

### 385. Topochemistry. Part III.<sup>1,2</sup> The Crystal Chemistry of some *trans*-Cinnamic Acids.

By G. M. J. SCHMIDT.

The crystal structures of substituted cinnamic acids can be divided into three groups ( $\alpha, \beta, \gamma$ ) according to their cell dimensions. These structure groups coincide with the three types of photochemical behaviour reported in Part II: dimerisation to (1)  $\alpha$ -truxillic or (2)  $\beta$ -truxinic acid, and (3) light-stability.

X-Ray analyses of members of the  $\alpha$ - and  $\beta$ -classes indicate that in these photo-active structures the conformation of the dimers can be correlated with the packing arrangement of nearest-neighbours in the monomer lattice: dimerisation takes place at  $\text{>C=C<}$  separations of 3.6–4.1 Å and preserves in the (molecular) symmetry of the cyclobutane derivative the (crystallographic) symmetry element relating nearest-neighbour monomers. The separation between  $\text{>C=C<}$  of 4.7–5.1 Å in the light-stable  $\gamma$ -structures is interpreted as too long for dimerisation to be possible.

WE discuss in this Paper the second line of approach outlined in Part I<sup>1</sup> to the problem of solid-state reactions, namely the correlation of the molecular packing arrangement of the reactant species with the chemical and stereochemical structure of the reaction product. The examples that follow are drawn from the chemistry of substituted cinnamic acids reported in Part II.<sup>2</sup> We recall the main results reported there: first, each crystalline phase of the *trans*-acids is either light-stable or gives its characteristic dimer ( $\alpha$ -truxillic or  $\beta$ -truxinic acid); secondly, no mixing of dimers occurs unless dimerisation takes place under conditions permitting a demonstrable transformation of the monomer such that the new phase accounts for the second dimer species formed; thirdly, even where such a phase transformation occurs no dimers other than  $\alpha$ -truxillic and  $\beta$ -truxinic acids are detectable, at any rate by our present techniques. Fourthly, no correlation could be found between ring-substituent and photochemical behaviour. These results suggest that photo-reactivity of cinnamic acids is crystal-structure dependent.

Table I lists the crystallographic constants of 28 *trans*-acids of which six occur in two, and one in three, crystal modifications; also included in this Table are the photochemical reaction products of these acids. The first sharply defined crystal-structure type, with a shortest axis of  $3.9 \pm 0.2$  Å, is exemplified by the  $\beta$ -form of *trans*-cinnamic acid and will be referred to as the  $\beta$ -type. In the remaining, less homogeneous, group the shortest axes vary from 4.7 Å upwards. We shall show from structure analyses of selected compounds that the second group can be subdivided into two classes which we denote as  $\alpha$  and  $\gamma$ , respectively, and that members of the  $\gamma$ -class have their shortest axes lying within the range  $4.9 \pm 0.2$  Å, while the  $\alpha$ -type structures have axes greater than 5.1 Å.

To provide quantitative information on the packing arrangements within these three types we present structural data on representative compounds. It had proved difficult to prepare entirely satisfactory crystals of  $\beta$ -*trans*-cinnamic acid; further work on this compound was stopped when we became aware of the analysis of *p*-chlorocinnamic acid by Patterson and Clark;<sup>3</sup> we are grateful to Professor Patterson for permission to quote his (unpublished) results from which we have drawn Fig. 1 showing the packing arrangement seen along [010].\*

\* In our packing diagrams we have used the convention of full circles for the molecular pair centred at the origin and its centrally related neighbours; molecules related to these by screw axes, etc., are represented by open circles.

<sup>1</sup> Part I, *J.*, 1964, 1996.

<sup>2</sup> Part II, preceding paper.

<sup>3</sup> Patterson and Clark, private communication.

TABLE I.

Crystallographic constants and photoproducts of some *trans*-cinnamic acids.

	Cinnamic acid	Packing type	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	$\beta$	Space group	$d_{\text{calc}}$ (g./cm. <sup>3</sup> )	<i>n</i>	Photo-product
MT1	H-	$\alpha$	7.79	18.07	5.67	97.0°	$P2_1/n$	1.242	4	I
MT2	"	$\beta$	31.3	4.04	6.05	90.3	$P2_1/a$	1.286	4	<i>m</i>
MT3	<i>o</i> -HO-	$\alpha$	16.31	5.52	8.83	93.6	$P2_1/a$	1.375	4	I
MT4	<i>o</i> -MeO-	$\alpha$	7.93	17.68	7.13	114.8	$P2_1/c$	1.304	4	I
MT5	<i>o</i> -EtO-	$\alpha$	8.87	6.82	10.36	94.7 90.5	$P\bar{1}$	1.244	2	$\bar{I}$
MT6	"	$\beta$	37.7	—	4.08	—	$R\bar{3}$	1.144	18	<i>m</i>
MT7	"	$\gamma$	17.25	5.45	24.0	111.8	$C2/c$	1.222	8	stable
MT8	<i>o</i> -PrO-	$\alpha$	38.0	8.68	21.0	94.5	$P2_1/c$	1.19	24	I
MT9	<i>o</i> -PrO-	$\alpha$	16.54	8.22	8.34	96.7	$P2_1/a$	1.21	4	$\bar{I}$
MT10	<i>o</i> -Allyloxy-	$\alpha$	9.67	8.09	10.79	115 83	$P\bar{1}$	1.18	2	I
MT11	5-Br-2-HO-	$\beta$	24.70	9.22	3.94	97.5	$P2_1/a$	1.802	4	<i>m</i>
MT12	5-Cl-2-MeO-	$\beta$	26.19	3.92	28.82	136.6	$A2/a$	1.382	8	<i>m</i>
MT13	5-Br-2-MeO-	$\beta$	26.1	4.02	24.6	104.5	$C2/c$	1.627	8	<i>m</i>
MT14	"	$\gamma$	23.1	4.73	18.8	90.8	$A2/a$	1.664	8	stable
MT15	<i>m</i> -HO-	$\alpha$	5.39	18.73	8.99	118.0	$P2_1/c$	1.360	4	I
MT16	<i>m</i> -MeO-	$\gamma$	8.77	4.92	22.6	105.6	$P2_1/c$	1.260	4	stable
MT17	<i>p</i> -HO-	$\alpha$	8.79	5.27	17.25	101.0	$P2_1/c$	1.386	4	$\bar{I}$
MT18	<i>p</i> -MeO-	$\gamma$	8.35	4.80	11.87	94.6 110.1	$P\bar{1}$	1.330	2	stable
MT19	<i>o</i> -NO <sub>2</sub> -	$\beta$	31.5	7.22	3.76	91.6	$P2_1/a$	1.501	4	<i>m</i>
MT20	<i>m</i> -NO <sub>2</sub> -	$\beta$	24.8	9.50	3.82	99.7	$P2_1/a$	1.446	4	<i>m</i>
MT21	"	$\gamma$	12.28	4.93	8.0	112.8 76.6	$P\bar{1}$	1.46	2	stable
MT22	<i>p</i> -NO <sub>2</sub> -	$\beta$	7.2	3.9	31.4	102.6 90	$P2_1/c$	1.46	4	<i>m</i>
MT23	"	$\gamma$	6.13	5.06	27.8	99.5	$P2_1/c$	1.510	4	stable
MT24	<i>o</i> -Cl-	$\beta$	*	*	*	94.5 90	$P\bar{1}$	1.47	2	<i>m</i>
MT25	<i>m</i> -Cl-	$\beta$	13.0	8.6	3.9	90 117.5	$P\bar{1}$	1.47	2	<i>m</i>
MT26	"	$\gamma$	12.5	4.93	14.1	94.0	$P2_1/a$	1.414	4	stable
MT27	<i>p</i> -Cl- <sup>a</sup>	$\beta$	32.9	3.87	6.56	83.0	$P2_1/a$	1.460	4	<i>m</i>
MT28	<i>o</i> -Br-	$\beta$	15.11	7.84	3.95	112.4 85.5	$P\bar{1}$	1.766	2	<i>m</i>
MT29	<i>m</i> -Br-	$\beta$	19.4	4.01	24.9	101.2 113.3	$C2/c$	1.700	8	<i>m</i>
MT30	"	$\gamma$	12.46	4.97	14.45	96.3	$P2_1/a$	1.693	4	stable
MT31	<i>p</i> -Br-	$\beta$	33.0	3.97	6.66	94.6	$P2_1/a$	1.739	4	<i>m</i>
MT32	2,4-di-Cl-	$\beta$	3.88	6.44	36.8	90.5	$P2_1/c$	1.568	4	<i>m</i>
MT33	2,6-di-Cl-	$\beta$	3.87	16.4	15.1	93.8	$P2_1/c$	1.505	4	<i>m</i>
MT34	3,4-di-Cl-	$\beta$	*	*	*	94.5 94.2	$P\bar{1}$	1.215	4	stable
MT35	<i>o</i> -Me-	$\gamma$	7.28	24.7	4.93	104.5 94.2	$P2_1/a$	1.215	4	stable
MT36	<i>p</i> -Me-	$\alpha$	7.75	7.20	9.18	107.1 115.6	$P\bar{1}$	1.223	2	I
	$\alpha$ -Br-Cinnamide	$\gamma$	18.80	5.14	19.61	108.3	$C2/c$	1.621	8	stable
		$\alpha$	9.56	5.14	16.01	94.1	$P2_1/c$	1.243	4	I

\* Crystals very poorly developed; shortest axis approximately 4 Å.

The structure consists of hydrogen-bonded pairs of acid molecules with the centres of the  $\text{—C}=\text{O} \cdots \text{HO—C—}$  system coinciding with sets of symmetry centres. Shortest approach between  $\text{>C=C<}$  groups occur along the 4 Å axis; all other contacts across centres or screw axes are longer than 5 Å.

This structure type closely resembles that of the halogenobenzoic acids<sup>4,5</sup> (e.g.,

<sup>4</sup> Toussaint, *Acta Cryst.*, 1951, **4**, 71; Pollock and Wood, *ibid.*, 1954, **7**, 605.

<sup>5</sup> Groth, "Chemische Krystallographie," IV, 463 ff., Engelmann, Leipzig, 1917.

*p*-chlorobenzoic acid:  $a = 14.190$ ,  $b = 6.213$ ,  $c = 3.852$  Å;  $\alpha = 91^\circ 14'$ ,  $\beta = 95^\circ 19'$ ,  $\gamma = 92^\circ 56'$ ; space group  $P\bar{1}$ ; see also *o*-bromobenzoic acid<sup>6</sup> ( $a = 14.82$ ,  $b = 4.10$ ,  $c = 15.90$  Å,  $\beta = 118^\circ 15'$ ; space group  $C2/c$ ), and 1-naphthoic acid<sup>7</sup> ( $a = 31.12$ ,  $b = 3.87$ ,  $c = 6.92$  Å,  $\beta = 92.2^\circ$ ; space group  $P2_1/a$ ) and certain  $\beta$ -substituted acrylic acids such as furoic acid<sup>8</sup> ( $a = 10.24$ ,  $b = 6.80$ ,  $c = 3.81$  Å;  $\alpha = 92^\circ 57'$ ,  $\beta = 96^\circ 16'$ ,  $\gamma = 106^\circ 10'$ ; space group  $P\bar{1}$ ). This structure type is characterised by the close packing of parallel, nearly planar, and centrosymmetric acid pairs arranged in stacks with a 4 Å repeat distance, the number of such stacks and the relation between them in the unit cell being determined by the symmetry elements present, such as screw axes and/or centres of symmetry (monoclinic or triclinic).

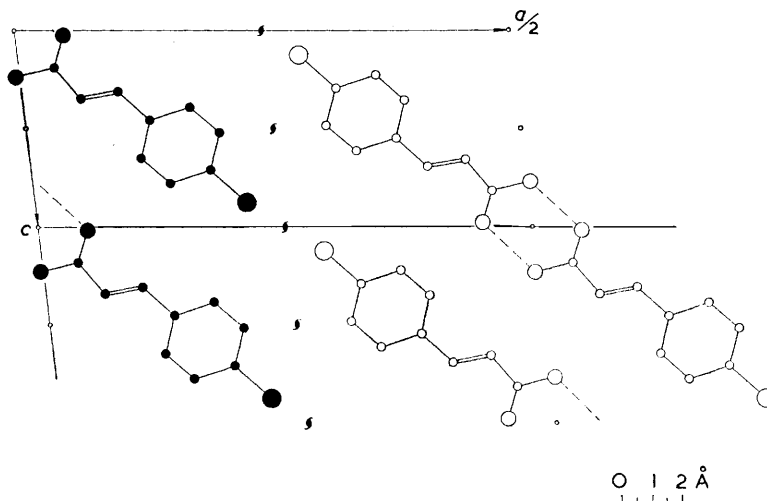


FIG. 1. *p*-Chloro-*trans*-cinnamic acid; packing arrangement seen along [010] (Patterson and Clark, unpublished).

The cluster of shortest axes in the region of  $4.9 \pm 0.2$  Å suggests that these structures belong to a common packing type; two such compounds have been partially analysed. The ( $h0l$ ) projections of  $\alpha$ -bromocinnamic acid<sup>9</sup> and of one of the two modifications of *m*-chlorocinnamic acid<sup>10</sup> are shown in Figs. 2 and 3, respectively. By assigning symmetry elements as shown in the Figures\* we can estimate separation of centres of screw- and rotation axis related  $>C=C<$  groups from the projected distances: in the  $\alpha$ -bromo-acid these are nowhere shorter than 5.1 Å; in the *m*-chloro-acid such contacts are not less than 4.93 Å.

Examples of the  $\gamma$ -type structure in chemically homologous series are salicylic acid<sup>11</sup> ( $a = 11.52$ ,  $b = 11.21$ ,  $c = 4.92$  Å;  $\beta = 90^\circ 50'$ ;  $P2_1/a$ ) and 2-naphthoic acid<sup>12</sup> ( $a = 30.59$ ,  $b = 5.00$ ,  $c = 5.63$  Å;  $\beta = 92.6^\circ$ ;  $P2_1/n$ ).

As examples of the remaining crystal structures we have analysed the  $\alpha$ -form of cinnamic

\* The ambiguity in only partially solved structures as to the origin of the cell and hence to the location of centres and screw axes (as, e.g., in the  $h0l$  zones of  $P2_1/a$ ) has been resolved on the assumption that the centres of hydrogen-bonded carboxyl groups coincide with centres of symmetry of the unit cell. The further ambiguity in the  $h0l$  projection of  $C2/c$  of the positions of the twofold rotation and screw axes has been resolved tentatively by the argument that a twofold axis at  $\frac{1}{2}y\frac{1}{2}$  rather than at  $0y\frac{1}{2}$  implies abnormally short contacts at the benzene rings close to this axis.

<sup>6</sup> Ferguson and Sim, *Acta Cryst.*, 1962, **15**, 346.

<sup>7</sup> Trotter, *Acta Cryst.*, 1960, **13**, 732.

<sup>8</sup> Goodwin and Thomson, *Acta Cryst.*, 1954, **7**, 166.

<sup>9</sup> Osaki and Schmidt, to be published.

<sup>10</sup> Rim and Schmidt, to be published.

<sup>11</sup> Cochran, *Acta Cryst.*, 1953, **6**, 260.

<sup>12</sup> Trotter, *Acta Cryst.*, 1961, **14**, 101.

acid<sup>13</sup> and cinnamide.<sup>14</sup> The molecular arrangement of the former is shown in Fig. 4. The structure consists of glide-plane related stacks along [100] of hydrogen-bonded pairs of acid molecules centred at (000) and  $(\frac{1}{2}\frac{1}{2}0)$ , respectively; each stack is made up of parallel and nearly planar molecules whose long axes are inclined at about 50° to [100]. The packing arrangement of cinnamide is shown in Fig. 5; this structure consists of glide-plane related stacks of amide molecules along [100] pair-wise linked by hydrogen bonds across centres of symmetry at (000) and  $(0\frac{1}{2}\frac{1}{2})$ . The requirement of a second hydrogen bond

FIG. 2.  $\alpha$ -Bromo-*trans*-cinnamic acid; packing arrangement seen along [010] (Osaki and Schmidt, to be published).

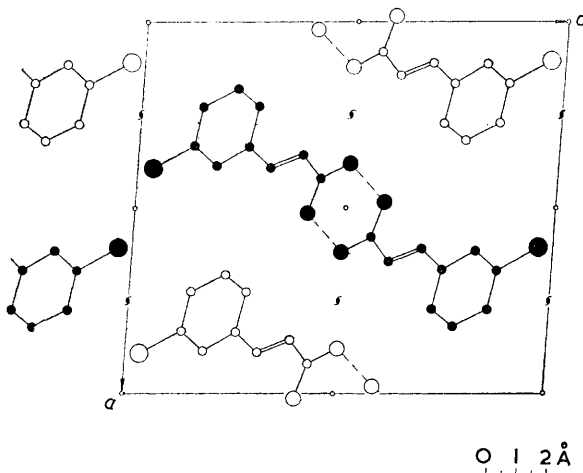
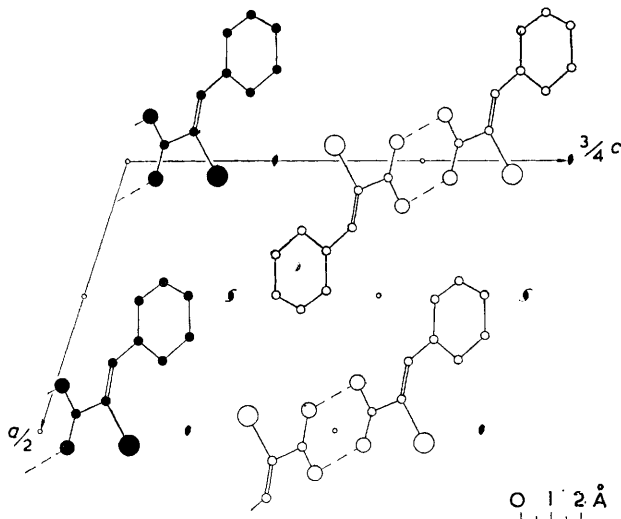


FIG. 3. *m*-Chloro-*trans*-cinnamic acid; packing arrangement seen along [010] (Rim and Schmidt, to be published).

from the amino-group to the oxygen of the identity-related molecule along [010] causes a twist of the CONH<sub>2</sub> group out of the mean plane of the PhCH:CH moiety, which is absent in the acid itself. However, this change in molecular structure does not significantly affect the contact between nearest-neighbour >C=C< groups, for these are essentially the same in the acid and amide. In both a nearest-neighbour contact occurs between >C=C< groups related by centres of symmetry, with centre-to-centre distances between nearest double bonds of 3.6 and 4.1 Å in the acid and amide, respectively. All other contacts whether along the identity period, glide plane, or screw axis exceed 5 Å.

<sup>13</sup> Ladell, McDonald, and Schmidt, *Acta Cryst.*, 1956, **9**, 195; full structure analysis to be published.

<sup>14</sup> Osaki, to be published.

The  $\alpha$ -type, too, occurs in the benzoic acid series. Thus, the structure of benzoic acid itself<sup>15</sup> ( $a = 5.52$ ,  $b = 5.14$ ,  $c = 21.90$  Å;  $\beta = 97^\circ$ ;  $P2_1/c$ ) belongs to this packing type; again, the structure of benzamide<sup>16</sup> ( $a = 5.59$ ,  $b = 5.01$ ,  $c = 21.93$  Å;  $\beta = 90^\circ 45'$ ;  $P2_1/c$ ) is homologous to that of cinnamide. The stability relation of the  $\alpha$ - and  $\beta$ -types in the two acids and their derivatives is maintained in the two series; in the unsubstituted

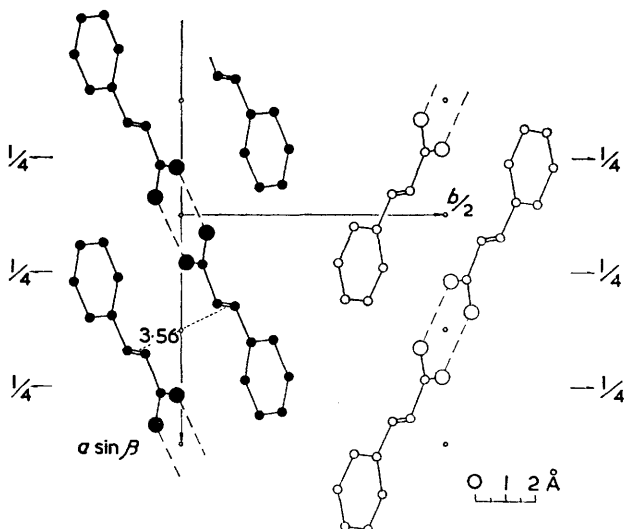
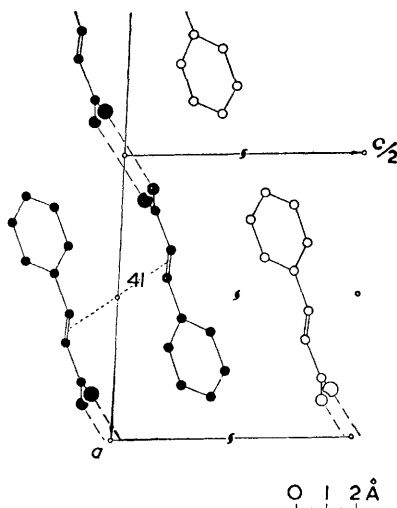


FIG. 4.  $\alpha$ -*trans*-Cinnamic acid; packing arrangement seen along [001] (Ladell, MacDonald, and Schmidt, to be published).

FIG. 5. *trans*-Cinnamide; packing arrangement seen [010] (Osaki and Schmidt, to be published).



acids the  $\beta$ -form is either unknown (benzoic), or metastable (cinnamic) with respect to the  $\alpha$ -form; in the halogeno-acids on the other hand the  $\alpha$ -type has not yet been observed.\*

Our chemical results can now be interpreted in terms of the structural data presented here. According to Table 1, correlation between the  $\beta$ -type and the photochemical formation of  $\beta$ -truxinic acids is complete. According to structure analyses nearest-neighbour contacts between  $>C=C<$  groups occur in this structure type between parallel

\* The relations between the various crystal structure types of cinnamic acid and their homologues briefly noted here will be discussed more fully elsewhere.

<sup>15</sup> Sim, Robertson, and Goodwin, *Acta Cryst.*, 1955, **8**, 157.

<sup>16</sup> Penfold and White, *Acta Cryst.*, 1959, **12**, 130.

molecules separated by a short ( $3.9 \pm 0.2 \text{ \AA}$ ) axis. The exclusive formation of the dimer of symmetry  $m$  from the  $\beta$ -lattice fits the assumption that this lattice consisting of parallel molecules constrains the reacting pair of monomers to form a cyclobutane dimer in which the two units are joined head-to-head while retaining the *trans*-configuration.

As for the  $\alpha$ -type, we have shown that, in cinnamic acid and in cinnamide at least, nearest-neighbour contact between  $\text{>C=C<}$  groups occurs between centrically related bonds at distances of the order of  $3.8 \text{ \AA}$ . Since, according to Table 1, all  $\alpha$ -type cinnamic acids dimerise to  $\alpha$ -truxillic acids we assert that formation of the centric dimer from the  $\alpha$ -lattice fits the assumption that this lattice, in which pairs of molecules are related by centres of symmetry, constrains the reacting monomers to form a cyclobutane dimer in which two units are joined head-to-tail while retaining the *trans*-configuration. In both lattices therefore reaction occurs between nearest neighbours; further, it takes place without change of configuration of the reaction partners except for the adjustment required by the passage from trigonal to tetrahedral bond angles at the reacting carbon atoms; finally, the crystallographic symmetry element relating the parent monomer pair is reproduced in the conformation of the dimer ( $\beta$ -lattice: translation  $\rightarrow m$ ;  $\alpha$ -lattice:  $\bar{1} \rightarrow \bar{1}$ .)

Since in the  $\alpha$ - and  $\beta$ -lattices reaction occurs between nearest neighbours separated by maximally  $4.1 \text{ \AA}$  we interpret photo-stability of the  $\gamma$ -form, in which nearest  $\text{>C=C<}$  groups make contact at  $4.7\text{--}5.1 \text{ \AA}$ , as due to lattice constraint which does not permit potentially reactive centres to move sufficiently close together to form a stable chemical compound.

The crystallographic data so far presented adequately interpret the chemical conclusions reached in the previous paper and summarised above. In particular the absence of dimers other than  $\alpha$ -truxillic and  $\beta$ -truxinic acids is in accord with the observation that so far only two (light-active) lattice types have been observed whose packing arrangements account for the formation of just these two dimers. The limited results of this Paper do not of course exhaust either geometry of contact between double bonds or stereochemistry of reaction products: according to de Jong<sup>17</sup> certain heavy-metal salts of *trans*-cinnamic acid can yield  $\delta$ -truxinic and  $\epsilon$ -truxillic acids, both of molecular symmetry 2. Further Papers in this series will show that sufficiently close  $\text{>C=C<}$  contact over screw axes or glide planes can initiate solid-state polymerisation. We shall also suggest that contact in the region between  $4.1$  and  $4.7 \text{ \AA}$  can lead to *cis-trans*-interconversion (Part IV).<sup>18</sup>

Finally, Sadeh and Schmidt<sup>19</sup> have pointed out that dimerisation of fumaric acid derivatives whose photochemistry has been studied by Griffin and his co-workers<sup>20,21</sup> follows the general principles derived for the cinnamic acids. Table 2 lists the cell constants of several derivatives in the series *trans*- $R^1CH=CHR^2$ . The crystal structure of fumaric acid<sup>22</sup> is unknown, and its light-stability cannot therefore be interpreted. On the other hand, the mono-<sup>19</sup> and di-methyl esters<sup>23</sup> and the dinitrile<sup>24</sup> of fumaric acid crystallise in cells having  $4 \text{ \AA}$  axes ( $\beta$ -type analogues); the formation of cyclobutane derivatives is in keeping with the arguments presented here, which are strongly supported by the conformation (symmetry  $m$ ) of the dimer of the monoester.<sup>19</sup> The light-stability of tetracyanoethylene<sup>25</sup> is in accord with its crystal structure<sup>26</sup> in which all  $\text{>C=C<}$  groups are more than  $5 \text{ \AA}$  apart. We have found that *trans,trans*-muconic<sup>27</sup> and sorbic

<sup>17</sup> de Jong, *Ber.*, 1923, **56**, 818.

<sup>18</sup> Part IV, following paper.

<sup>19</sup> Sadeh and Schmidt, *J. Amer. Chem. Soc.*, 1962, **84**, 3970.

<sup>20</sup> Griffin, Basinski, and Velluro, *Tetrahedron Letters*, 1960, No. 3, 13.

<sup>21</sup> Griffin, Velluro, and Furukawa, *J. Amer. Chem. Soc.*, 1961, **83**, 2725.

<sup>22</sup> Yardley, *J.*, 1925, **127**, 2207.

<sup>23</sup> Knaggs and Lonsdale, *J.*, 1942, 417.

<sup>24</sup> Post, private communication.

<sup>25</sup> Sadeh, unpublished observation.

<sup>26</sup> Bekoe and Trueblood, *Z. Krist.*, 1960, **113**, 1.

<sup>27</sup> Bregman and Schmidt, *J. Amer. Chem. Soc.*, 1962, **84**, 3785.

acids<sup>28</sup> (4 Å axes<sup>24</sup>) react on irradiation with ultraviolet light (<3000 Å); their photo-products are being studied. Dimethyl *trans,trans*-muconate and all-*trans*-hexatriene-1,6-dicarboxylate,<sup>19</sup> which do not belong to the β-type, appear to be light-stable.<sup>27</sup> Their crystal structures are being investigated.

TABLE 2.

	Ref.	a (Å)	b (Å)	c (Å)	β	Space group	$d_{\text{calc}}$ (g./cm. <sup>3</sup> )	n
Fumaric acid .....	22	7.56	15.00	6.20	90.7° 88.5 89.7 72.6	P $\bar{1}$	1.63	6
Methyl hydrogen fumarate .....	19	14.14	3.99	5.60	98.8 83.8 108.1	P $\bar{1}$	1.50	2
Dimethyl fumarate .....	23	3.92	9.24	5.93	112.8 109.3	P $\bar{1}$	1.47	1
Fumaronitrile .....	24	3.89	5.60	11.54	121.9	P2 <sub>1</sub> /n	1.21	2
Tetracyanoethylene .....	26	7.51	6.21	7.00	97.2 123.2	P2 <sub>1</sub> /n	1.30	2
<i>trans-trans</i> -Muconic acid .....	27	6.98	3.76	7.01	88.5 101.7	P $\bar{1}$	1.56	1
Sorbic acid .....	28	20.00	4.03	15.83	103.5 88.0	C2/c	1.19	8
Dimethyl <i>trans-trans</i> -muconate ...	19	7.74	5.81	5.82	121.8 106.1 81.4	P $\bar{1}$	1.33	1
Dimethyl hexatrienedicarboxylate	19	7.60	5.99	13.06	107.7 105.9	P $\bar{1}$	1.19	2

In conclusion we comment on the second stage of solid-state reactions, namely the appearance of the product phase. It is reasonable to assume that the dimer goes into solid solution in the lattice of the monomer and that as the dimer concentration rises the solubility limit is exceeded and the new phase precipitated. However, since the solubility of dimers in the monomer lattice and the stability of this solid solution must vary from compound to compound and within the polymorphs of each compound no generalisations are as yet possible. Indeed a wide variety of effects have been observed: powder lines of the product phase appear at low concentration (<10%) of dimer or only after higher concentration have been reached. The β-truxinic acids in particular show a wide variation of recrystallisation behaviour: several of these acids crystallise during the course of reaction in a metastable form not identical with the modification obtained by crystallisation from solvent. Alternatively, only a few diffuse or broad lines appear during exposure; in extreme cases no powder lines of the dimer can be seen even after 70% conversion. These phenomena are probably related to the fact that several β-truxinic acids crystallise with solvent of crystallisation, and that their solvent-free phases are either metastable or incapable of existence.

Two further points currently being worked on deserve brief mention. Concerning the yield of these dimerisation reactions it is clear that the α- and β-types differ in the theoretical maximum possible conversion into dimer. Whereas in the α-type two monomer units are paired (across crystallographic centres of symmetry), and therefore capable of dimerisation so long as they can maintain this alignment irrespective of progress of dimerisation elsewhere in the lattice, in the β-type a monomer molecule may find itself eventually isolated: a parallel stack designated by M ··· M ··· M ··· M ··· may react to form M<sub>2</sub> ··· M ··· M<sub>2</sub> in which the remaining monomer molecule is temporarily removed from reaction until recrystallisation has returned it to the monomer lattice. Significantly, the yield of photo-dimer is low and dimerisation rate exceptionally slow (5-bromo-2-hydroxycinnamic acid) where the product does not appear as a separate phase,

<sup>28</sup> Lonsdale, Robertson, and Woodward, *Proc. Roy. Soc.*, 1940, *A*, **178**, 43.



conceivably as the result of intermolecular hydrogen bonding which slows down the rate of recrystallisation. If this picture is correct then yields, particularly in the  $\beta$ -series, must be a function of temperature. Experiments to test this hypothesis are under way.

Secondly, the question arises whether photochemical reactions can take place in such a way that the product phase appears in an oriented form. We agree with the findings of Eanes and Donnay<sup>29</sup> that in the dimerisation of  $\alpha$ -cinnamic acid to  $\alpha$ -truxillic acid the product phase shows no signs of orientation; however, we suggest that the absence of orientation is due to too large a difference between the crystal structures of the monomers and dimers and that, where two structures are sufficiently closely related, as *e.g.*, in the system cinnamide  $\rightarrow$   $\alpha$ -truxillamide,<sup>14</sup> direct single-crystal transitions are in fact possible. This problem will be discussed elsewhere.

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DEPARTMENT OF X-RAY CRYSTALLOGRAPHY,  
WEIZMANN INSTITUTE OF SCIENCE, REHOVOTH, ISRAEL.

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<sup>29</sup> Eanes and Donnay, *Z. Krist.*, 1959, **111**, 368.

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