Crystal Engineering *via* Cl···Cl Non-bonded Interactions. The Novel 2 : 1 Complex, 6-Chloro-3,4-(methylenedioxy)cinnamic Acid–2,4-Dichlorocinnamic Acid. Topochemical Conversion into an Unsymmetrical Cyclobutane and Kinetics of the Reaction

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Two chloro-substituted cinnamic acids have been induced to co-crystallise as a molecular complex which is converted, at different rates, into one unsymmetrical and two symmetrical cyclobutanes during solid-state topochemical 2 + 2 photoaddition.

Crystal engineering of organic structures to forms that will permit topochemical conversion can often result in new solid-state reactivity patterns and much attention has therefore been paid to the manipulation of subtle intermolecular forces that can effectively steer an organic crystal structure into a particular form.[1—3] In this respect, the device of chlorosubstitution has been one of the more reliable ways of steering the packing of at least sixty or so planar organic molecules to the highly overlapped 4 Å-repeat β-structure.[2] This concept has been recently extended to some alkoxy-aromatic compounds.[4]

In this communication we report the novel 2 : 1 molecular complex (**1**) made up of 6-chloro-3,4-(methylenedioxy)-cinnamic acid (**2a**) and 2,4-dichlorocinnamic acid (**2b**), where Cl···Cl interactions between *different* molecules have been optimised in the same crystal so as to cause a β-structure to be adopted. Acids (**2a**) (m.p. 246 °C, space group $P\bar{1}$, $Z = 2$, $a = 9.05$, $b = 12.94$, $c = 4.10$ Å, $\alpha = 93.3$, $\beta = 95.5$, $\gamma = 74.4°$) and (**2b**) (m.p. 229 °C, $P2_1/c$, $Z = 4$, $a = 3.88$, $b = 6.44$, $c = 36.8$ Å, $\beta = 90.5°$) both crystallise in the β-structure and yield the topochemically expected β-truxinic acids (**3a**) and (**3b**) respectively on irradiation at *ca.* 350 nm.[4,5] However, the relative rates of dimerisation as well as the final yields of (**3a**) from (**2a**) and (**3b**) from (**2b**) are different. Under similar conditions, (**2a**) reacts significantly slower than (**2b**) while the maximum yields are respectively 70 and 90%.

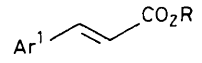
When (**2a**) and (**2b**) are dissolved in EtOH in approximately equimolar quantities and the solvents carefully evaporated, white crystals of complex (**1**) (m.p. 225—226 °C) are the first to crystallise. Complex (**1**) is distinct from either (**2a**) or (**2b**) or from a physical 2 : 1 mixture of (**2a**) and (**2b**) (m.p. 207—210 °C) while admixture of (**1**) with either (**2a**) or (**2b**) results in a considerable m.p. depression. Crystals of (**1**) were irradiated with the Hg lamp (Pyrex filter), until no further change was seen in the i.r. spectrum. Esterification

Table 1. Relative molar amounts[a] of cinnamic acid monomers and cyclobutane dimers at various stages in the solid-state photoirradiation of complex (**1**).

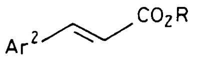
Time/h	% Overall conversion	(**2a**) : (**2b**)[b]	(**5a**)	(**5b**)	(**4a**)	(**4b**)	(**4c**)
0	0	2	2	1	0	0	0
2	47	2.10	1.037	0.555	0.385	0.115	0.193
3	66	1.997	0.627	0.404	0.530	0.142	0.314
4	72	2.03	0.551	0.287	0.540	0.164	0.371
32 (∞)	94	2.09	0.150	0.044	0.626	0.164	0.598
—	100[c]	2	0	0	0.667[d]	0.166[d]	0.667[d]

[a] As estimated by u.v. spectra of fractions obtained from preparative t.l.c. of methylated, partially reacted solids. [b] The ratio is defined as [(**5a**)+2(**4a**)+(**4c**)]/[(**5b**)+2(**4b**)+(**4c**)] and provides a cross-check on the separation and estimation procedures, since it should ideally be equal to 2.00. [c] A 100% conversion is impossible for this reaction. [d] These values are calculated assuming an ideally disordered structure for complex (**1**).

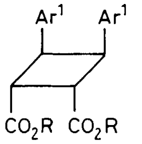
(1) = $(2a)_2 \cdot (2b)$



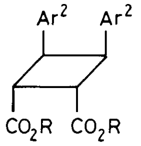
(2a) R = H
(5a) R = Me



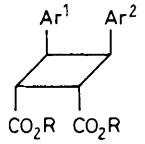
(2b) R = H
(5b) R = Me



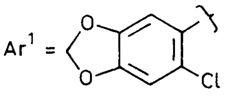
(3a) R = H
(4a) R = Me

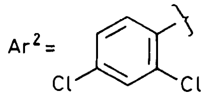


(3b) R = H
(4b) R = Me



(3c) R = H
(4c) R = Me





with CH_2N_2 followed by preparative t.l.c. (silica gel, $CHCl_3$) showed the presence of the three cyclobutane diesters (**4a**) (m.p. 181 °C), (**4b**) (m.p. 108 °C), and (**4c**) (m.p. 76 °C) and small amounts of the monoesters (**5a**) and (**5b**). Most interestingly, the rates of formation of the cyclobutanes (**3a**), (**3b**), and (**3c**) from solid (**1**) (as monitored by u.v. analyses of partially reacted samples) are quite different. The relative rates of appearance of (**3a**) and (**3b**) closely parallel the behaviour of pure (**2a**) and (**2b**) on solid-state irradiation while dimer (**3c**) is formed more slowly than (**3a**) and (**3b**) (Table 1). Crystals of (**1**) were extremely small, but Weissenberg photographs showed that they were distinct from those of either (**2a**) or (**2b**) and further revealed a triclinic space group with two molecules in the unit cell, a short axis of *ca.* 3.88 Å, and other cell dimensions which bear a resemblance to those of (**2a**). Although the crystal quality did not permit the collection of counter data, the chemical, kinetic, and crystallographic evidence is sufficient to propose a structure for complex (**1**).

The formation of all three *m* or pseudo-*m*-symmetry cyclobutanes (**3a**), (**3b**), and (**3c**) shows that, in the solid complex, (**2a**) and (**2b**) molecules are related by a 4 Å translation with all three types of contacts (**2a**)···(**2a**), (**2b**)···(**2b**), and (**2a**)···(**2b**) being possible (Figures 1 and 2). Clearly, a short axis of 3.88 Å shows that there is a random occupation of crystallographic sites by (**2a**) and (**2b**) molecules. In accordance with this, the relative amounts of the three cyclobutanes formed at maximum conversion are very close to the theoretically expected 4 : 1 : 4 ratio for a statistical 2 : 1 distribution of acids (**2a**) and (**2b**) in the solid complex (Table 1). The cell dimensions show that the minor component (**2b**) has been induced to co-crystallise in the crystal structure of the major component (**2a**). Equal amounts of (**3a**) and (**3c**) can be rationalised by a variety of models but the formation of (**3b**) and the 4 Å axis are difficult to explain unless (**2a**) and (**2b**) are disordered. Now, the volumes of the individual molecules in the crystal are quite similar and one can understand why these chemically and structurally similar molecules co-crystallise with a disordered site occupancy. However, the 2 : 1 stoicheiometry [where (**2a**) has one Cl atom while (**2b**) has two] perhaps indicates that intermolecular interactions also have directional character. There is evidence that in the β-structures, maximum Cl···Cl non-bonded forces between laterally adjacent molecules favour the formation of sheets which can stack along a 4 Å axis so as to optimise C···C inter-sheet interactions.[6] We suggest that intra-sheet Cl···Cl interactions between (**2a**) and (**2b**) molecules are the driving force in the adoption of the disordered, fixed-stoicheiometry β-structure by complex (**1**).

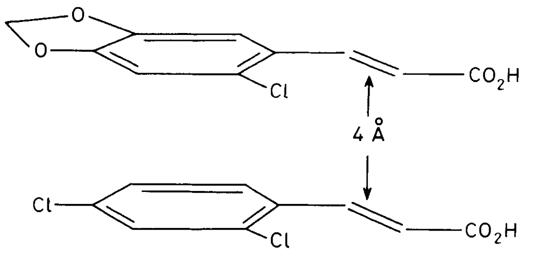


Figure 1. Schematic representation of the (**2a**)···(**2b**) interaction in complex (**1**) which leads to the formation of the unsymmetrical cyclobutane (**3c**).

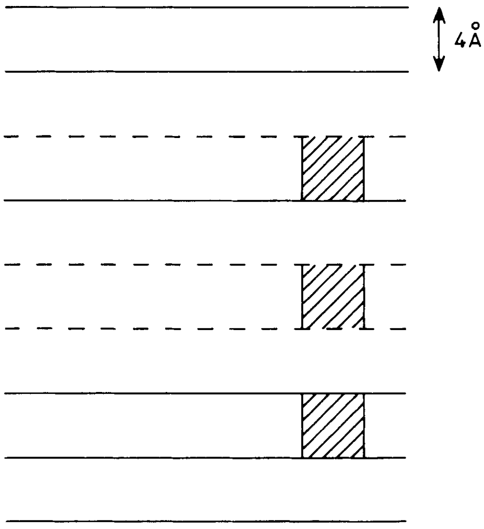


Figure 2. Disordered-stack structure in complex (**1**). Acids (**2a**) (——) and (**2b**) (- - -) occur in 2 : 1 ratio with a stack repeat of 4 Å. Each of the three contacts that lead to (**3a**), (**3b**), and (**3c**) are shown. Note that the number of molecules shown is too small to depict the 4 : 1 : 4 distribution of dimers actually observed.

Since the dimers (**3a**), (**3b**), and (**3c**) are all produced in the same crystal, their relative rates of formation are a measure of intrinsic solid-state reactivity differences. Factors such as crystal history and the role of defects, which would normally preclude a discussion of solid state kinetics, need not be considered here. Since the formation rates of (**3a**) and (**3b**) from (**1**) closely match the solid-state reactions of pure (**2a**) and (**2b**), we feel that the nature of the (**2a**)···(**2a**) solid-state reaction is the same, whether in pure (**2a**) or in (**1**), and the same applies for (**2b**). Certainly, the three rates in (**1**) are different at various stages of the reaction and these differences in the pairs (**2a**)···(**2a**), (**2b**)···(**2b**), and (**2a**)···(**2b**) could be electronic or because the three stack spacings are all slightly but significantly different.

These aspects as well as the role of intra- *vs.* inter-stack Cl···Cl interactions in the stabilization of such structures will be discussed in further detail elsewhere.[6] The formation of the unsymmetrical (**3c**) is of added interest in connection with topochemical asymmetric syntheses.[7]

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