

386. *Topochemistry. Part IV.*¹ *The Crystal Chemistry of some cis-Cinnamic Acids.*

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The solid-state photochemistry of *cis*-cinnamic acids substituted in the ring and/or at C_α is reported, and interpreted as lattice-controlled isomerisation to the *trans*-isomer which, after a recrystallisation step, is either trapped in a light-stable structure or reacts to give the dimer(s) characteristic of its crystal structure(s).

Structure data for three *cis*-acids are given. These suggest that lattice control is exerted through a mechanism of isomerisation which requires interaction of an excited >C=C< group in one *cis*-molecule with a nearest-neighbour (4.0—4.4 Å) >C=C< group.

WE have shown in Part III¹ that the photochemistry of crystalline *trans*-cinnamic acids is directly dependent on the geometrical relation between nearest-neighbour molecules in their crystal lattices. The combined chemical and crystallographic work has been summarised in the correlations shown in Table I.

TABLE I.

Packing type	Nearest-neighbour relation	Double-bond separation	Photoproduct
α	Centric	3.6—4.1 Å	α-Truxillic acid
β	Translation	3.9—4.1	β-Truxinic acid
γ	Translation	4.7—5.1	No reaction

We now report work on the photochemistry of *cis*-cinnamic acids, which is being undertaken to explore further the extent of lattice control of solid-state reactions, and to test the validity of the postulate (presented in Part I² and supported by the evidence of Part III¹) that these reactions occur with a minimum of atomic and molecular movements. Table 2 lists 12 *cis*-acids, their crystallographic constants, and photochemical behaviour.

¹ Part III, preceding paper.

² Part I, *J.*, 1964, 1996.

TABLE 2.

Crystallographic constants and photoproducts of some <i>cis</i> -cinnamic acids.										
	Cinnamic acid	Packing type	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	β	Space group	$d_{\text{calc.}}$ (g./cm. ³)	<i>n</i>	Photo-product
MC1	<i>o</i> -MeO-	α_1	11.97	10.71	7.29	93.5°	$P2_1/a$	1.269	4	D4
MC2	„	α_2	8.88	7.52	8.09	112.4 101.7 72.9	$P\bar{1}$	1.246	2	D4
MC3	<i>o</i> -EtO-	α	12.34	15.34	10.79	—	$Pbca$	1.250	8	D5, D6, MT7
MC4	<i>o</i> -PrO-	β	19.99	13.61	4.05	92.6	$P2_1/a$	1.247	4	D8
MC5	<i>o</i> -PrO-	β	18.28	14.33	4.27	95.3	$P2_1/a$	1.224	4	D9
MC6	<i>o</i> -Allyloxy-	β	19.98	13.39	4.07	91.2	$P2_1/a$	1.246	4	D10
MC7	5-Cl-2-MeO-	α	8.72	11.55	11.02	117.4	$P2_1/c$	1.434	4	D12
MC8	5-Br-2-MeO-	β	17.99	4.10	13.99	96.8	$P2_1/a$	1.666	4	D13, D38
MC9	α -Br-	α	18.64	11.48	8.20	—	$Pbca$	1.662	8	<i>trans</i> -acid
MC10	α -Br- <i>o</i> -MeO-	β	14.39	17.86	4.08	98.0	$P2_1/a$	1.645	4	<i>trans</i> -acid
MC11	α -Br- <i>m</i> -MeO-	α	21.3	11.74	8.05	—	$Pbca$	1.694	8	<i>trans</i> -acid
MC12	α -Br- <i>p</i> -MeO-	β	23.87	4.05	11.14	109.8	$P2_1/a$	1.685	4	<i>trans</i> -acid
MC13	<i>p</i> -MeO-	α	9.59	16.38	12.63	105.5	$A2/a$	1.150	8	<i>trans</i> -acid
MC14	β -Me-		16.49	7.46	7.51	98.8	$P2_1/n$	1.182	4	light-stable

EXPERIMENTAL

The *cis*-acids studied were prepared by standard methods; coumarinic acids were obtained from the corresponding coumarins by hydrolysis under conditions sufficiently mild to prevent isomerisation, followed by treatment with an alkylating agent and hydrolysis of the resulting ether esters; α -bromo-acids, prepared by dehydrobromination of the corresponding cinnamic acid dibromides, were split into their *cis*- and *trans*-isomers *via* the barium salts or by differential precipitation of the two isomeric acids in characteristic pH ranges; other *cis*-acids were obtained by ultraviolet irradiation of solutions of the *trans*-acids and separation of the resulting *cis-trans* mixtures by one of the two methods just mentioned.

For methods of preparation of polymorphic forms, checks of crystallographic purity, techniques of irradiating, and of following reaction progress, reference should be made to the Experimental section of Part II.³

o-Methoxy-*cis*-cinnamic Acid (MC1, MC2).—The acid⁴ crystallises from ethyl acetate, ether, ether-petroleum (b. p. 60–80°) in a modification (MC1), m. p. 94°. A second form (MC2), m. p. 89°, can be obtained from hot aqueous solutions which have been freed from seeds of the first form by filtration; large crystals can be obtained by vacuum sublimation (80°/25 mm.). When these are slowly heated on a microscope hot stage they melt at 89°, resolidify, and melt again at 94°. [Stoermer⁵ erroneously attributed the two melting points (89 and 94°) to acids of differing degrees of purity.]

Soxhlet extraction with ether of monomer MC1 irradiated for 20 days (4.80 g., m. p. 87–165°) gave a residue of D4,* 2,2'-dimethoxy- α -truxillic acid [1.48 g., 31%; m. p. 264–265° (from acetic acid)]. The extract consisted of *cis*-acid; no *trans*-acid could be isolated from either fraction of the Soxhlet treatment. The powder lines of MC1 did not change during irradiation; a few diffuse lines identified as belonging to the D4 pattern emerged in the course of irradiation.

The rapid change of MC2 could be followed on powder photographs taken at regular intervals during irradiation (20 days). The *trans*-monomer lines which appeared during the early stages of irradiation were subsequently replaced by the pattern of the dimer D4. Soxhlet extraction with ether of the irradiated material (4.9 g.) gave a residue (87%), identified as D4.

o-Ethoxy-*cis*-cinnamic Acid (MC3).—The acid⁵ had m. p. 101–102° (from benzene). On powder pictures taken at regular intervals during irradiation (44 days) there appeared the weak pattern of the γ -form of the *trans*-isomer superimposed on the original monomer pattern; the latter persisted throughout the entire irradiation period. No other new lines could be observed. Soxhlet extraction with petroleum (b. p. 60–80°) split the irradiated material (8.95 g.) into an insoluble fraction (2.85 g., 32%), m. p. 258–263° after softening at 130°, and an extract from

* The numbering of the α -truxillic and β -truxinic acids follows the system adopted in Part II.

³ Part II, *J.*, 1964, 2000.

⁴ Reimer and Howard, *J. Amer. Chem. Soc.*, 1928, **50**, 196.

⁵ Stoermer and Friderici, *Ber.*, 1911, **44**, 644.

which a crystalline solid (2.22 g., 25%), m. p. 128—130°, separated on cooling: *o*-ethoxy-*trans*-cinnamic acid [m. p. 133—134° (from ethanol-water)]. The solid obtained from the extract by evaporation of the solvent consisted of about equal amounts (21%) of *cis*- and *trans*-monomers. On Soxhlet extraction with ether of the petroleum-insoluble fraction, 2,2'-diethoxy- α -truxillic acid (D5) (1.42 g., 16%) was isolated as the residue, m. p. 285—287° (from acetic acid); the ether-soluble extract gave a crystalline solid (1.20 g., 13%), m. p. 206—208°, identified as 2,2'-diethoxy- β -truxinic acid (D6), m. p. 210—212° [from ether-petroleum (b. p. 60—80°)]. The material balance (96%) of the reaction follows: 16% of centric dimer, 13% of mirror-dimer, 46% of *trans*-monomer, and 21% of recovered *cis*-monomer.

o-Propoxy-*cis*-cinnamic Acid (MC4).—The acid was prepared by Stoermer's method⁵ with the minor modification that the ethanol-water solution of coumarinic acid was not concentrated before addition of propyl iodide so as to minimise isomerisation of the coumarinic acid; after addition of the alkylating agent the solution was refluxed for 3 hr. The acid, recrystallised from petroleum (b. p. 60—80°), had m. p. 82—83°. During irradiation (55 days) the monomer powder pattern was gradually replaced by that of the dimer. Soxhlet extraction with ether of the irradiation product gave an insoluble fraction (5.84 g., 82%), m. p. 258—260° (from acetic acid), of 2,2'-dipropoxy- α -truxillic acid (D8). Powder photographs indicated a content of about 50% of D8 in the solid obtained by evaporation of the ether extract. Total conversion thus amounted to approximately 90%.

o-Isopropoxy-*cis*-cinnamic Acid (MC5).—The acid, prepared analogously to MC4, had m. p. 59—60° [from petroleum (b. p. 60—80°)] (Found: C, 70.1; H, 6.7. C₁₂H₁₄O₃ requires C, 69.9; H, 6.8%). The powder pattern of the *trans*-monomer which appeared during the initial stages of exposure was gradually replaced by the dimer pattern on continued irradiation (36 days). Soxhlet extraction with ether of the irradiated material (6.85 g.) gave 2,2'-di-isopropoxy- α -truxillic acid (D9) (6.08 g., 89%), m. p. 271—273°.

o-Allyloxy-*cis*-cinnamic Acid (MC6).—Allyl bromide (83 g.) was added dropwise to a boiling solution of coumarin (50 g.) in aqueous (520 ml.) ethanolic (130 ml.) sodium hydroxide (30 g.). The solution was refluxed for another 2 hr., and the ester hydrolysed with 10% aqueous sodium hydroxide. The acid (49 g., 70%) was precipitated with hydrochloric acid after evaporation of the alcohol *in vacuo*; it had m. p. 82—83° [from petroleum (b. p. 60—80°)] (Found: C, 70.8; H, 5.8. C₁₂H₁₂O₃ requires C, 70.6; H, 5.9%). From the product (16.86 g.) of irradiation (30 days) 2,2'-diallyloxy- α -truxillic acid (D10) was separated by ether extraction as the insoluble fraction (12.06 g., 72%), m. p. 237—238° (from acetic acid). The remainder of the material obtained by evaporation of the ether was a yellow viscous liquid which eventually solidified and was not characterised further.

5-Chloro-2-methoxy-*cis*-cinnamic Acid (MC7).—The acid, prepared analogously to MC1 from 6-chlorocoumarin by methylation (dimethyl sulphate) and hydrolysis, had m. p. 151—152° (from ethanol-water) (Found: C, 56.5; H, 4.2; Cl, 16.8. C₁₀H₉ClO₃ requires C, 56.5; H, 4.3; Cl, 16.7%). During irradiation (40 days) the powder lines of the monomer were replaced by the dimer pattern while the melting point rose to about 230°. The dimer, 5,5'-dichloro-2,2'-dimethoxy- β -truxinic acid (D12), m. p. 242—245°, was isolated from the irradiation product in 81% yield by two recrystallisations from acetic acid.

5-Bromo-2-methoxy-*cis*-cinnamic Acid (MC8).—The acid prepared from 6-bromocoumarin had m. p. 161—162° (from ethanol) (Found: C, 46.7; H, 3.5; Br, 31.2. C₁₀H₉BrO₃ requires C, 46.7; H, 3.5; Br, 31.1%). The slow reaction occurring on irradiation (40 days) was characterised by the gradual disappearance of the monomer powder pattern; no new lines appeared. The irradiation product (16.92 g., m. p. 140—260°) was extracted with hot ethanol leaving an insoluble fraction which was split by Soxhlet treatment with ether into an extract from which 5,5'-dibromo-2,2'-dimethoxy- β -truxinic acid (D13) was isolated (1.32 g., 7.8%), m. p. 241—244° (from dioxan-water). The ether-insoluble residue (1.30 g., 7.7%), m. p. 313—314° (from acetic acid), was identified as 5,5'-dibromo-2,2'-dimethoxy- α -truxillic acid (D38) since on debromination in the presence of 2% Pd-CaCO₃ catalyst⁶ it gave quantitatively 2,2'-dimethoxy- α -truxillic acid (D4). Dimethyl 5,5'-dibromo-2,2'-dimethoxy- α -truxillate had m. p. 167.5—168.5° (from methanol) (Found: C, 48.8; H, 4.2; Br, 29.25. C₂₂H₂₂Br₂O₆ requires C, 48.7; H, 4.1; Br, 29.5%). The ethanolic extract of the irradiated material gave on evaporation a non-crystalline residue (14.2 g., 84%); attempts to recrystallise this material or to

⁶ Busch and Stove, *Ber.*, 1916, **49**, 1063.

separate it into crystalline fractions were unsuccessful; X-ray photographs of the product showed a diffuse ring with a spacing of about 4.2 Å.

p-Methoxy-*cis*-cinnamic Acid (MC9).—*p*-Methoxy-*trans*-cinnamic acid ⁷ (14.0 g.), dissolved in a solution of sodium carbonate (14.0 g.) in water (2.7 l.), was irradiated for 24 hr. with a high-pressure 300W mercury immersion lamp. The solution was de-aerated before irradiation with a stream of nitrogen. The residual *trans*-acid was precipitated with hydrochloric acid and filtered off. The *cis*-acid, which had remained in solution, was extracted from the filtrate with ether. Evaporation of the CaSO₄-dried solution gave *p*-methoxy-*cis*-cinnamic acid ⁷ (10.3 g., 74%), m. p. 67—68°.

The fast reaction which occurred on irradiation of the *cis*-acid in sunlight could be followed by the replacement of the *cis*-powder lines by the pattern of the *trans*-isomer. *p*-Methoxy-*trans*-cinnamic acid, m. p. and mixed m. p. 173°, was obtained by recrystallisation of the irradiation product from ethanol (yield 78%).

α -Bromo-*cis*-cinnamic Acid (MC10).—The acid ⁸ had m. p. 119—120° [from benzene-petroleum (b. p. 60—80°)]. Powder pictures taken during irradiation (24 days) showed the gradual replacement of the *cis*-acid powder-lines by the pattern of the *trans*-acid; the irradiation product was further identified as α -bromo-*trans*-cinnamic acid by mixed m. p. and ultraviolet spectra. Another sample of the *cis*-acid was irradiated through a filter passing light of wavelength between 3000—4000 Å, in an unsuccessful attempt to accumulate any unstable intermediate dimer which might have been formed in the isomerisation to the *trans*-acid.

α -Bromo-*o*-methoxy-*cis*-cinnamic Acid (MC11).—The acid ⁴ had m. p. 137° (from benzene). Irradiation produced a fast reaction accompanied by replacement of the powder lines by the *trans*-acid pattern and a rise in m. p. to 167—170°. Recrystallisation from aqueous ethanol gave the *trans*-isomer (80%), m. p. 171—172°.

α -Bromo-*m*-methoxy-*cis*-cinnamic Acid (MC12).—The acid ⁹ had m. p. 91° (from chloroform). The replacement of the powder pattern of the *cis*-acid by that of the *trans*-isomer occurred in the early stages of irradiation. On continued irradiation (50 days) no further change of pattern could be observed. The irradiation product had m. p. 121—123°; the mixed m. p. with the *trans*-monomer (m. p. 122°) ⁹ was unchanged.

α -Bromo-*p*-methoxy-*cis*-cinnamic Acid (MC13).—The acid ¹⁰ was obtained in yellow crystals, m. p. 102—103° [from chloroform-petroleum (30—60°)]. Irradiation produced a very fast change (1 day) to the *trans*-isomer, observable by the change in powder pattern and of colour from yellow to white. On continued irradiation (21 days) the powder turned brownish because of decomposition, occurring under the conditions of exposure. The powder pattern of the *trans*-isomer remained unchanged. Recrystallisation of the irradiation product from aqueous ethanol gave the pure *trans*-isomer (80%), m. p. 188—189°; mixed m. p. with an authentic sample (m. p. 188—189°) was unchanged.

β -Methyl-*cis*-cinnamic Acid (MC14).—The acid was prepared, in 14% yield, by irradiation with a low-pressure mercury lamp of a benzene solution of the *trans*-isomer; ¹¹ it had m. p. 131.0—131.5° (from carbon disulphide). Irradiation (35 days) produced no change in m. p., powder pattern, or u.v. spectrum. The mixed m. p. of the irradiation product with the starting material was unchanged.

The experimental data can be summarised as follows: with the exception of 5-bromo-2-methoxy-*cis*-cinnamic acid discussed in detail below, photoactive *cis*-acids give either the light-stable *trans*-acid or the known photo-dimer(s) of the *trans*-acid. Where the *trans*-acid is polymorphic the end products are frequently all the compounds expected from the various crystal forms of the *trans*-isomer.

We may therefore assume that the first stage in the photo-reaction of solid *cis*-cinnamic acids is the formation of the *trans*-acid, and that this is followed by the crystallisation of the *trans*-acid into its polymorphic forms which in turn undergo their characteristic photo-reactions. Thus the products of irradiation of *o*-ethoxy-*cis*-cinnamic acid are the light-stable (γ) form of the *trans*-acid (identified in the mixture by powder photography), and the 2,2'-diethoxy-derivatives of α -truxillic and β -truxinic acids which can be accounted for as the photo-dimers of the α - and

⁷ Stoermer, *Ber.*, 1911, **44**, 656.

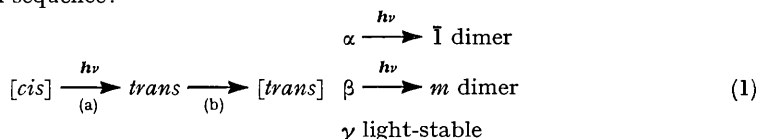
⁸ Sudborough and Thompson, *J.*, 1903, **83**, 675.

⁹ Jones and James, *J.*, 1935, 1600.

¹⁰ Hariharan and Sudborough, *Chem. Zentr.*, 1926, **I**, 70.

¹¹ Stoermer, Grimm, and Laage, *Ber.*, 1917, **50**, 966.

β -forms of the *trans*-monomer, respectively. No other products could be isolated. The absence (at least within the limits of our experimental techniques) of dimers other than those α -truxillic and β -truxinic acids which are known to be derived from the *trans*-acids must be stressed as confirming this crystallisation step. The two-step mechanism is further supported by the fact that in many of the photo-reactions yielding dimers the photo-active *trans*-acid could be detected by powder photography in the early stages of reaction. Eqn. (1) summarises the suggested reaction sequence:



where the species in square brackets indicate a molecule in its crystalline assembly, and the species without brackets a molecule in solid solution or some other "disordered" state.

This formulation accounts satisfactorily for the absence in the *solid state* of the photo-equilibrium between *cis*- and *trans*-acids characteristic of the solution reaction: the crystallisation step (b) removes the *trans*-acid from the system by fixing it in a light-stable (γ) lattice or as a stable *dimer* molecule *via* the photo-reaction of the α - or β -lattice.

We next enquire whether step (a) in the reaction scheme of eqn. (1) is lattice controlled. Our qualitative evidence is threefold: first, the difference in the photo-behaviour of the two modifications of *o*-methoxy-*cis*-cinnamic acid is *prima facie* evidence for the operation of topochemical factors [criterion (3), Part I²]. While the α_1 -phase shows neither X-ray nor chemical evidence of the *trans*-acid at any time during the formation of the centric dimer the powder pattern of the α_2 -phase develops the lines of the *trans*-isomer after short exposure.

Our next argument is based on the second criterion for lattice control, namely on differences in behaviour of chemically closely related compounds. Solid 5-chloro-2-methoxy-*cis*-cinnamic acid gives exclusively the β -truxinic acid expected from its *trans*-isomer; the bromo-acid on the other hand yields the α -truxillic acid and non-crystalline material as well as the β -truxinic acid. This difference cannot be explained by polymorphism of the *cis*- or *trans*-bromo-acids. The crystallographic purity of the *cis*-acid was established by an indexing check of the powder pattern from single-crystal data; variations of recrystallisation conditions did not produce a second phase. The *trans*-acid had already been shown to be dimorphic, with a light-stable form and a β -modification responsible for the β -truxinic acid. The formation of this latter dimer can thus be explained by the intermediate isomerisation to, and subsequent reaction of, the β -modification of the *trans*-monomer. An α -form of the *trans*-acid which would be responsible for the α -truxillic acid could not be found; this negative result though not conclusive is given weight by the observation that we have not found a single ring-halogenated cinnamic acid crystallising in the α -modification. We may accept the conclusion that the centric dimer and the non-crystalline material do not stem from the *trans*-isomer; the difference in photochemical behaviour of the chloro- and bromo-*cis*-acids must therefore be due to different topochemical factors operating in these two crystal structures.

Our third argument is based on the light-stability of certain *cis*-acids in the *solid state*. Thus, solid β -methyl-*cis*-cinnamic acid is unaffected by irradiation lasting several weeks although the *cis*-acid is thermodynamically less stable than the *trans*-acid: it is quantitatively isomerised in solution by treatment with boiling sodium hydroxide¹¹ or with cold sulphuric acid.¹¹ The light-stability of the crystalline *cis*-acid can only be interpreted in terms of topochemical factors.

We now consider the nature of the topochemical factors controlling *cis*-acid reactions. Proceeding as in Part III with an analysis of the crystal structure types presented by the *cis*-acids for the presence of short double-bond contacts, we note from Table I that the cell constants of the *cis*-acids fall into two major groups, characterised by shortest axes of $4.1 \pm 0.1 \text{ \AA}$ and $> 5.5 \text{ \AA}$, to be referred to as β - and α -types, respectively, in analogy with the *trans*-acids. We have so far analysed α -bromo-*cis*-cinnamic acid,¹² as an example of the α -type; packing diagrams, projected down [001] and [010], are shown in Fig. 1 (see footnote on page 2014, Part III). The structure has nearest-neighbour $>C=C<$ groups lying across centres of symmetry with the midpoints of the double-bonds separated by 4.4 \AA . All other double-bond contacts are greater than 6 \AA .

¹² Osaki and Schmidt, to be published.

The β -type packing presents a more complicated situation than in the *trans*-acid case. Because of the *cis*-configuration at the double bond, there exists the possibility of close-neighbour contacts essentially in the molecular plane as well as from above and below it. The simple β -type packing is exemplified by the structure of α -bromo-*p*-methoxy-*cis*-cinnamic acid,¹³ whose

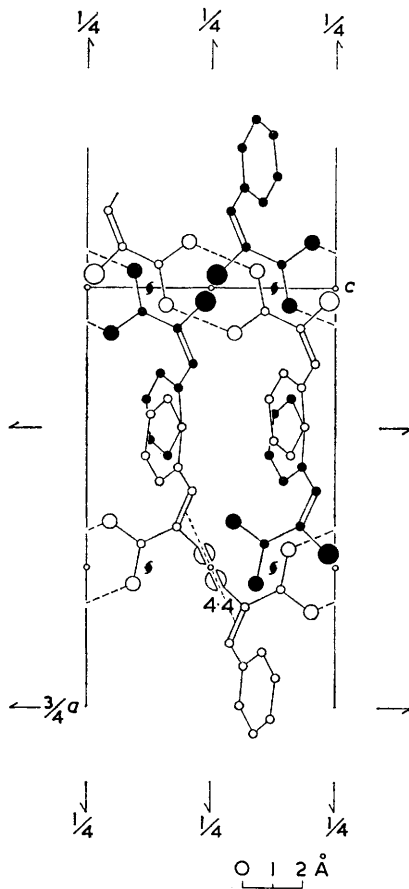


FIG. 1. α' -Bromo-*cis*-cinnamic acid; packing arrangement seen along [010] (Osaki and Schmidt, to be published).

packing arrangement projected down the 4 Å axis is shown in Fig. 2. This projection indicates no short >C=C< contacts other than along [010]; all other contacts, centric and screw-axis related, are longer than 5 Å. No structural data have been obtained for the *n*- and iso-propyl and allyl ethers of *o*-hydroxy-*cis*-cinnamic acid. An example of the β -type structure with more than one kind of double-bond contact has been found in 5-bromo-2-methoxy-*cis*-cinnamic acid¹⁴ whose packing arrangement projected down the 4 Å axis is shown in Fig. 3. The additional short >C=C< contact in this structure produced by the twofold screw axis parallel to [010], can be calculated directly from the projection to be 3.9 Å.

The results of these structure analyses would, in the light of our conclusions on the crystal chemistry of the *trans*-acids, lead to the following predictions: β -type: short contact along the 4 Å axis dimerises to all-*cis*-truxinic acid of symmetry *m*; α -type short contact across centre of symmetry dimerises to α -truxillic acid. Actually, neither of these predictions is fulfilled. We now suggest that the short translation and centric contacts, while not permitting dimerisation, are responsible for the photo-activity, *i.e.*, isomerisation, of these *cis*-acids, and suggest a mechanism which interprets topochemical control in terms of these contacts. The process of isomerisation is pictured as photo-excitation of a >C=C< group, followed by a movement of the excited molecule towards the double bond of a suitable close and correctly aligned nearest

¹³ Bregman and Schmidt, to be published.

¹⁴ Osaki and Schmidt, to be published.

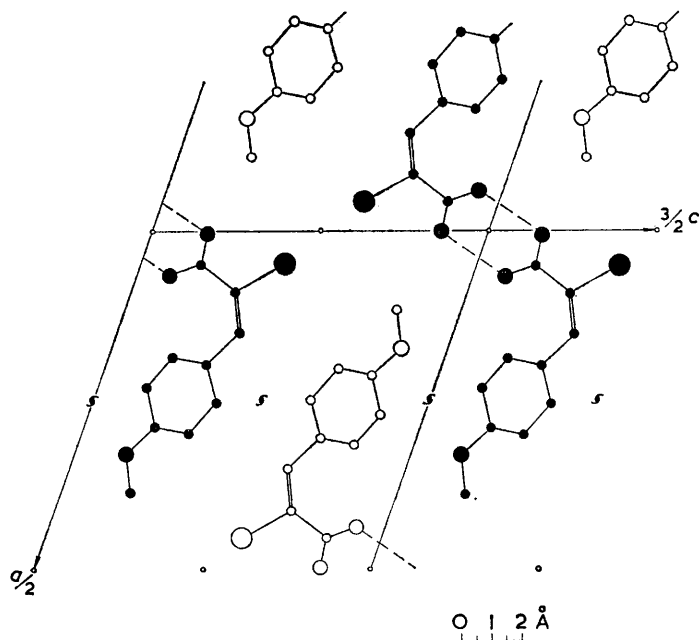


FIG. 2. α -Bromo-*p*-methoxy-*cis*-cinnamic acid; packing arrangement seen along [010] (Bregman and Schmidt, to be published).

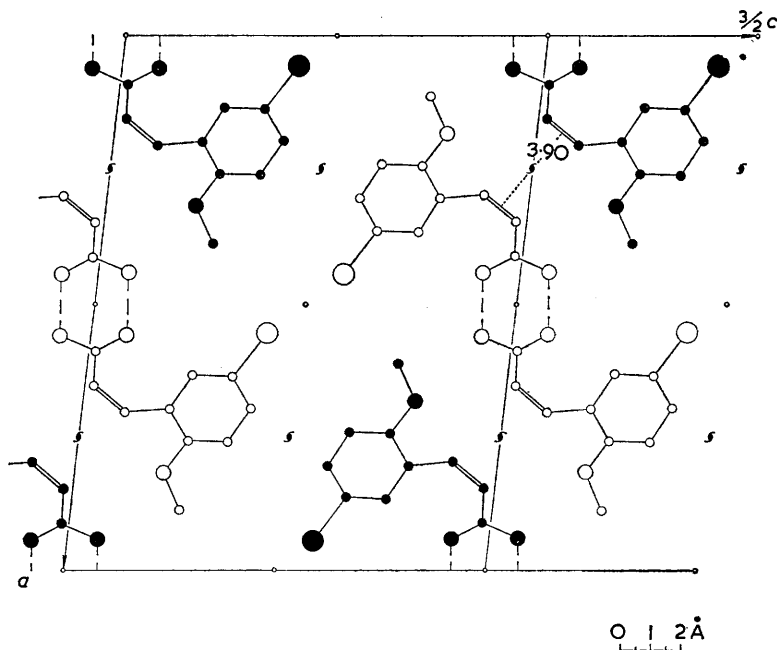


FIG. 3. 5-Bromo-2-methoxy-*cis*-cinnamic acid; packing arrangement seen along [010]. (Osaki and Schmidt, to be published).

neighbour. Interaction between the two double bonds may establish new covalent bonds between the two molecules (irreversible dimerisation); alternately, if dimerisation does not take place, for reasons to be established, we assume that the movement of the excited molecule towards its nearest neighbour releases at least one of the two reaction partners from the

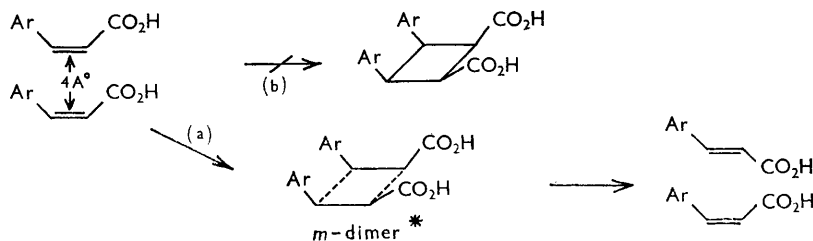


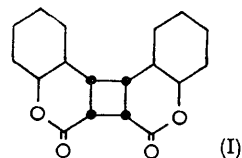
FIG. 4. Suggested mechanism of *cis*-to-*trans*-conversion in the β -packing type.

restraint of the crystal lattice forces and thereby permits its isomerisation. We further assume that the required double-bond separation is comparable with that permitting dimerisation. We suggest the bimolecular mechanism



in which dimer* represents a metastable complex formed between the excited molecule and its closest neighbour.

Returning now to our structural data and considering first the short translational contact in the β -type we suggest that isomerisation occurs *via* an unstable dimer [Fig. 4 (a)] and that this isomerisation successfully competes with direct dimerisation to the overcrowded *cis-syn*-truxinic acid to be expected from process (b). That the latter process is possible in the absence of the competing process (a), *i.e.*, in molecules incapable of isomerisation, is shown by the photochemistry of coumarin: its unstable (4 Å) modification¹⁵ as well as its complex with mercuric chloride ($C_9H_6O_2 \cdot HgCl_2$; $a = 23.63$, $b = 11.27$, $c = 4.03$ Å, $\beta = 97^\circ 40'$; space group $P2_1/a$; see Fig. 5 for a packing diagram along the short axis)¹⁶ give bicoumarin¹⁷ (I) whose configuration as *cis-syn* has been established by Anet.¹⁸



The behaviour of 5-bromo-2-methoxy-*cis*-cinnamic acid in the β -type packing with two kinds of short double bond contacts is now explicable. The β -truxinic acid is formed through known reactions of the *trans*-isomer which itself arises *via* the isomerisation mechanism of eqn. 2. The α -truxillic acid which, as we have shown, cannot arise from either of the known dimorphs of the *trans*-acid, can be formed directly from pairs of *cis*-molecules correctly oriented across screw axes as regards double-bond separation (3.9 Å between bond centres) and symmetry relation (double bonds nearly parallel to the projection plane and therefore nearly parallel to each other). We consider this acid to be of cardinal importance to the overall picture of lattice control presented here: it is so far the only *cis*- (or *trans*-) acid to yield two dimers whose formation cannot be accounted for by dimorphism but follows from the presence within one crystal structure of two geometrically distinct $>C=C<$ contacts. We shall point out elsewhere¹⁹ that the formation of non-crystalline material from this *cis*-acid can also be understood in terms of the crystal structure.

In the one α -type *cis*-acid crystal structure analysed so far geometrical conditions for reaction (eqn. 2) are fulfilled in the centric approach of nearest-neighbour $>C=C<$ groups though at a distance (4.4 Å) exceeding those found in the α -type *trans*-acid structures. In interpreting the instability of the postulated dimer* [Fig. 6 (a)] we reject the possibility that the centric dimer of α -bromocinnamic acid is too overcrowded to be stable; instead we prefer

¹⁵ Bregman, unpublished.

¹⁶ Struchkov, Kitaigorodskii, and Khotsyanova, *Doklady Akad. Nauk S.S.R.*, 1953, **93**, 675.

¹⁷ de Jong, *Rec. Trav. chim.*, 1924, **43**, 316; Sonntag, unpublished.

¹⁸ Anet, *Canad. J. Chem.*, 1962, **40**, 1249.

¹⁹ Hirshfeld and Schmidt, *J. Polymer Sci.*, in the press.

at this stage to attach significance to the difference between 4.4 Å (isomerisation) and 4.1 Å (maximum separation observed in dimerisation). This argument is qualitatively supported by the observation that of the two *o*-methoxy-*cis*-acid modifications, both of which occur in the α -type, one dimerises directly to the α -truxillic acid while the second isomerises to the *trans*-acid which then forms the α -truxillic acid. This difference between the two forms may be explained

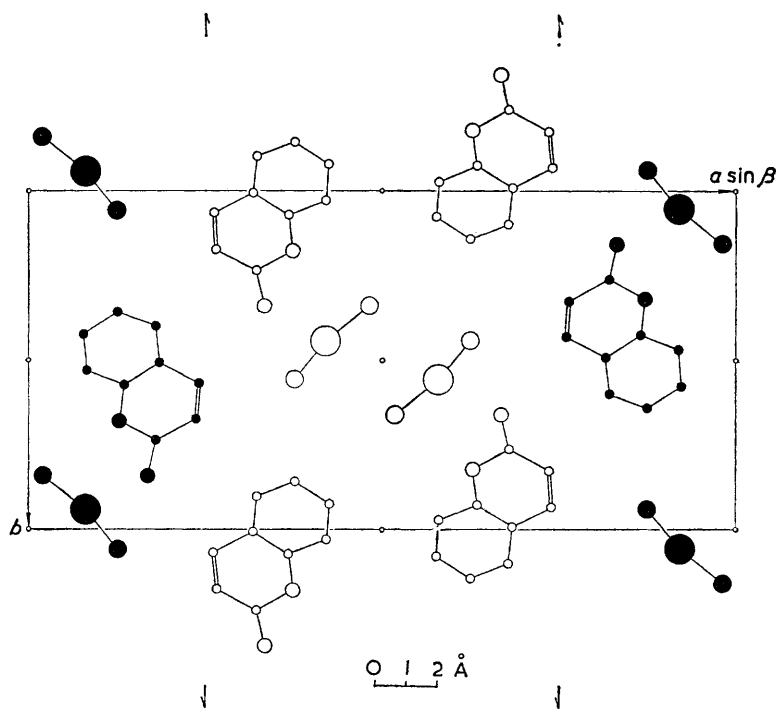


FIG. 5. Coumarin-mercuric chloride adduct; packing arrangement seen along [001].¹⁶

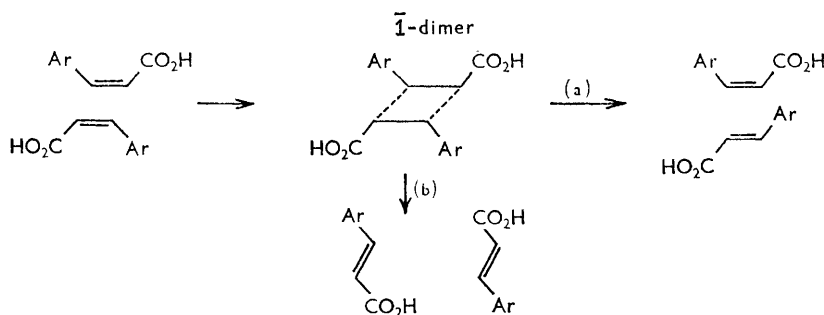


FIG. 6. Suggested mechanisms of *cis*-to-*trans*-conversion in the α_2 -packing type.

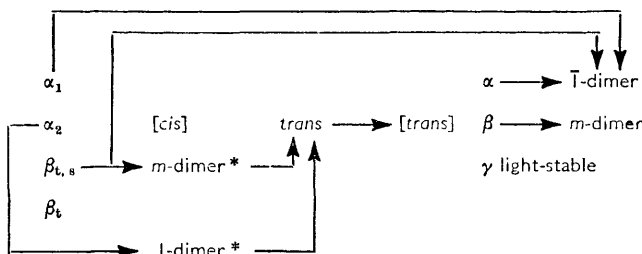
by the assumption, which fits readily into our reaction scheme, that in the first modification, α_1 , the >C=C< contacts are sufficiently short to lead to direct dimerisation whereas in the second form, α_2 , these contacts are too long to permit formation of the stable dimer though not too long for interaction of the kind postulated in Fig. 6 (a).

The possibility is envisaged that isomerisation in the centric dimer* can alternatively occur by the "cross-over" mechanism of Fig. 6 (b). This mechanism has been suggested by House²⁰

²⁰ House, *J. Org. Chem.*, 1959, **24**, 1374.

and rejected by him in liquid-phase isomerisation; we are currently studying the photo-isomerisation of double-labelled *p*-methoxy-*cis*-cinnamic acid, which crystallises in the α -type packing, to determine whether such crossing-over takes place in the solid state.

Summarising, we arrive at the following reaction scheme:



In this scheme β_t and $\beta_{t,s}$ refer to the two β -types established in this Paper, with translational, and translational and screw-axis, contacts of 4 Å, respectively. The separation of the α -type into the two classes α_1 and α_2 is conjectural, and requires verification by structure analyses. We point out that this reaction scheme may well turn out to be more symmetric; work is now in progress on the *trans-cis*-isomerisation in the solid state of β -substituted cinnamic acids. We predict the possibility that the α -type in the *trans*-series too may require classification into α_1 and α_2 with the latter permitting, as in the *cis*-acid series, isomerisation rather than dimerisation.

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