15} \text{ Crystal structure of 7 (BERGAG) to show the linear arrangement of molecules linked through C–H, O hydrogen bonded synthon VIIIa} \]
hemihydrogen phosphate. Such observations lead to the idea that it should also be possible to design related AAA DDD and AAD DDA supramolecular synths with C-H...O hydrogen bonds. Finally, this work also shows that π-π interactions are important in determining the stoichiometry of molecular components and in turn in governing crystal packing.

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References


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