C–H · · · O Hydrogen Bonding and Topochemistry in Crystalline 3,5-Dinitrocinnamic Acid and Its 1 : 1 Donor–Acceptor Complex with 2,5-Dimethoxycinnamic Acid

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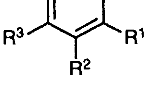
3,5-Dinitrocinnamic acid adopts an unusual crystal structure wherein C–H · · · O hydrogen bonds dictate the symmetry of the O–H · · · O network while its 1 : 1 molecular complex with 2,5-dimethoxycinnamic acid is photoreactive in the solid state to yield an unsymmetrical cyclobutane dimer.

That C–H · · · O hydrogen bonds exist in organic solids is well-accepted[1,2] but it is also assumed that these weak interactions only concur with and cannot compete with stronger O–H · · · O bonds in establishing stable crystal packings. Such an assumption, however, need not always be valid. By discriminating between energetically similar yet geometrically dissimilar O–H · · · O patterns, C–H · · · O bonds may actually be crystal-structure-determining. In this communication, we describe 3,5-dinitrocinnamic acid, **1a**, which crystallises as an O–H · · · O dimer wherein the hydrogen-bonded molecules are related, not by an inversion centre, as is typical,[3] but by a twofold rotation axis. This curious phenomenon arises because of an abundance of C–H · · · O interactions.

Such studies of the C–H · · · O bond are chemically relevant, because the energy of this interaction (1–5 kcal mol^{-1}) (1 cal = 4.184 J) is just in the range where it can compete with conformational processes in small molecules[4] and with forces responsible for the tertiary structure in macromolecules.[5]

In the novel crystal structure of **1a**† (Fig. 1), the eight-membered O–H · · · O ring is reasonably planar, but because of the twofold symmetry, the 28° intramolecular twist between carboxy and aromatic groups leads to an inclination of 56° between the two aromatic rings in the dimer. Fig. 1 provides a rationale for this observation. There is an extensive C–H · · · O bond network (7 contacts with C · · · O $\leqslant$ 3.75 Å), confirmed by the ordered carboxy group [C–O, 1.308(6), 1.226(6) Å]. A relatively high cut-off has been used here for the C · · · O distances because it has been observed that systematic gradations in these distances extend to well beyond 'conventional' van der Waals limits.[6,7] The C–H · · · O contact is, in essence, electrostatic rather than van der Waals, falling off much more slowly with distance. Even so, the



1a; $R^1 = R^3 = R^5 = H$; $R^2 = R^4 = NO_2$
b; $R^1 = R^4 = OMe$; $R^2 = R^3 = R^5 = H$
c; $R^1 = R^3 = NO_2$; $R^2 = R^4 = R^5 = H$
d; $R^1 = R^4 = R^5 = H$; $R^2 = R^3 = OMe$
e; $R^1 = R^4 = R^5 = H$; $R^2 = OMe$; $R^3 = OH$
2; **1a** : **1b**

3; Ar^1 = 3, 5-dinitrophenyl
Ar^2 = 2, 5-dimethoxyphenyl

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† *Crystal structure determination* of acid **1a**, Nicolet R3m, Mo-Kα, monoclinic, $C2/c$, $Z = 8$, $a = 15.767(15)$, $b = 7.796(3)$, $c = 16.155(5)$ Å, $\beta = 95.61(6)°$, 545 non-zero (2σ) reflections out of 866 collected with $4° < 2\theta < 45°$, SHELXTL, $R = 0.038$, hydrogens calculated, C, N and O anistropic.

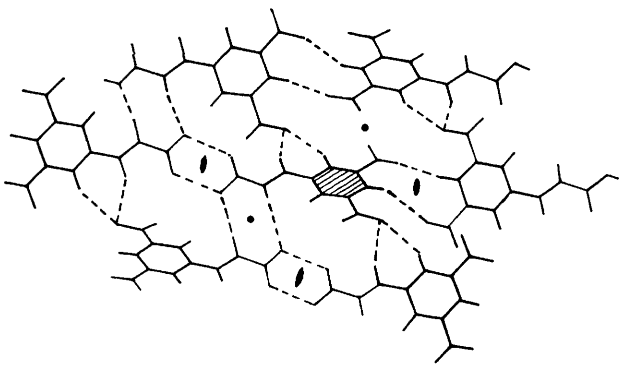

Fig. 1 Crystal structure of acid **1a** showing O–H · · · O and C–H · · · O hydrogen bonds. The reference molecule is shaded and is linked to its twofold axis-related-neighbours by O–H · · · O bonds and to its *c*-glide, inversion and other twofold-related-neighbours by C–H · · · O bonds (H atoms are in idealised positions, see ref. 1).

shortest C · · · O distances probably represent fairly good C–H · · · O hydrogen bonds (C · · · O, C–H · · · O, 3.19 Å, 123°; 3.41 Å, 144°; 3.45 Å, 152°, all H atom positions corrected). Acid **1a** is particularly well-suited for the formation of these C–H · · · O bonds. The alkenic hydrogens are unusually acidic when compared with aliphatic hydrogens. Since it is believed that C–H acidity is more important than O atom basicity in a C–H · · · O bond, the weak acceptor nature of the nitro group is probably not critical. Additionally, cooperative effects[8] could enhance nitro group basicity. The C–H · · · O bonds dominate the structure and their directional requirements appear to be incompatible with an O–H · · · O inversion-dimer. Simple calculations (MOPAC) show that there is an energy difference of *ca.* 0.55 kcal mol^{-1} between an all-planar conformation (which might have led to an inversion-dimer) and the more energetic, twisted conformation observed here. The total energy of the C–H · · · O bonds should be at least equal to this difference. The planarity and conformational flexibility of **1a** increases its C–H · · · O bond-forming ability in the crystal since rotations of the substituent groups to optimise C–H · · · O bonds are facile. In contrast, 2,4-dinitrocinnamic acid, **1c**, crystallises as a 'normal' inversion-symmetry O–H · · · O dimer.‡ Here, the 2-nitro group does not participate effectively in C–H · · · O bonding, probably because of its conformational inflexibility caused by steric hindrance and accordingly, the possibilities of distortions in the O–H · · · O network are reduced.

Acid **1a** is also of interest because it forms a 1 : 1 molecular complex, **2** with 2,5-dimethoxycinnamic acid, **1b**, deep-yellow crystals (m.p. 159 °C) being obtained from a mixed solution of **1a** and **1b** in 2 : 3 benzene–toluene. The crystal structure of complex **2** is of limited accuracy (poor crystal quality)§ but is of interest for two reasons: (*i*) There is again an extensive network of C–H · · · O hydrogen bonds (Fig. 2) and these seem mostly to involve **1a** molecules in that the number of contacts with C · · · O ≤ 4.00 Å are 10, 5 and 6 for **1a** · · ·**1a**, **1a** · · · **1b** and **1b** · · · **1b** (C · · · O, C–H · · · O; 3.06 Å, 133°; 3.16 Å, 134°; 3.29 Å, 105°; 3.41 Å, 133°). The **1a** molecules are held thus in a non-planar sheet to which are attached **1b** molecules employing O–H · · · O and π–π interactions. (*ii*) O–H · · · O bonds link **1a** and **1b** molecules into pseudo-inversion-symmetry dimers which are efficiently π–π stacked (Fig. 3). Such overlap of aromatic donor and acceptor rings ensures that the alkenic bridges also overlap and are within the threshold distance (4 Å) for [2 + 2] cycloaddition.[9] In complex **2**, the double bond centre-to-centre separation is 3.54 Å and accordingly, solid state irradiation **2** (sunlight, 30 °C, 5 days) results in a good (60%) yield of the pseudo-mirror-symmetry cyclobutane, **3** [m.p. 169 °C, IR ν/cm^{-1} 1700, 1530, 1340, 905, 660, NMR ([^{2}H$_6$]-acetone) δ 3.6, 3.9 (dimethoxy), 4.1, 4.6 (cyclobutane)]. Such chiral donor–acceptor truxinic acids have not been reported hitherto and are of interest for the following reasons: (*i*) solid state topochemical asymmetric synthesis,[10] (*ii*) as models for intramolecular charge transfer and (*iii*) as clathrating hosts.[11]

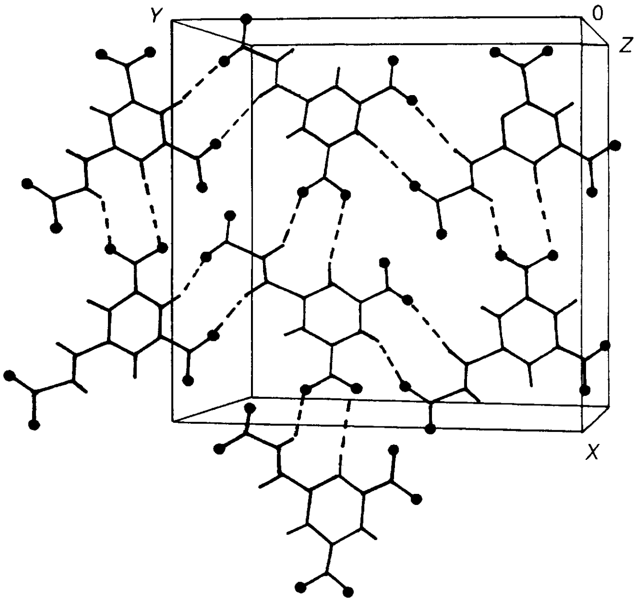

Fig. 2 Sub-structure of **1a** molecules in the crystal structure of complex **2**. Oxygen atoms are shaded. Notice the favourable angular approaches of the C–H groups (idealised H atom positions) towards the oxygen atoms.

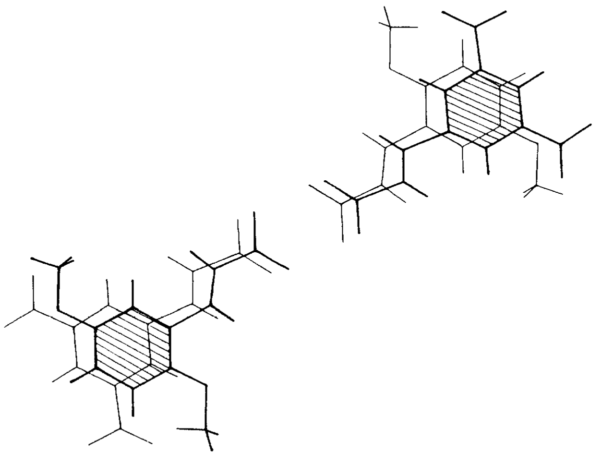

Fig. 3 Molecules of acid **1a** and **1b** related by O–H · · · O hydrogen bonds and π–π donor–acceptor interactions in complex **2**. Unsymmetrical dimer **3** is formed by a topochemical [2 + 2] cycloaddition of the stacked molecules.

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‡ *Crystal structure determination* of acid **1c**, Nicolet R3m, Mo-Kα, monoclinic, $P2_1/n$, $Z = 4$, $a = 8.760(9)$, $b = 7.869(5)$, $c = 14.040(10)$ Å, $\beta = 93.12(7)°$, 1137 non-zero (3σ) reflections out of 1785 collected with $4° < 2\theta < 50°$, SHELXTL, $R = 0.034$, hydrogens calculated, C, N and O anisotropic.

§ *Crystal structure determination* of complex **2**, Nicolet R3m, Mo-Kα, orthorhombic, *Pbca*, $Z = 8$, $a = 16.859(10)$, $b = 17.277(10)$, $c = 13.993(6)$ Å, 852 non-zero (3σ) reflections out of 3144 collected with $4° < 2\theta < 45°$, SHELXTL, $R = 0.114$, hydrogens calculated, C, N, and O anisotropic. Atomic coordinates, bond lengths and bond angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre for **1a**, **1c** and **2**. See Notice to Authors, Issue No. 1.

The complex-forming ability of acid **1a** seems to be quite general and we have isolated its 1 : 1 photoreactive complexes with acids **1d** and **1e**. The structural chemistry of these acids and complexes is being investigated at present.

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