

Predictable solid state structures incorporating the $C\equiv C-H\cdots O_2N$ supramolecular synthon

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Terminal alkynes interact with nitro groups in a symmetrically bifurcated manner to form ribbon-like structures in the solid state.

It is widely accepted that although C–H groups are relatively poor hydrogen bond donors, many C–H \cdots O interactions share some of the characteristics of stronger hydrogen bonds that are formed with more conventional hydrogen bond donors such as N–H and O–H.¹ Attempts to quantify donor and acceptor strengths in C–H \cdots O interactions have shown^{2,3} that, as expected, the strongest interactions are formed by pairing the most acidic C–H hydrogens, such as Cl_3C-H and $C\equiv C-H$, with the best oxygen acceptors, which include P=O and H_2O . Although the oxygens of the nitro group appear to be poor hydrogen bond acceptors when compared to oxygen atoms in other bonding environments, they do participate in other noteworthy interactions such as the polarisation-induced halogeno \cdots nitro motif. In particular, the iodo \cdots nitro supramolecular synthon⁴ **1** has been utilised in several recent examples⁵ of crystal engineering. Recently, our analysis⁶ of the structures of substituted benzene derivatives containing alkynes and/or halogens has suggested that there may be recognition characteristics which are shared between terminal alkynes and halogen atoms. For this reason, we felt that a logical development of the iodo \cdots nitro synthon **1** (Fig. 1) would be the substitution of the iodine by a terminal alkyne to give the synthon **2**, with the expectation that it would retain the novel bifurcated interaction. Furthermore, such studies should provide additional insight into the characteristics of C–H \cdots O hydrogen bonds to nitro groups. Here we describe the crystal structures of 1-ethynyl-4-nitrobenzene **3** and the 1:1 co-crystal [4·5] of 1,4-dinitrobenzene **4** and 1,4-diethynylbenzene **5**; both structures contain the supramolecular synthon **2**.

Small needle-like crystals of **3** were grown by the slow evaporation of solvent from a solution of **3** in a MeOH– H_2O mixture. However, poor crystal quality, coupled with a tendency for crystal twinning, made structure solution impossible from single crystal X-ray diffraction data. Therefore, the structure was solved from powder X-ray diffraction data using the Monte Carlo method.⁷ The crystal structure of **3** \ddagger contains (Fig. 2a) linear ribbons of **3** which are connected by the alkynyl \cdots nitro motif **2** to create infinite chains of molecules linked by $C\equiv C-H\cdots O$ hydrogen bonds as the major inter-

molecular interaction. The two C–H \cdots O distances ($d_{H\cdots O} = 2.47$ and 2.36 Å) are significantly less than the sum of the van der Waals radii,⁸ ($\Sigma_{vdw} = 2.65$ Å). The adjacent ribbons of molecules are not coplanar, but are stepped to form corrugated layers. Thus, the aromatic protons of each molecule in a ribbon form a number of minor C–H \cdots O interactions with the nitro groups of the molecules in adjacent ribbons ($d_{H\cdots O}$ range 2.4–2.9 Å).

In order to assess whether the alkynyl \cdots nitro interaction in motif **2** could be used as a robust supramolecular synthon in crystal engineering applications, we attempted a co-crystallisation between two molecular components with the potential to form motif **2**. Whereas the structure of **3** contains *da* \cdots *da* \cdots *da* interaction arrays based on one molecular component (where *da* is a component containing self-complementary donor and acceptor sites), we aimed to design and construct a structure based on *dd* \cdots *aa* \cdots *dd* arrays using two molecular components (Fig. 1).

Single crystals of [4·5] suitable for single crystal X-ray diffraction studies were grown by slow evaporation of solvent from a solution of a 1:1 mixture of **4** and **5** in benzene. The crystal structure of [4·5] \ddagger (Fig. 2b) bears a strong resemblance to that of **3** in that linear molecular ribbons arise from infinite chains of molecules linked by motif **2**. Again, the alkynyl \cdots nitro interaction is not symmetrically bifurcated, with a small difference between the two C–H \cdots O distances ($d_{H\cdots O} = 2.54$ and 2.61 Å); additional C–H \cdots O contacts ($d_{H\cdots O}$ 2.6–2.7 Å) are also formed between ribbons, as seen for **3**.

The C–H \cdots O distances observed in the alkynyl \cdots nitro motifs in both **3** and [4·5] are relatively long compared to other C–H \cdots O interactions involving terminal alkynes.³ This observation can be attributed to the acknowledged poor hydrogen bond accepting properties of the oxygens of the nitro group, although distance alone cannot be taken as a quantitative indication of the interaction strength. Therefore, we have attempted to further characterise the alkynyl \cdots nitro interaction using infra-red spectroscopy and *ab initio* quantum mechanical calculations.

The difference (denoted $\Delta\nu_{C-H}$) between the C–H stretching frequency for the ‘free’ alkyne (as determined for a dilute solution of the alkyne in CCl_4) and for the hydrogen bonded alkyne in the solid gives a qualitative indication of the strength of the C–H \cdots O interaction. Typically, the range in magnitude of $\Delta\nu_{C-H}$ for alkynyl C–H \cdots O interactions vary from long, and

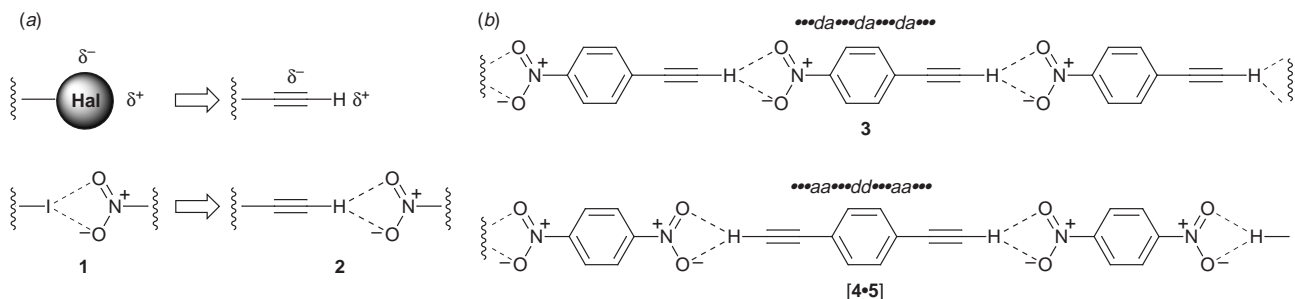


Fig. 1 (a) The polarisation pattern found in terminal alkynes is similar to that for halogens. Thus, the established iodo \cdots nitro synthon **1** can be evolved into the alkynyl \cdots nitro synthon **2**. (b) The synthon **2** can be used to form linear molecular ribbons, either using one molecular component as in **3** or two components as in [4·5].

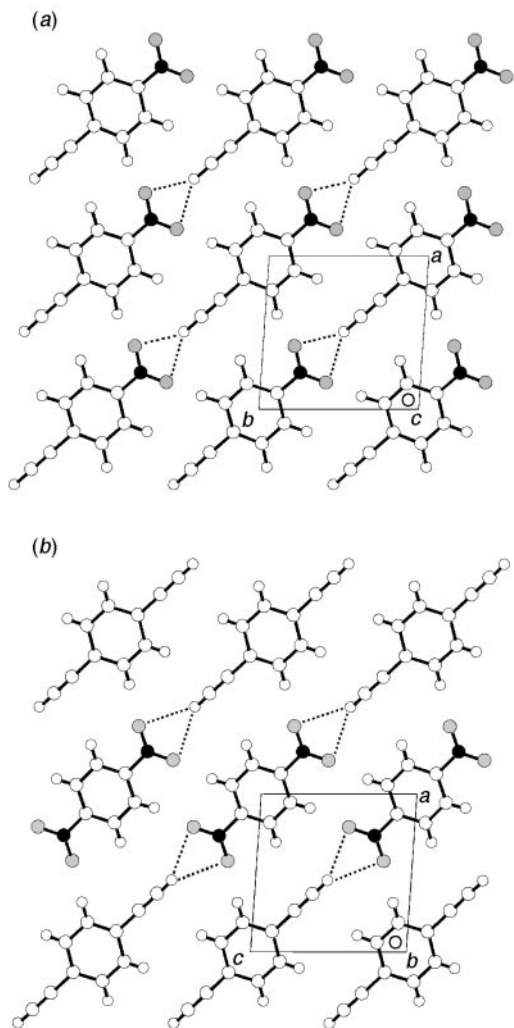


Fig. 2 The crystal structures of (a) **3** and (b) **[4-5]** both show linear molecular ribbons which are held together by the alkyne-nitro synthon **2**. The black and shaded spheres represent nitrogen and oxygen atoms respectively; the dotted lines represent C≡C-H...O₂N interactions.

thus presumably very weak, interactions (*ca.* 15 cm⁻¹, $d_{\text{H}\cdots\text{O}} = 2.92 \text{ \AA}$)⁹ to much shorter, stronger interactions (*ca.* 145–200 cm⁻¹, $d_{\text{H}\cdots\text{O}} < 2.0 \text{ \AA}$)¹⁰ with most red-shifts falling⁹ in the range 40–100 cm⁻¹. The infra-red spectra for polycrystalline samples of **3** and **[4-5]** obtained from the same batches used for the X-ray diffraction data collections were measured§ in KBr disks. The $\Delta\nu_{\text{C-H}}$ for **3** (57 cm⁻¹) and **[4-5]** (50 cm⁻¹) represents an appreciable red shift of indicative of a moderately strong interaction, which is comparable to alkyne C-H...O interactions which involve supposedly much better oxygen acceptors (such as OH groups).

Ab initio quantum mechanical calculations were performed¶ at the MP2/6-31G(d,p) level using an ethyne-nitrobenzene aggregate as a model system for the alkyne-nitro interactions. The energy of interaction (ΔE_{int}), corrected for basis set superposition error (BSSE), for the alkyne-nitro C-H...O₂N interaction was calculated to be -8.0 kJ mol⁻¹. Although this interaction energy is less than that calculated¹¹ for the alkyne-water C-H...O interaction (-12.2 kJ mol⁻¹), surprisingly, it is comparable to the estimated¹² interaction energy for the bifurcated iodo-nitro motif (-10 kJ mol⁻¹).

In conclusion, we have demonstrated that, by virtue of common recognition features, halogens and terminal alkynes can be exchanged to create a new supramolecular synthon incorporating a C≡C-H...O₂N interaction which, by FTIR spectroscopy and quantum mechanical calculations, has been shown to possess a significant binding energy.

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Notes and references

† *Crystal data* for **3**: [C₈H₅NO₂], $M = 147.13 \text{ g mol}^{-1}$, triclinic, space group $P\bar{1}$, $a = 6.8261(8)$, $b = 7.9213(9)$, $c = 7.4743(7) \text{ \AA}$, $\alpha = 116.581(4)$, $\beta = 91.556(4)$, $\gamma = 92.749(9)^\circ$, $V = 360.5(1) \text{ \AA}^3$, $Z = 2$, $\lambda = 1.3 \text{ \AA}$, $T = 295(2) \text{ K}$. The sample was loaded into a capillary (1.0 mm diameter). Data were measured on the high-resolution powder diffraction station 2.3 at the Synchrotron Radiation Source, Daresbury Laboratory, for a total of 100 min. Data were recorded in the 2θ range 5 to 67° in 0.01° steps. The powder diffraction pattern was indexed using ITO (ref. 13) and the structure was solved by the Monte Carlo method (ref. 7). The geometry of the molecule was restrained during the Rietveld refinement which was carried out using GSAS (ref. 14). Non-hydrogen atom positions were refined with fixed isotropic displacement parameters (0.025 Å²) and hydrogen atoms were placed in calculated positions. Final refinement gave $R_p = 0.067$, $R_{wp} = 0.097$.

‡ *Crystal data* for **[4-5]**: [C₆H₄N₂O₄·C₁₀H₆], $M = 294.26 \text{ g mol}^{-1}$, triclinic, space group $P\bar{1}$, $a = 7.059(3)$, $b = 7.555(2)$, $c = 6.939(3) \text{ \AA}$, $\alpha = 91.86(4)$, $\beta = 93.849(9)$, $\gamma = 89.669(9)^\circ$, $V = 369.0(3) \text{ \AA}^3$, $Z = 1$, $\lambda = 0.71069 \text{ \AA}$, $T = 296(2) \text{ K}$, $\mu = 0.097 \text{ mm}^{-1}$, 1142 independent reflections ($R_{\text{int}} = 0.065$), $R = 0.061$, $wR_2 = 0.155$. CCDC 182/1108.

§ Infra-red spectra were recorded on a Perkin-Elmer Paragon 1000 FTIR spectrometer at 293 K. Solid state spectra were recorded as KBr disks. Solution spectra (concentration *ca.* 2 mM) were recorded in CCl₄ in an Aldrich Demountable liquid-cell kit with a pathlength of 0.5 mm. All spectra were recorded at a resolution of 2 cm⁻¹.

¶ *Ab initio* quantum mechanical calculations, including geometry optimisations, were performed using GAMESS (ref. 15) (the version dated 18 May 1997 was used for all calculations). Corrections for BSSE for the optimised coordinates were obtained by the full counterpoise procedure using CADPAC (ref. 16).

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