# Solid-state Supramolecular Assembly *via* C–H···O Hydrogen Bonds: Crystal Structures of the Complexes of 1,3,5-Trinitrobenzene with Dibenzylideneacetone and 2,5-Dibenzylidenecyclopentanone

**Kumar Biradha,**[a] **C. V. Krishnamohan Sharma,**[a] **Kaliyamoorthy Panneerselvam,**[a] **Liat Shimoni,**[b] **H. L. Carrell,**[b] **David E. Zacharias**[b] **and Gautam R. Desiraju***[a]

[a] *School of Chemistry, University of Hyderabad, PO Central University, Hyderabad 500 134, India*
[b] *Fox Chase Cancer Center, 7701 Burholme Avenue, Philadelphia, PA 19111, USA*

Dibenzylidene ketones are shown to form stoicheometric complexes with 1,3,5-trinitrobenzene wherein the molecular components are held together with C–H···O hydrogen bonds.

A crystal has been termed a 'supramolecule *par excellence*'[1] and if molecular recognition is 'the strategy by which a molecule bears supramolecular functions',[2] the very process of crystallisation (of either single or poly component crystals) is one of the most impressive and precise examples of molecular recognition. Closely related to these ideas is the concept of crystal engineering[3] through which 'recognition-directed spontaneous assembly of a supramolecular strand'[4] is possible. Indeed, crystal engineering and molecular recognition are two related facets of supramolecular chemistry that depend on multiple matching of functionalities among molecular components so as to optimise a number of intermolecular interactions which may be of different strengths and directionalities.[3,5]

A number of recent papers on crystal engineering and molecular recognition are concerned with 'conventional' N–H···O and O–H···O hydrogen bonds and typical examples include molecular complexes of aminopyrimidines, pyrimidines, pyridones and carboxylic acids (network **1**).[6–8]

Continuing this line of thought, is it possible to design crystalline molecular complexes which are held exclusively *via* forces such as C–H···O hydrogen bonds which are weaker than O–H···O and N–H···O bonds by a factor of typically 3 to 5?[9] We have described a system where both O–H···O and C–H···O bonds are involved[10] as have others,[11] but an exclusive C–H···O receptor has not yet been reported. In this communication, we describe such an example which contains network **2** with the C–H···O bonds directed inwards (convergent binding).[8]†

The choice of 1,3,5-trinitrobenzene **3a** for these crystal engineering studies was quite deliberate. It is known that the

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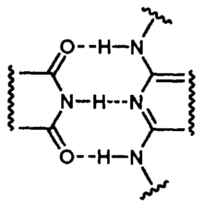
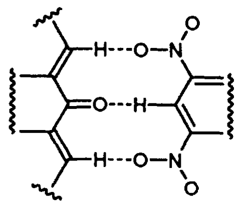
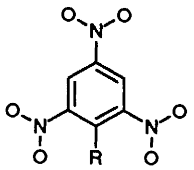
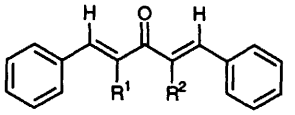
† This is true if the two-component entity is treated as a supermolecule. If, on the other hand, the entire crystal is treated as a supermolecule, many recognition sites will, in the limit, be directed outwards because each molecule is surrounded by many others.

–$NO_2$ group is a good C–H···O acceptor[12] and further, the H atoms in **3a** are very acidic, a factor that favours the formation of short and linear C–H···O bonds.[13] Previous studies with 3,5-dinitrocinnamic acid had shown that the C–H···O network is significant enough to deform the O–H···O network.[14] If anything, the C–H···O bonds in **3a** were expected to be even more important because of the presence of the third –$NO_2$ group. The choice of the second molecular component of the supermolecule was made by matching complementary groups with C–H···O bonds as in network **2** and molecules like dibenzylideneacetone **4a**, and related derivatives 2,5-dibenzylidenecyclopentanone **4b** and 2,6-dibenzylidenecyclohexanone **4c** suggested themselves naturally. Additionally, the fact that networks such as **8** have been observed elsewhere[15] strengthened the reasons for the choice of **4a**, **4b** and **4c**.

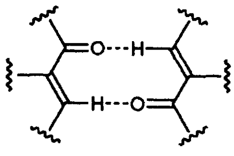

**1**

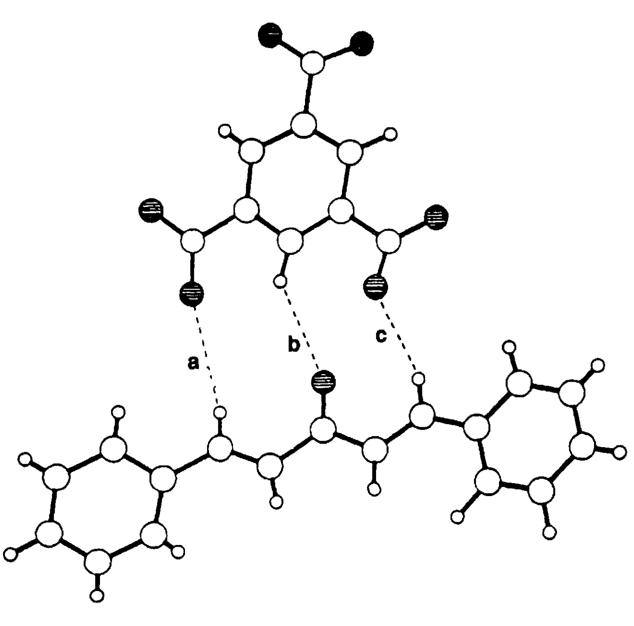

**2**


**3a**; R = H
**3b**; R = $CH_3$


**4a**; $R^1 = R^2 = H$
**4b**; $R^1 = R^2 = –[CH_2]_2–$
**4c**; $R^1 = R^2 = –[CH_2]_3–$

**5** = $(\mathbf{3a})_2$ . **4a**
**6** = $(\mathbf{3a})_2$ . **4b**
**7** = $(\mathbf{3a})_2$ . **4c**


**8**

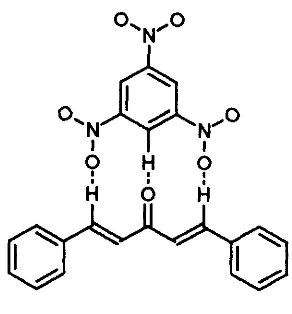


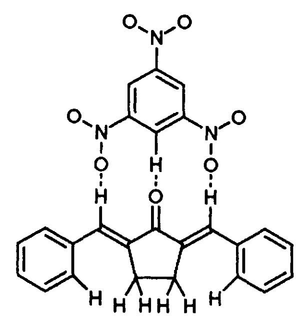
| | C···O (Å) | H···O (Å) | C–H···O (°) |
|---|---|---|---|
| **a** | 3.66 | 2.81 | 155 |
| **b** | 3.33 | 2.59 | 132 |
| **c** | 3.17 | 2.45 | 137 |

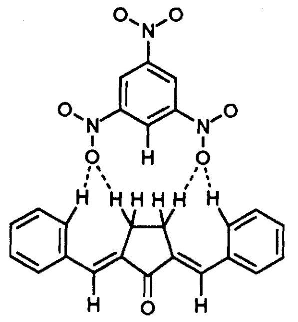
**Fig. 1** Molecular recognition pattern of **3a** with **4a** *via* C–H···O bonds in complex **5**. Oxygen atoms are shaded.

Yellow crystals of the 2:1 complex **5** (m.p. 125–127 °C) were obtained readily from an equimolar solution of **3a** and **4a** in 1:1 dichloromethane–hexane. A view of the crystal structure‡ is shown in Fig. 1. Molecules of **3a** and **4a** are linked by a group of three strong C–H···O bonds. It is important to note that the H atoms in these crystal structures were located with difference Fourier syntheses and refined independently. It is therefore possible to state confidently that these C–H···O hydrogen bonds are crucial to stabilising network **2** and in turn the entire structure.

Compound **3a** also forms 2:1 crystalline complexes with ketones **4b** and **4c**. The crystal structure of complex **6**‡ (m.p. 169 °C) is shown in Figs. 2 and 3. Network **2** is found again and the C–H···O bonds are shorter and even more linear than in







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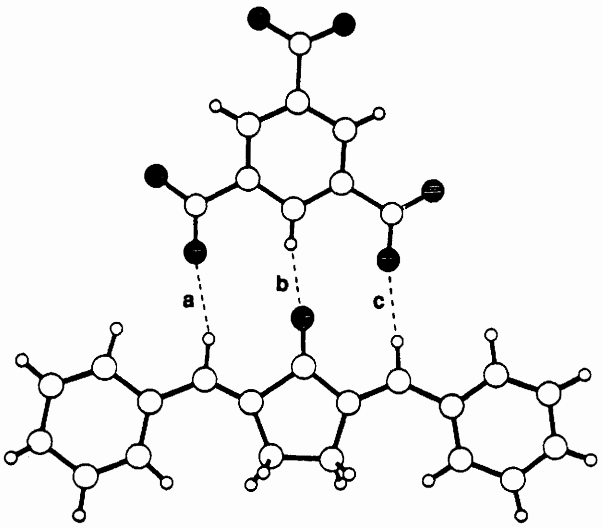
‡ *Crystal data* for complex **5**: $C_{17}H_{14}O:(C_6H_3N_3O_6)_2$ $M_r$ = 660.52, Mo-Kα radiation, monoclinic, $P2_1$, $Z$ = 2, $a$ = 7.092(2), $b$ = 27.927(4), $c$ = 7.569(2) Å, β = 96.67(2)°, $V$ = 1488.9(5) Å$^3$, $F$(000) = 680, $D_c$ = 1.47 Mg m$^{-3}$, μ = 0.76 cm$^{-1}$, 1828 observed (3σ) reflections out of 2931 collected with 2 < 2θ < 55°, Enraf-Nonius FAST area detector with rotating anode X-ray source, solution SHELXS86, refinement SHELX76, $R$ = 0.038, $R_w$ = 0.041, C, N, O anisotropic, H isotropic, maximum and minimum final difference electron density 0.13 and −0.19 e Å$^{-3}$.

*Crystal data* for complex **6**: $C_{19}H_{16}O:(C_6H_3N_3O_6)_2$ $M_r$ = 686.56, Mo-Kα radiation, monoclinic, $P2_1/c$, $Z$ = 2, $a$ = 7.493(2), $b$ = 27.384(6), $c$ = 7.491(2) Å, β = 92.39(2)°, $V$ = 1535.8(6) Å$^3$, $F$(000) = 708, $D_c$ = 1.484 Mg m$^{-3}$, μ = 0.76 cm$^{-1}$, 1328 observed (3σ) reflections out of 3532 collected with 2 < 2θ < 55°, CAD4 diffractometer, solution SHELX86, refinement SHELX76, $R$ = 0.048, $R_w$ = 0.050, C, N, O anisotropic, H isotropic, maximum and minimum final difference electron density 0.13 and −0.13 e Å$^{-3}$; the **4b** molecule is disordered.

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



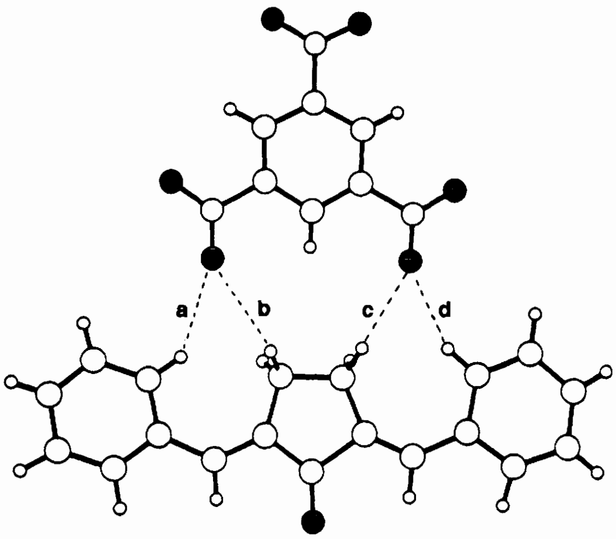
| | C···O (Å) | H···O (Å) | C–H···O (°) |
|---|---|---|---|
| **a** | 3.44 | 2.48 | 157 |
| **b** | 3.18 | 2.30 | 160 |
| **c** | 3.31 | 2.39 | 156 |

**Fig. 2** Molecular recognition pattern of **3a** with **4b** in complex **6**. Oxygen atoms are shaded.

complex **5**. Curiously, the **4b** molecules are disordered because there is an alternative C–H···O recognition motif which involves the 'hydrocarbon' side of the molecule. The occupancies of the two orientations of **4b** in complex **6** are constrained by crystallographic symmetry to be 0.5 and 0.5 indicating that the C–H···O patterns are of comparable significance. In this respect, ketone **4a** binds more specifically to **3a** than does ketone **4b**. Complex **7** was crystallised to examine if the dual recognition motif in complex **6** could be disrupted by increasing the ring size from five to six. Unfortunately, this compound gave twinned crystals which so far have resisted structural analysis.

Competition experiments were carried out where equimolar amounts of **3a** and trinitrotoluene **3b** were allowed to compete for half the equivalent amount of **4a** (*i.e.* 1 : 1 : 0.5 moles of **3a**, **3b** and **4a**). Only crystals of complex **5** were formed, with **3b** remaining in solution. The separation of **3a** and **3b** was essentially quantitative. The presence of the $-CH_3$ group in **3b** hinders the coplanarity of at least two of the $-NO_2$ groups with the aromatic ring, effectively shutting out the possibility of the formation of network **2**. Similar results were obtained when **3a** and **3b** were allowed to compete for **4b** or **4c**. When solution experiments on molecular recognition are carried out, the magnitude of association constants give some idea concerning the efficiency and specificity of binding. This is not possible for the equivalent events in solution preceding crystallisation especially because (as in the present case) the intermolecular forces are very weak. However the solid state equivalents of an association constant are the distance and angle characteristics of the intermolecular interactions. By this token there is specific molecular binding in complexes **4** and **5** because the C–H···O bonds are short and linear.

The C–H···O patterns reported here have not, in general, been observed in the many complexes of **3a** with aromatic hydrocarbons that have been investigated crystallographically.[16] We have also crystallised complexes of **4a**, **4b** and **4c** with picric acid and picryl chloride and these solids are under investigation. This work shows that exclusive C–H···O (and/or O–H···C?)[17] receptors may be designed and that these may form the basis for new schemes of molecular recognition with special importance in biological systems.



| | C···O (Å) | H···O (Å) | C–H···O (°) |
|---|---|---|---|
| **a** | 3.60 | 2.79 | 142 |
| **b** | 3.57 | 2.83 | 132 |
| **c** | 3.52 | 2.84 | 123 |
| **d** | 3.31 | 2.66 | 122 |

**Fig. 3** An alternative recognition pattern of **3a** with **4b** in complex **6**. Oxygen atoms are shaded.

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