Crystal Engineering *via* Donor–acceptor Interactions. *X*-Ray Crystal Structure and Solid State Reactivity of the 1:1 Complex, 3,4-Dimethoxycinnamic Acid–2,4-Dinitrocinnamic Acid

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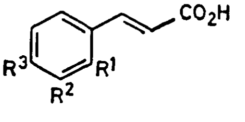
Donor–acceptor interactions can be used to engineer a crystal structure where solid state topochemical photodimerisation is permitted.

Topochemical control in organic solid state reactions can profoundly enhance product selectivity and specificity. Thus there have been several efforts, in recent years, towards systematically steering or engineering the crystal structures of organic molecules to packing modes that are conducive to a desired reactivity.[1] The general strategy in these efforts has been established by a discussion of the crystalline forms of some organic molecules (*e.g.*, the α, β, and γ-forms of crystalline substituted cinnamic acids) where a directional though usually weak intermolecular interaction is often only possible in one of several structural alternatives.[2] Dichloro-substitution of cinnamic acid has led to a general method by which the β-modification is engineered by the presence of a maximum Cl–Cl non-bonded interaction between adjacent molecules.[3] Other methods using dipole–ring interactions or hydrogen bonding as a steering device have been reviewed.[4] More recently, the application of crystal engineering to the 2-benzyl-5-benzylidenecyclopentanone family of structures has been described.[5]



(1) is (2a).(2b)
(2a); R^1 = H, R^2 = R^3 = OMe
(2b); R^1 = R^3 = NO_2, R^2 = H

In this communication we report the novel 1:1 complex (1) of 3,4-dimethoxycinnamic acid (2a) and 2,4-dinitrocinnamic acid (2b), where π–π donor–acceptor interactions have been used as a steering device to a β-type potentially photoreactive structure.

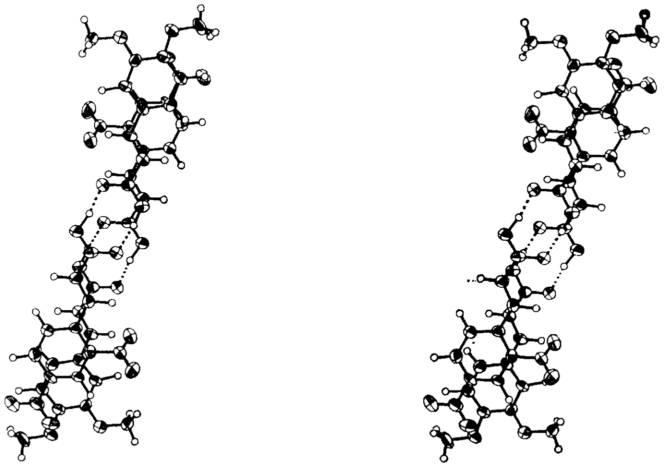


Figure 1. Stereoscopic view of the crystal structure of (1) showing hydrogen bonding and π-complexing between four molecules, two each of (2a) and (2b). There is a close approach of a 4-nitro-oxygen atom and a 4-methoxy-hydrogen atom of 3.05 Å.

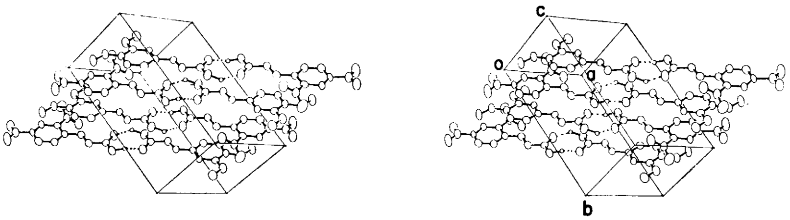


Figure 2. Stereoscopic view of the structure of (**1**) showing the stack direction [001]. Molecules of (**2a**) and (**2b**) alternate with unequal spacings (*ca.* 3.80 and 4.97 Å).

The acids (**2a**) and (**2b**), when dissolved in ethanol in equimolar quantities, exclusively yielded orange crystals of the 1 : 1 complex, (**1**). The crystal cell dimensions of (**1**) are different from those of either (**2a**) or (**2b**) while its solid state electronic spectrum [λ_{max} (charge transfer) 460 nm] is characteristic of a donor–acceptor complex. The structure determination of (**1**) was carried out to analyse its implications on the solid state reactivity.

Crystal data for (**1**): $C_{11}H_{12}O_4.C_9H_6N_2O_6$, $M = 446$, triclinic, space group $P\bar{1}$, $a = 8.857(5)$, $b = 13.872(8)$, $c = 8.578(4)$ Å, $\alpha = 101.11(4)$, $\beta = 100.98(4)$, $\gamma = 95.98(4)°$, $U = 1004.3(9)$ Å^3, $F(000) = 463.9$, $Z = 2$, $D_c = 1.47$ g cm^{-3}, $\mu(\text{Mo-}K_\alpha) = 1.13$ cm^{-1}. The data, collected on a Syntex P2$_1$ diffractometer, gave 1315 independent reflections with $I > 3\sigma(I)$. The structure was solved with the program MULTAN 80, which revealed the positions of all but six of the non-hydrogen atoms.[6] Least-squares refinement[7] and difference-Fourier syntheses yielded the rest of the structure. The final refinement cycle employed anisotropic thermal parameters for the non-hydrogen atoms, while the hydrogen atoms were placed as found in the difference map. The hydrogen positions and isotropic thermal parameters were not varied. The final R value was 0.054 (R_w 0.068).†

Figure 1 shows the arrangement of four molecules, two each of the donor and the acceptor, around a centre of symmetry. Molecules of (**2a**) are hydrogen bonded to molecules of (**2b**) to form cyclic unsymmetrical dimers. This is unusual, since hydrogen-bonded dimer rings in carboxylic acid structures normally lie on centres of symmetry. Here, however, the centres relate pairs of dimers that are, in turn, π-bonded. A consequence of this optimal π-overlap is that olefinic double bonds of adjacent donor and acceptor molecules in the stack are within photoreactive distance of each other (3.80 Å). However, the spacing between molecules in the stack is unequal; in addition to this close approach that permits photoreaction, there is a longer spacing of about 4.97 Å between the cinnamic double bonds (Figure 2). This latter arrangement does not permit topochemical photoaddition and corresponds to the situation in a γ-structure. The molecular dimensions of (**2a**) in the complex are very similar to those in the crystal structure of (**2a**) itself. This structure will be reported elsewhere.[8]

Since the topochemically expected photodimer from (**1**) is an unsymmetrically substituted cyclobutane with four chiral centres per molecule, the solid state photochemistry of (**1**) is of obvious interest. However, irradiation of (**1**) (Pyrex filter) with sunlight or an Hg lamp yielded only a small amount of a coloured, intractable substance and no photodimer, the bulk of the material being unchanged. Interestingly, the two acids (**2a**) (short axis, 8.44 Å) and (**2b**) (short axis, 6.75 Å) were found to undergo topochemical 2 + 2 addition when irradiated separately. It is therefore possible that the photostability of complex (**1**) can be accounted for by its crystal structure. Since one of the oxygen atoms on the 4-nitro-group is located only 3.05 Å from one of the hydrogen atoms on the 4-methoxy-group of the adjacent molecule, hydrogen abstraction by the n–π^*-excited nitro-group could be a complication, with the bulk of the light energy being lost through radiationless decay or emission from the lowest lying excited states of the nitro-groups. This view is supported by preliminary photoacoustic spectral data.

Even if complex (**1**) had yielded some of the 2 + 2 photodimer, the product would have been racemic since the space group of the starting material is $P\bar{1}$; for each chiral molecule of unsymmetrical cyclobutane produced there would have been formed another molecule of the enantiomer. Experiments are therefore under way to design donor–acceptor complexes, similar to (**1**), where the yields of photodimer are expected to be high and which can be induced to crystallise in non-centrosymmetric space groups. Such compounds should offer convenient routes, through topochemical solid state syntheses to chiral materials from achiral precursors.

We thank the C.S.I.R., New Delhi for financial assistance, and the School of Chemical Sciences, University of Illinois, Urbana, and Professor I. C. Paul for the use of their diffractometer for data collection.

Received, 30th September 1982; Com. 1153

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.