The Novel 1 : 1 Donor–Acceptor Complex, 3,4-Dimethoxycinnamic Acid–2,4-Dinitrocinnamic Acid. Crystal Engineering, Structure, and Anomalous Lack of Solid-state Topochemical Reactivity

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Donor–acceptor interactions have been exploited to engineer a crystal structure of a 1 : 1 molecular complex (**2a**) of the title acids (**1a**) and (**1d**), where solid-state topochemical 2 + 2 photoaddition to yield pseudo-symmetrical cyclobutanes is permitted. Orange crystals of (**2a**) are triclinic, $P\bar{1}$, a = 8.857(5), b = 13.872(8), c = 8.578(4) Å, α = 101.41(4), β = 100.98(4), γ = 95.98(4)°, Z = 2, R = 0.054 on 1 315 non-zero reflections. The crystal structure consists of interleaving donor and acceptor molecules in the stack with two unequal separations of 3.80 and 4.97 Å with the former overlap relating 'potentially reactive' double bonds. Contrary to expectation, complex (**2a**) is photostable. This inertness is shared by several other aromatic nitro compounds and some mechanistic possibilities are discussed. A classification of solid-state 2 + 2 cycloaddition reactions is attempted on the basis of how far topochemical predictions match with observed photochemical behaviour.

In view of the repeated confirmation of the topochemical principle in a wide variety of 2 + 2 cycloadditions and other organic solid-state reactions, there has recently been a shift in emphasis from the reactions and the crystallographic details to the larger question of what factors and forces direct and determine the crystal structures of organic solids. While there is as yet no simple answer to this question, the usual strategy in the well known method of crystal engineering has been to study a series of closely related compounds so that a unifying structural principle may be made to emerge.[1–4] Since the original coining of the phrase by Schmidt, there have been several elegant demonstrations of it, using such techniques as the device of dichloro substitution, methods employing hydrogen bonding and dipole–ring interactions, and the use of volume and packing arguments, as for example in the 2-benzyl-5-benzylidenecyclopentanone series[5] and for the 1,4-disubstituted phenylenediacrylates.[6] In addition, it has been shown that the scope of chloro-substitution may be significantly extended to the domain of molecular complexes[7] while another recent extension has been the identification of the methylenedioxy fragment as a group that will preferentially steer the crystal structure of a planar aromatic compound to a form which has a crystallographic short axis of *ca.* 4 Å (β-structure).[8]

In this paper, it is shown that donor–acceptor interactions may be used as a steering device to a β-type structure where *two* distinct molecules have been induced to co-crystallise such that solid-state topochemical dimerisation between them is permitted. However, we have observed that such a reaction, though theoretically possible from a consideration of topochemical factors, does not in fact take place. We have given reasons for this anomalous lack of reactivity and have also classified solid-state 2 + 2 cycloadditions on the basis of how predictions based on the topochemical principle match with or deviate from the actual behaviour of the compound on irradiation.

Experimental

All the cinnamic acids were prepared from the corresponding aldehydes by literature procedures and were satisfactorily characterised. I.r. spectra were recorded on a Perkin-Elmer model 580 spectrometer. N.m.r. spectra were recorded on a JEOL FX-100 Fourier transform instrument. Photoacoustic spectra were recorded on an EG and G Princeton Applied Research model 6001 or an EDT model spectrometer. Solid-state u.v. spectra were recorded on a Beckmann 5260 spectrophotometer. *X*-Ray single-crystal data were collected at the School of Chemical Sciences, University of Illinois, Urbana, on a Syntex $P2_1$ diffractometer. The physical characteristics and the cell dimensions of the compounds studied are given in Table 1. Spectral details are given in Table 2.

3,4-*Dimethoxycinnamic Acid*–2,4-*Dinitrocinnamic Acid* 1 : 1 *Complex* (**2a**).—The acids (**1a**) and (**1d**), when dissolved in ethanol in equimolar quantities, yielded exclusively orange crystals, m.p. 202 °C, of complex (**2a**). The molecular stoicheometry was confirmed by n.m.r. and u.v. spectroscopy. The solid-state electronic spectrum is characteristic of a donor–acceptor [$\lambda_{max.}$(CT) = 460 nm] while the crystallographic unit-cell dimensions of (**2a**) are different from those of either (**1a**) or (**1d**), $\nu_{max.}$(KBr) 1 693, 1 631, 1 516, 1 350, and 1 266 cm^{-1}.

3,4-*Dihydroxycinnamic Acid*–2,4-*Dinitrocinnamic Acid* 1 : 1 *Complex* (**2b**).—This complex was crystallised from EtOH from equimolar (**1b**) and (**1d**), orange crystals, m.p. 206 °C. The characterisation was as for complex (**2a**), $\nu_{max.}$(KBr) 3 500(br), 1 697, 1 633, 1 525, and 1 345 cm^{-1}.

3-*Methoxy*-4-*hydroxycinnamic Acid*–2,4-*Dinitrocinnamic Acid* 1 : 1 *Complex* (**2c**).—This complex was prepared exactly as complexes (**2a**) and (**2b**) but from acids (**1c**) and (**1d**) in equimolar quantities. Orange crystals, m.p. 204 °C, were obtained. Characterisation was as above, $\nu_{max.}$(KBr) 3 550 (sharp) 1 698, 1 630, 1 525, and 1 335 cm^{-1}.

Methyl 4-*Hydroxy*-3-*nitrocinnamate* (**1f**).—This ester was prepared using literature procedures.[9] However, the nitration of *p*-hydroxybenzaldehyde with HNO_3 and AcOH yielded a mixture of hydroxy- and acetoxy-nitrobenzaldehyde. Hydrolysis of the product (aqueous KOH) yielded pure 4-hydroxy-3-nitrobenzaldehyde which was converted into (**1f**) either by the Doebner modification of the Perkin condensation and esterification or by a Wittig procedure. Yellow leaflets, m.p. 142—144 °C, were obtained from EtOH, $\nu_{max.}$(KBr) 1 730, 1 650, 1 530, 1 330, and 1 180 cm^{-1}.

X-*Ray Structure Determination of Complex* (**2a**).—Crystal data: $C_{11}H_{12}O_4 \cdot C_9H_6N_2O_6$, M = 446, triclinic, space group

Table 1. Crystallographic data and solid-state reactivity behaviour for some cinnamic acid derivatives

Compound	Unit-cell parameters		Space group	Z	Solid-state photoreactivity u.v. 300 nm	Topochemically allowed	Ref.
	a b (Å) c	α β (°) γ					
(**1a**)	8.448 15.072 8.437	99.44 94.71 101.59	$P\bar{1}$	4	Yes	Yes	8
(**1b**)	6.711 11.833 5.837	104.99 90.04 103.79	$P\bar{1}$	2	No	[a]	8
(**1c**)	4.68 17.01 12.14	90 90.0 90	$P2_1/c$	4	No	No	[b]
(**1d**)	9.11 6.75 15.53	90 92.3 90	$P2_1/c$	4	No	[c]	[b]
(**1e**)	17.91 22.44 3.79	92.2 95.3 94.6	$P\bar{1}$	4	No	Yes	8
(**1g**)[d]	7.2 3.9 31.4	90 90.0 90	$P2_1/c$	4	Yes	Yes	15
(**1f**)	3.873 21.342 12.15	90 90.9 90	$P2_1/c$	4	No	Yes	24,[b]
(**2a**) (**1a**) · (**1d**)	8.857 13.872 8.578	101.11 100.98 95.8	$P\bar{1}$	2 + 2	No	Yes	4,[b]
(**2b**) (**1b**) · (**1d**)	Crystals of complexes (**2b**) and (**2c**) were of too poor a quality for Weissenberg photography				No	[c]	[b]
(**2c**) (**1c**) · (**1d**)					No	[c]	[b]

[a] Crystal structure determination in progress. [b] This work. [c] Crystal structure unknown. [d] This compound exhibits dimorphism. The cell dimensions of the photoactive modification are given here.

Table 2. Solid-state u.v. and PAS π–π^*, $n\pi^*$ and CT bands for some compounds in this study.

Compound	$\pi\pi^*$	$n\pi^*$	Charge transfer
(**1d**)	325[a]	360	
	320[b]	370	
(**1g**)	280	375[c]	
	275	380[c]	
(**1f**)	280	370	420
	275	380	430
(**2a**)	320	380	460
	325	390	470
(**2b**)	295	390	460
	300	400	475
(**2c**)	280	380	470
	270	390	480

[a] The upper values in all cases refer to the optical solid-state spectra in nm. [b] The lower values refer to the photoacoustic spectra in nm. [c] This peak is of very weak intensity and is obtained as a shoulder of the $\pi\pi^*$ peak.

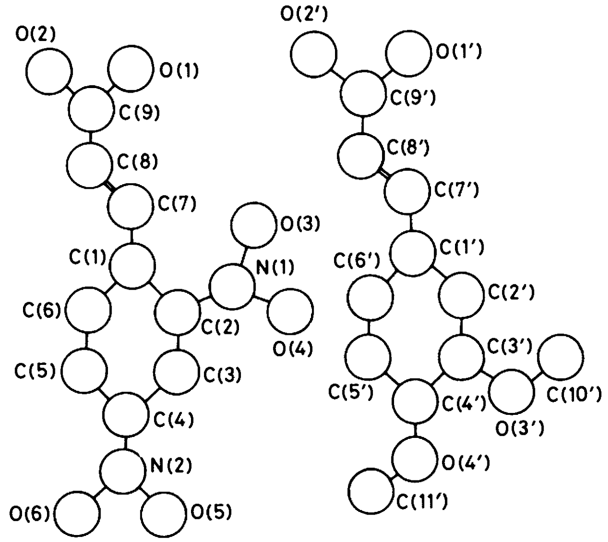

Figure 1. Atom-numbering scheme for complex (**2a**)

$P\bar{1}$, $a = 8.857(5)$, $b = 13.872(8)$, $c = 8.578(4)$ Å, $\alpha = 101.11(4)$, $\beta = 100.98(4)$, $\gamma = 95.98(4)^\circ$, $V = 1\,004.3(9)$ Å^3, $F(000) = 463.9$, μ(Mo-K_α) = 1.13 cm^{-1}, $Z = 2$, $D_c = 1.47$ g cm^{-3}, $D_m = 1.46$ g cm^{-3} (Mo-K_α, $\lambda = 0.710\,69$ Å). Unit-cell parameters were determined by a least-squares fit to the settings for 15 accurately centred high-order reflections. A total of 1 315 reflections were considered non-zero at the 3.0 σ significance level out of 2 628 possible reflections in the 2θ range 3—45°. No absorption corrections were applied and there was no evidence for crystal decomposition. The weights were taken as $5.516\,\{[\sigma(F_o)]^2 + (0.026\,F_o)^2\}$ where $\sigma(F_o)$ is the standard deviation based on the

Table 3. Atomic co-ordinates in fractional crystal co-ordinates for complex (**2a**),*·† $a = 8.857(5)$, $b = 13.872(8)$, $c = 8.578(4)$ Å, $\alpha = 101.11(4)$, $\beta = 100.98(4)$, $\gamma = 95.98(4)$.

Atom	*x*	*y*	*z*
2,4-Dinitrocinnamic acid			
C(1)	0.896 0(6)	0.266 4(4)	0.685 9(7)
C(2)	0.858 7(6)	0.177 3(4)	0.733 6(7)
C(3)	0.966 5(7)	0.134 4(4)	0.827 7(7)
C(4)	1.115 0(6)	0.184 2(5)	0.876 3(7)
C(5)	1.159 9(7)	0.271 9(5)	0.835 1(7)
C(6)	1.052 1(7)	0.312 1(4)	0.739 9(8)
C(7)	0.784 4(6)	0.340 4(4)	0.582 9(7)
C(8)	0.810 5(7)	0.396 8(5)	0.540 7(7)
C(9)	0.691 4(8)	0.434 1(5)	0.434 4(7)
O(1)	0.555 9(5)	0.385 9(3)	0.386 4(5)
O(2)	0.732 1(4)	0.514 8(3)	0.394 6(5)
O(3)	0.591 1(5)	0.172 2(4)	0.687 6(6)
O(4)	0.683 2(6)	0.034 6(4)	0.666 6(8)
O(5)	1.185 1(5)	0.068 5(4)	1.029 8(6)
O(6)	1.362 0(6)	0.184 4(4)	1.020 8(7)
N(1)	0.699 3(6)	0.124 7(5)	0.690 6(6)
N(2)	1.228 2(7)	0.142 1(4)	0.983 0(6)
H(3)	0.934	0.061	0.857
H(5)	1.285	0.299	0.870
H(6)	1.085	0.380	0.706
H(7)	0.666	0.261	0.539
H(8)	0.925	0.443	0.575
H(O)	0.640	0.530	0.304
3,4-Dimethoxycinnamic acid			
C(1′)	0.189 9(6)	0.697 6(4)	−0.115 3(7)
C(2′)	0.246 8(6)	0.784 4(4)	−0.157 8(7)
C(3′)	0.150 1(7)	0.832 0(4)	−0.252 5(7)
C(4′)	−0.010 6(7)	0.793 4(4)	−0.306 3(7)
C(5′)	−0.068 1(6)	0.707 7(4)	−0.266 4(7)
C(6′)	0.032 1(7)	0.659 1(4)	−0.171 1(7)
C(7′)	0.298 7(6)	0.651 5(4)	−0.012 8(6)
C(8′)	0.269 3(6)	0.567 3(4)	0.037 6(7)
C(9′)	0.388 6(7)	0.531 5(4)	0.144 5(7)
C(10′)	0.358 0(7)	0.953 5(5)	−0.258 7(8)
C(11′)	−0.260 7(7)	0.810 0(5)	−0.452 3(9)
O(1′)	0.524 0(5)	0.578 4(3)	0.191 1(5)
O(2′)	0.347 7(5)	0.451 8(3)	0.189 1(5)
O(3′)	0.195 0(5)	0.914 3(3)	−0.305 0(5)
O(4′)	−0.097 4(5)	0.845 1(3)	−0.400 3(5)
H(2′)	0.393	0.801	−0.133
H(5′)	−0.196	0.664	−0.327
H(6′)	−0.016	0.585	−0.168
H(7′)	0.420	0.685	0.003
H(8′)	0.158	0.522	−0.006
H(31′)	0.370	1.014	−0.314
H(32′)	0.390	0.979	−0.115
H(33′)	0.428	0.897	−0.328
H(41′)	−0.306	0.863	−0.497
H(42′)	−0.289	0.727	−0.538
H(43′)	−0.340	0.799	−0.377
H(O′)	0.439	0.403	0.227

* Estimated standard deviations are given in parentheses. † For atom numbering, see Figure 1.

counting statistics. The scattering factors were taken from the expression in ref. 10.

The structure was solved with the program MULTAN 80, which revealed the positions of all but six of the non-hydrogen atoms.[11] Least-squares refinement and difference Fourier synthesis yielded the rest of the structure.[12] Refinement began at an R value of 0.34 and when positional and anisotropic thermal parameters for all the non-hydrogen atoms were varied, R 0.077 was obtained. An electron density difference map at this stage revealed the positions of all hydrogen atoms except the two carboxy hydrogen atoms. A few intense low-angle reflections had F_o significantly less than F_c. Thus, the empirical extinction parameter in the program SHELX 76 was varied.[12,*] This somewhat improved the agreement between F_o and F_c for those reflections. When the reflections (022) and (372) were omitted in the refinement, the value of R fell to 0.054 and of R_w to 0.056 for 290 refined parameters. The final atomic co-ordinates for complex (**2a**) are listed in Table 3. The atom-numbering scheme is given in Figure 1. The values of the thermal parameters, the structure factors, and the intramolecular bond lengths are in a supplementary publication (SUP. No. 56328; 12 pp.).†

Results and Discussion

Crystal Engineering.—The engineering of a crystal structure of a molecular complex is inherently attractive for two reasons. First, dissimilar organic molecules prefer to crystallise separately when together in solution unless very specific electronic or geometrical factors are optimised.[13] Hence the very manifestation of co-crystallisation in a particular system implies that it is possible to dissect and analyse a few significant molecular interactions from amongst the larger number that actually determine the stable crystal structure. This is true for all kinds of molecular complexes, disordered or ordered and with fixed or variable stoicheiometry. In other words, it is usually easier to understand why two molecules may co-crystallise rather than why a single molecule adopts a particular crystal structure in preference to another.

Secondly, in those cases where the crystal structure may be linked to solid-state reactivity, a molecular complex may be used to study a solid-state reaction of the type A + B⟶products. This offers much more scope than reactions such as A⟶products or A + A⟶products or A + A + ····⟶polymer which are the only types possible for crystals of a pure compound.[14] One ventures to add that the reason that a great deal of effort in organic solid-state chemistry has been directed towards the study of a single reaction, the 2 + 2 cycloaddition of olefins, is because it is of the A + A⟶product type. The more numerous and diverse A + B⟶product reactions have been largely unexplored perhaps because co-crystallisation is still an imperfectly understood phenomenon. Photodimerisation reactions of the type A + B⟶dimer have, however, been used successfully in a solid-state asymmetric synthesis[6] while it will be seen that the complex described in this paper is another case where a dissymetric environment for a solid-state reaction is only possible because two *different* molecules are within reacting distance.

Our strategy for crystal engineering uses donor–acceptor (DA) interactions and is based on the fact that the crystal structures of a large majority of stoicheiometric complexes involving π-donors (D) and π-acceptors (A) consist of mixed stacks of D and A molecules where the planes of the molecules are at the van der Waals separation of 3.4 Å (Figure 2). This means that if a potentially reactive grouping such as a double bond is attached to each of D and A, the preferential stabilisation of the D····A interactions could have the secondary result of bringing the double bonds on adjacent D and A molecules to within 4 Å of one another and thus within photoreactive distance for cyclobutane formation on u.v. irradiation, while the different D and A substituents would necessarily result in a product having four asymmetric carbon atoms (Figure 3).

Examination of Figure 3 will show that substituted cinnamic

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* $R = ||F_o| - |F_c||/|F_o|$; $R_w = [w||F_o| - |F_c||^2/w|F_o|^2]^{\frac{1}{2}}$

† For details of the Supplementary Publications Scheme, see Instructions for Authors, *J. Chem. Soc., Perkin Trans. 2*, 1985, Issue 1.

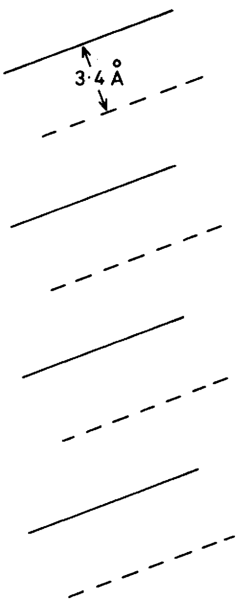


Figure 2. Schematic view of a ππ donor–acceptor complex

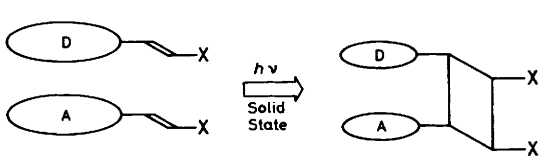
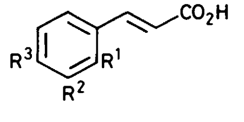
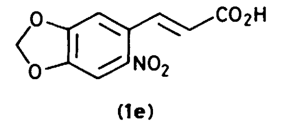


Figure 3. Conceptual view of a donor–acceptor complex where 2 + 2 topochemical addition is possible





(1e)

(1a) R^1 = H, R^2 = R^3 = OMe
(1b) R^1 = H, R^2 = R^3 = OH
(1c) R^1 = H, R^2 = OMe, R^3 = OH
(1d) R^1 = R^3 = NO_2, R^2 = H
(1g) R^1 = R^2 = H, R^3 = NO_2

acids may be conveniently employed to test the hypothesis in the preceding paragraph. Not only is it possible to obtain a large number of such acids, substituted with D and A groups, but there is a considerable wealth of information on the crystal chemistry of the simpler derivatives and a classification into α, β, and γ structural types by Schmidt.[15] This classification is based on unit-cell lengths and solid-state photoreactivity. Adapting Schmidt's terminology, the structure in Figure 3 would correspond to a pseudo-β variant since the expected product cyclobutane would have pseudo rather than true mirror symmetry.

Co-crystallisation was therefore attempted on a large number of D and A cinnamic acid pairs. The crucial factors which determine whether a DA complex is formed seem to be the high electron-withdrawing ability of the A substituents and the comparative solubilities of the two acids in the solvent system of choice. Monosubstituted A-acids (p-NO_2, p-Cl) would not co-crystallise with D-acids (**1a**)—(**1c**). An early report by Pfeiffer[16] on 2,4-dinitrocinnamic acid (**1d**), however, comments on its 1:1 complex with benzene and suggested that perhaps D···· A interactions could be optimised in this case. Indeed it was found that crystals of the 1:1 DA complexes, (**2a**)—(**2c**) could be isolated with varying degrees of ease from mixed solutions of (**1d**) and any of (**1a**)—(**1c**), respectively. The complexes were easily distinguished from the constituent acids on account of their deep orange-red colour. Table 1 gives the relevant data for these complexes and for other related compounds studied.

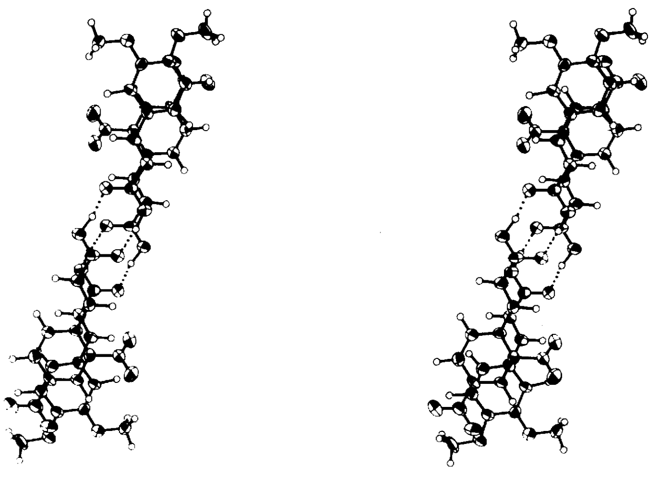


Figure 4. Stereodrawing of complex (**2a**) to show π-bonded and hydrogen-bonded molecules

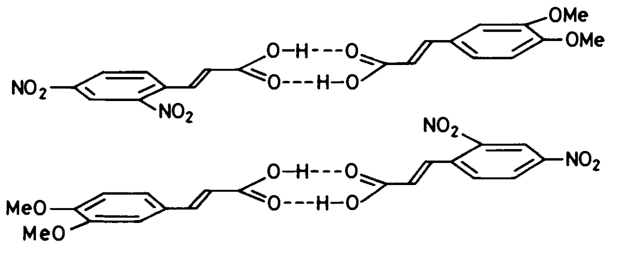


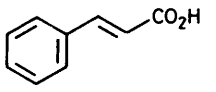
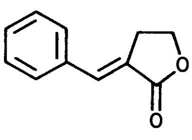
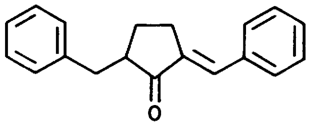
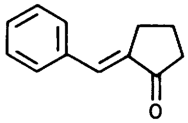
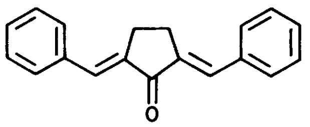
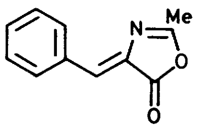
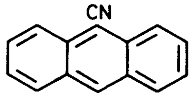
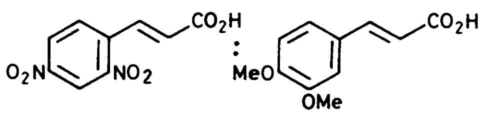
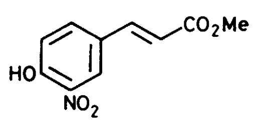
Figure 5. Schematic view of the (**2a**) crystal structure to show π-bonding and hydrogen-bonding

The crystal cell dimensions of the complex (**2a**), 3,4-dimethoxycinnamic acid–2,4-dinitrocinnamic acid are different from those of the constituent acids (**1a**) and (**1d**). The structure determination, which we have already reported in brief,[4] was carried out using diffractometer data and MULTAN 80 with the positional and thermal parameters refined to a final R-value of 0.054. Table 3 lists the positional parameters.

Figure 4 shows the arrangement of four molecules, two each of D and A around a centre of symmetry and looking down the stack direction. Molecules of (**1a**) are hydrogen-bonded to molecules of (**1d**) to form cyclic unsymmetrical dimers. A schematic view of these four molecules looking at the stack is given in Figure 5. Such an arrangement is unusual since hydrogen-bonded dimer rings in carboxylic acid structures usually lie on centres of symmetry. Here, however, these centres relate *pairs* of dimers that are, in turn, π-bonded. Such a juxtaposition of hydrogen-bonding and π-bonding in a DA complex may also be seen in the crystal structures of quinone–hydroquinone and quinone–phenol complexes.[17]

The marked resemblance between Figure 5 and the left side of Figure 3 may be noted. As predicted in Figure 3, a consequence of optimal π–π overlap between adjacent (**1a**) and (**1d**) molecular planes is that olefinic double bonds on these molecules are within photoreactive distance of each other (3.80 Å). We note, however, that the spacing between molecules in the stack is unequal. In addition to this close approach between

Table 4. Classification of solid-state 2 + 2 cycloaddition and related reactions

Category	Double bonds parallel	Distance between double bond centres	Overlap *i.e.*, topo-chemically allowed	Reaction	Topo-chemical product	Examples	Energy transfer	Ref.
A	Yes	< 4.2	Yes	Yes	Yes	  	Slow	8, 15, 14, 19, 25
						$R{-}C{\equiv}C{-}C{\equiv}C{-}R$		[a]
B	Yes	*ca.* 4.2	No	No				14, 19
C	No	< 4.2	Yes	Yes	Yes	 	Slow	27, 28
D	Yes	> 4.2	No	Yes	No		Fast inter molecular	26, [b]
E	Yes	< 4.2	Yes	No		 	Fast intra molecular	This work

[a] Category A also includes reactions like diacetylene polymerisation, where topochemical reaction is permitted and occurs after co-operative molecular shearing has taken place. [b] Reaction in 9-cyanoanthracene may occur topochemically *via* another polymorph.

D(1 − *x*, 1 − *y*, 1 − *z*) and A(*x*, *y*, *z*) which permits photoreaction, there is a longer spacing of *ca.* 4.97 Å between double bonds of D(1 − *x*, 1 − *y*, −*z*) and A(*x*, *y*, *z*). This latter arrangement (Figure 6) does not permit topochemical photoaddition and corresponds to the situation in a γ-structure. Figure 7 is a projection of the molecular planes perpendicular to the stack direction and shows the molecular overlap for these two distinct situations. From the Figure, we note that the overlap for molecules at 3.80 Å separation is quite favourable in contrast to molecules at 4.97 Å separation for which there is poor π–π overlap. We have noted previously[8] that complex (**2a**) has structural features of both β and γ forms of cinnamic acid and also shows some similarities in unit-cell parameters, hydrogen-bonding, and symmetry characteristics to the crystal structure of acid (**1a**).

Solid-state Reactivity.—While the crystal structure of complex (**2a**) would seem to permit a topochemical cycloaddition, no reaction takes place when the solid is irradiated for times up to 150 h and at wavelengths above and below 300 nm (Hg lamp; Pyrex and quartz). In fact, the material is totally unaffected, there being no detectable amount of any product. It

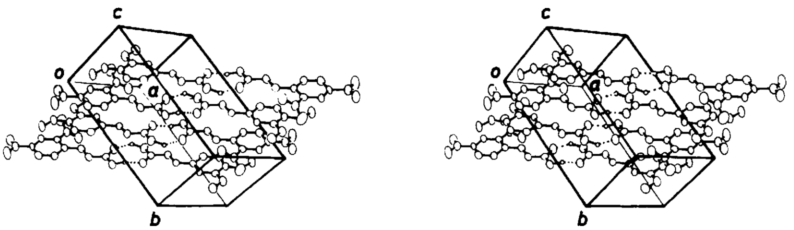


Figure 6. Stereodrawing of the (**2a**) crystal structure showing structural features of both β- and γ-polymorphs of *trans*-cinnamic acid

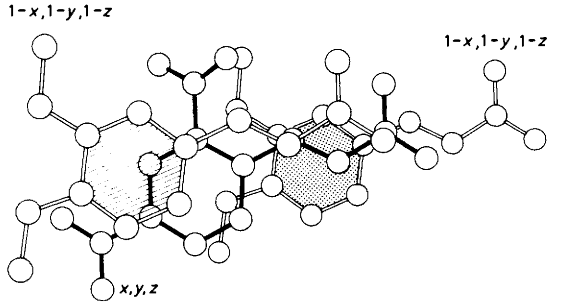


Figure 7. Projection drawing of the (**2a**) crystal structure down the stack direction

was observed that this anomalous lack of reactivity was not a peculiarity of complex (**2a**) but was part of a more general phenomenon in aromatic nitro compounds. For instance, complexes (**2b**) and (**2c**) behave exactly like (**2a**); there was no visible sign of reaction and no detectable product. Further, acid (**1e**) crystallising in the β modification should give the corresponding β-truxinic derivative on solid-state irradiation while acid (**1d**) which is presumably in the photoactive α-modification (short axis 6.75 Å) should be similarly converted to its α-truxillic dimer.[4,8] Yet these acids are merely darkened on irradiation, while the i.r. spectra and *X*-ray powder traces of the discoloured solids are identical to those of the starting material. On the other hand, it has been reported that the three nitrocinnamic acids[15] and *trans*-β-nitrostyrene[18] undergo solid-state photodimerisation.

An analysis of the crystal structure of (**2a**) indicates favourable overlap between 'potentially reactive' double bonds. In this sense, the non-reactivity of the complex cannot be ascribed to limited orbital overlap as in the case of the recently studied 2-benzylidenecyclopentanone which is photostable even though the distance between parallel double bonds is 4.14 Å.[14,19] Although crystals of complexes (**2b**) and (**2c**) were of too poor a quality for *X*-ray work, the similar stoicheiometries and physical and spectroscopic properties of (**2a**)—(**2c**) might indicate that the crystal structures of (**2b**) and (**2c**) are related to that of (**2a**). We therefore conclude that in these three cases, as well as for acids (**1d**) and (**1e**), the yield of topochemically expected product is vanishingly small, even though the crystal structure seemingly permits the formation of such a product.

The fact that several nitroaromatic compounds share this lack of reactivity towards a $\pi\pi^*$-mediated reaction indicates the possibility of a low lying easily accessible $n\pi^*$ level. Assuming, for the time being, that intramolecular energy-transfer between $\pi\pi^*$ and $n\pi^*$ levels is easy in complex (**2a**), the following possibilities, all mentioned in the literature, were considered:

1. Intramolecular hydrogen abstraction by the $n\pi^*$ excited *ortho*-nitro group to yield cyclic isatogens as in the case of 2,4-dinitro-*trans*-stilbene;[20]
2. Intermolecular abstraction of a methoxy hydrogen atom by the $n\pi^*$ excited *p*-nitro group (O • • • • H is 3.05 Å);[18]
3. Nitro–nitrite isomerisation in the manner of 9-nitroanthracene;[21]
4. Emission and/or non-radiative decay to the ground state.

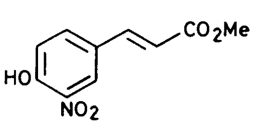
Nitro-group photochemistry has a long and well documented history.[18] Sachs' Rule (1904) mentions photochromism in aromatic compounds having a nitro group and a benzylic hydrogen in an *ortho*-orientation. The basis of this rule is now understood to be hydrogen abstraction by the $n\pi^*$ excited nitro group and such explanations have been used in many modern mechanistic approaches to nitro photochemistry.[1,18] We should also note here that *cis*-β-nitrostyrene is photochromic and cannot be photodimerised in the solid state like the *trans*-isomer,[18] that crystalline *p*-nitrophenol exists in two modifications and the stable form is photosensitive,[22] and that in both these examples hydrogen abstraction may be involved. Hence, the two first possibilities were considered. There is also ample precedence for the third possibility, *viz.* nitro–nitrite photochemical isomerisation in nitroaromatics where the nitro group is not coplanar with the aromatic ring.[21] In case there is no further chemical event following $n\pi^*$ excitation, reversion to the ground state must occur and hence the final possibility.

Since no products were detected for (**2a**)—(**2c**), (**1d**), and (**1e**), the first and third possibilities seem unlikely. The second option should also lead to products, but since these *aci*-nitro compounds are very unstable they are expected to revert rapidly to starting material and hence will not be detectable. Even so, this is a possibility, although rather specific to (**2a**) since it is difficult in complexes (**2b**) and (**2c**), both of which lack a *p*-methoxy group. Our attention was therefore shifted to the final possibility and to the primary question as to why energy transfer from the $\pi\pi^*$ to $n\pi^*$ level is so facile in these compounds.

An obvious structural difference between the reactive nitrocinnamic acids and the photostable nitroaromatics described above is that all the inert compounds have at least one nitro group that is *ortho* to a –CH= group and which therefore cannot be coplanar with the aromatic ring. Further, of the three nitrocinnamic acids, the *para*- and *meta*-isomer are converted into dimer in higher yield than the *ortho*-compound.[15] Although none of the three crystal structures have been determined, it is reasonable to assume a higher degree of nitro-group planarity with the aromatic ring for the *meta*- and *para*-acids compared with the *ortho*-isomer where coplanarity is impossible. In addition one may note that there is no intramolecular steric hindrance to the nitro group being coplanar with the conjugated system in photoreactive crystalline β-*trans*-nitrostyrene (crystal structure also unknown). It was felt therefore that if the nitro group was parallel to the aromatic ring, the $n\pi^*$ transition is somehow not so readily accessible and that, as a consequence, dimerisation becomes possible through $\pi\pi^*$ excitation. In line with this argument, it may be noted that it is not possible to assign the $n\pi^*$ band in the solid-state optical and photoacoustic (PA) spectra of the reactive *p*-nitrocinnamic acid. This band is readily discernible for the non-reactive compounds (Table 2).

It has been reported that for nitroaromatics, the nitro group is constrained to be in the plane of the aromatic ring if it is held in place by a device such as hydrogen-bonding to an adjacent hydroxy group.[23] It was sought to test the generality of this structural principle with the eventual aim of linking molecular planarity with solid-state reactivity. The Cambridge Crystallographic Database was searched to yield 51 compounds containing the $>C(OH)-C(NO_2)<$ fragment. In the 14 compounds where this group was part of an aliphatic residue there was no tendency for the nitro and hydroxy groups to be hydrogen-bonded. However, among the 37 aromatic compounds there was a clear trend for the nitro group *ortho* to a hydroxy group to be strongly intramolecularly hydrogen-bonded to the latter, with the mean O····O distance being 2.58 Å and, as a consequence, for it to be coplanar with the aromatic ring. Some typical compounds in this latter group are 2-nitrophenol, 4-chloro-2-nitrophenol, and 2,4-dinitrophenol. For compounds like picric acid where two nitro groups flank the hydroxy group, only one of them, as expected, was observed to be coplanar and hydrogen-bonded.

One of the 37 aromatic compounds identified in the Database Search Routine is methyl 3-nitro-4-hydroxycinnamate (**1f**) and it is of some relevance to the problem here. In the crystal, the (**1f**) molecules are quite planar and the O····O (nitro to hydroxy) distance is 2.596 Å. Further, the short crystallographic axis is 3.873 Å[24] which means that the compound is expected to form a mirror-symmetry cyclobutane upon topochemical dimerisation. Ester (**1f**) was therefore judged to be an ideal model and its behaviour upon solid-state irradiation was examined. Yet, it too was completely unaffected, indicating that coplanarity, or the lack of it, of the nitro group is not the crucial factor in determining the ease of energy transfer from the $\pi\pi^*$ to the $n\pi^*$ level.

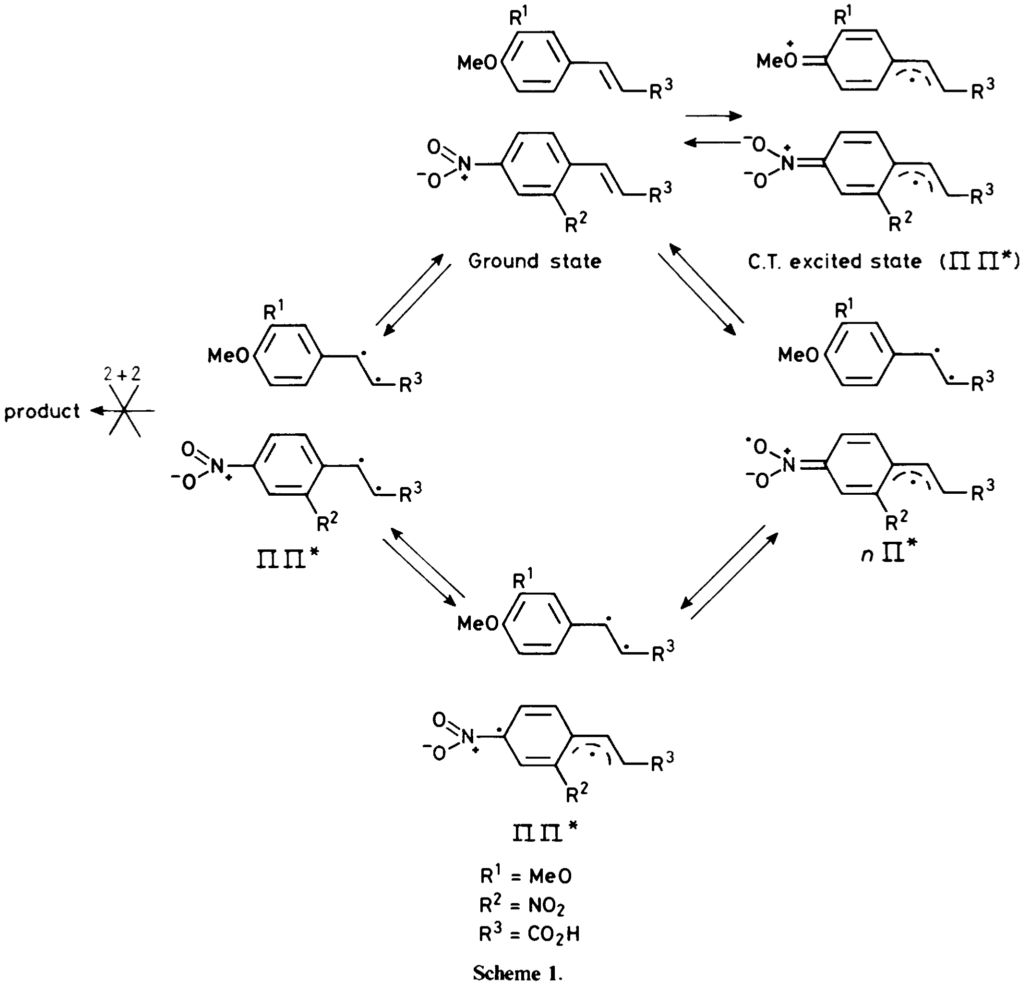


(**1f**)

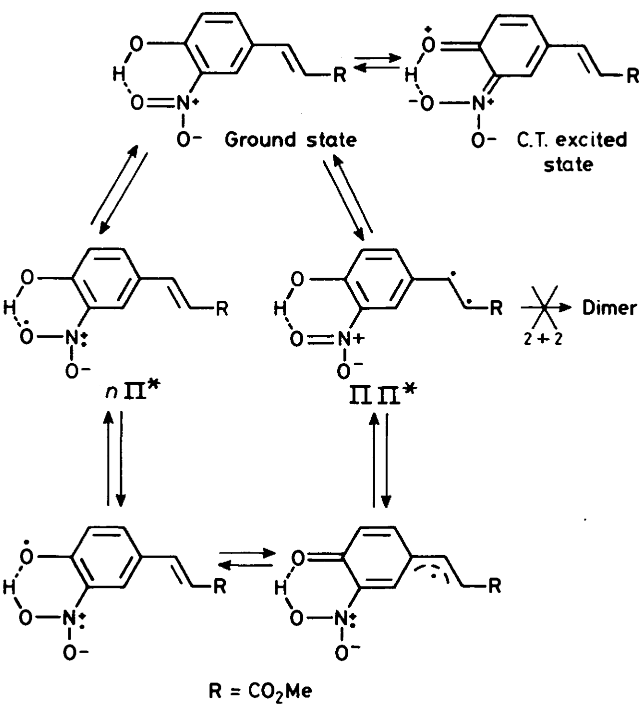
Photoacoustic and optical spectra were recorded for the inert solid compounds (**2a**)—(**2c**), (**1d**), and (**1f**) and for the reactive (**1g**). The former compounds showed the $\pi\pi^*$, $n\pi^*$, and charge transfer (CT) bands clearly while (**1g**) showed only the $\pi\pi^*$ band (Table 2). The CT band was especially prominent for ester (**1f**) and the complexes (**2a**)—(**2c**). It was not observed for acid (**1d**) (as expected).

Scheme 1 sets out a mechanistic possibility for the lack of reactivity in complex (**2a**) [and (**2b**), (**2c**)]; $\pi\pi^*$ excitation of the olefinic double bond may lead to a population of the $n\pi^*$ levels of the nitro group, since this group is conjugated with the double bond. Either the *o*- or *p*-nitro group could be involved. The $n\pi^*$ excited nitro group may revert to ground state (**2a**) with emission and/or non-radiative decay (PAS) with reversible abstraction of an adjacent methoxy hydrogen being a possible intermediate process.

In the case of ester (**1f**), lack of reactivity may be due to the



Scheme 1.



Scheme 2.

fact that the $\pi\pi^*$ and $n\pi^*$ levels are mutually accessible from a cyclic intramolecularly hydrogen-bonded species (Scheme 2). Any $\pi\pi^*$ excitation will lead to $n\pi^*$ emission or non-radiative decay to starting material (PAS), thus bypassing the 2 + 2 reaction. The hydroxy group, far from assisting topochemical reaction by adjusting the nitro-group geometry, may be actively involved in quenching the $\pi\pi^*$ state and therefore responsible for the lack of reactivity.

It has been noted previously that the presence of $n\pi^*$ and CT states of appropriate energy levels may serve as effective routes for non-radiative decay from the $\pi\pi^*$ states[2,25] and Schemes 1 and 2 are consistent with these possibilities.

From these results we conclude that even though a crystal structure may ideally permit a 2 + 2 reaction, it need not take place for nitroaromatic compounds if the $n\pi^*$ and $\pi\pi^*$ levels are close in energy and if the $n\pi^*$ state is particularly accessible through $\pi\pi^*$ excitation. Breakdown of topochemical principles in 9-cyanoanthracene has been correlated with efficient energy transfer in the crystal to defect sites.[26] In an analogous fashion, we suggest that the absence of experimentally detectable amounts of topochemical products, indeed of any products at all in the nitro compounds studied here, is also because of energy transfer; but this transfer is intramolecular and from a $\pi\pi^*$ to an $n\pi^*$ level.

Classification of Solid-state 2 + 2 *Reactions of Olefins*.—There has been much recent discussion as to what constitutes a deviation from topochemical rules, whether non-parallel double bonds can react,[27] and if orbital overlap rather than geometrical considerations should be the criterion for solid-state reactivity.[19] Table 4 attempts to summarise the present facts and to classify 2 + 2 solid-state processes. In A and B, topochemical and orbital overlap predictions are borne out, while in C the topochemical argument has been extended to non-parallel double bonds. In D, however, the reaction is non-topochemical because of defect-controlled energy transfer. A type-E process, hitherto unknown, has been described in this paper. Here again there are anomalies in the solid-state reaction, but because of an intramolecular process. These five situations describe all possible combinations of topochemical allowance or prohibition and the presence or lack of solid-state reactivity.

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