Crystal Structures of α-*trans*- and *p*-Methoxy-cinnamic Acids and their Relation to Thermal Mesomorphism

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p-Methoxycinnamic acid (I) is nematogenic but cinnamic acid (II), although as a hydrogen-bonded dimer it has the necessary molecular anisotropy, is not. The crystal structures of the two compounds have been determined at room temperature, and this difference can be directly attributed to differences in molecular packing.

Crystals of (II) are monoclinic, space group $P2_1/c$ with $a = 5.644(1)$, $b = 18.011(6)$, $c = 9.019(3)$ Å, $\beta = 121.47(2)°$, and $Z = 4$. The structure was solved by direct methods and refined by least squares to R 0.059 for 899 independent reflections whose intensities were measured by counter diffractometry. Crystals of (I) are triclinic, space group $P\bar{1}$ with $a = 8.336(2)$, $b = 12.026(4)$, $c = 4.842(2)$ Å, $\alpha = 81.80(3)$, $\beta = 99.28(2)$, $\gamma = 111.90(3)°$, and $Z = 2$. The structure was solved by a Fourier-transform method, and refined by least squares to R 0.048 for 1 675 independent reflections.

The molecular packing in crystals of (II) is zig-zag type with the long axes of the hydrogen-bonded dimers inclined at 45°. Crystals of (I) have all molecules parallel in a three-dimensionally interlocked arrangement characteristic of nematogenic crystals.

THERMOTROPISM of the *trans*-isomers of the *p*-n-alkoxycinnamic acids has long been known,[1] and the range of thermal stabilities of the mesophases for the acids with from C_1 to C_{16} side-chains has been established.[2] Unlike the corresponding C_1 and C_2 alkoxybenzoic acids, which melt to isotropic liquids directly at 183 and 196 °C, respectively,[2] *p*-methoxycinnamic acid (I) yields a nematic phase at 170 °C before melting to an isotropic liquid at 182 °C. Cinnamic acid (II), though as a hydrogen-bonded dimer it has the necessary molecular anisotropy, shows no thermal mesomorphism, melting to an isotropic liquid at 135—136 °C.

In order to obtain information bearing on these differences in thermal behaviour, we have determined the room-temperature crystal structures, since these are self-evidently the starting points from which a nematic phase or isotropic melt derives. The crystal structures of *p*-methoxy- and *p*-ethoxy-benzoic acids have been reported,[3] and evidence has been presented[4] that their high m.p.s, which alone inhibit a nematic transition,[2] arise from strong interactions between the phenyl rings of overlapping molecules. The thermotropism of *p*-methoxycinnamic acid, and the much lower m.p. of cinnamic acid, rule out such interactions and indicate a different mode of molecular packing in each, and between these two acids and the two alkoxybenzoic acids. Our results clearly demonstrate these differences, and explain the differences in thermal behaviour of these four compounds.

TABLE 1

(*a*) Atomic co-ordinates for (II) (C and O × 10^4, H × 10^3), and thermal parameters for H atoms *

Atom	x/a	y/b	z/c	B/Å^2
O(1)	3 270(5)	482(2)	826(3) †	
O(2)	7 631(5)	73(2)	2 122(3)	
C(1)	5 690(7)	392(2)	2 174(4)	
C(2)	6 207(7)	659(2)	3 859(4)	
C(3)	4 300(7)	1 015(2)	4 014(4)	
C(4)	4 634(6)	1 309(2)	5 630(4)	
C(5)	7 029(7)	1 196(2)	7 244(4)	
C(6)	7 269(7)	1 497(2)	8 729(5)	
C(7)	5 136(9)	1 900(2)	8 641(5)	
C(8)	2 747(8)	2 022(2)	7 048(5)	
C(9)	2 485(7)	1 725(2)	5 546(4)	
H(O)	282(8)	21(2)	−052(5)	6.6(10)
H(2)	808(7)	59(2)	488(5)	4.6(8)
H(3)	240(7)	110(2)	296(4)	4.7(8)
H(5)	875(7)	92(2)	743(4)	4.5(8)
H(6)	909(7)	141(2)	995(5)	5.3(9)
H(7)	530(8)	213(3)	975(6)	7.4(11)
H(8)	113(8)	234(2)	695(5)	5.7(9)
H(9)	78(8)	188(2)	543(5)	6.5(10)

(*b*) Thermal parameters (× 10^4) for non-hydrogen atoms. The exponent has the form: $-[h^2_i\beta_{ii} + \ldots 2h_ih_j\beta_{ij} + \ldots]$

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
O(1)	563(13)	59(1)	125(4)	56(3)	108(6)	−3(2)
O(2)	497(12)	62(1)	152(4)	36(3)	140(6)	−14(2)
C(1)	456(16)	33(1)	140(5)	8(3)	130(8)	3(2)
C(2)	434(15)	31(1)	149(6)	4(3)	132(8)	0(2)
C(3)	437(15)	31(1)	124(5)	1(3)	115(7)	−1(2)
C(4)	417(15)	23(1)	152(6)	4(3)	137(8)	4(2)
C(5)	523(18)	34(1)	186(7)	15(4)	181(9)	7(2)
C(6)	713(24)	38(1)	263(9)	24(5)	282(13)	1(3)
C(7)	844(27)	46(2)	214(8)	24(5)	260(13)	−13(3)
C(8)	702(23)	49(2)	160(7)	27(5)	156(10)	−10(3)
C(9)	487(17)	36(1)	143(6)	17(4)	109(8)	−10(2)

* Standard deviations, in parentheses, in this and other Tables are applicable to the least significant figure given. They are derived here as $\sigma(u_j) = a^{jj}\Sigma w(\Delta F)^2/(n - m)$. † To maintain conformity with Figure 7, 5 000 should be added to values for z/c.

RESULTS AND DISCUSSION

The atomic parameters defining the crystal structures are given in Tables 1 and 2, and the molecular structures are illustrated by Figures 1 and 2. Bond distances and angles are given in Table 3. Both compounds exist in the crystal as hydrogen-bonded dimers with O · · · O 2.630 in cinnamic acid (II) and 2.614 Å in the methoxy acid (I). For each compound, in the crystal, there is evidence, both from the near equivalence of C–O bond distances in the carboxy-group and from difference electron-density maps calculated in the carboxy-planes, that the $-CO_2H$ moiety is disordered by interchange of carbonyl and hydroxy-groups. This phenomenon is apparently common in the

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[1] R. Stoermer, *Ber.*, 1911, **44**, 637; R. Stoermer and F. Wodarg, *ibid.*, 1928, **61**, 2323.

[2] G. M. Bennett and B. Jones, *J. Chem. Soc.*, 1939, 420.

[3] R. F. Bryan, *J. Chem. Soc.* (*B*), 1967, 1311; R. F. Bryan and J. J. Jenkins, *J.C.S. Perkin II*, 1975, 1171.

TABLE 2

(*a*) Atomic co-ordinates for (I) (C and O × 10^4, H × 10^3), and thermal parameters for H atoms

Atom	*x*/*a*	*y*/*b*	*z*/*c*	*B*/Å^2
O(1)	10 397(2)	1 144(1)	7 322(3)	
O(2)	7 960(2)	−382(1)	8 198(3)	
O(3)	5 493(2)	4 079(1)	6 718(3)	
C(1)	8 791(2)	558(2)	13 282(4)	
C(2)	7 810(2)	959(2)	4 242(4)	
C(3)	8 531(2)	1 943(2)	2 598(4)	
C(4)	7 676(2)	2 443(2)	141(3)	
C(5)	5 917(2)	1 930(2)	−785(4)	
C(6)	5 130(3)	2 438(2)	−3 096(4)	
C(7)	6 120(2)	3 490(2)	−4 524(4)	
C(8)	7 882(2)	4 020(2)	−3 637(4)	
C(9)	8 646(2)	3 503(2)	−1 351(4)	
C(10)	3 665(3)	3 620(2)	−7 658(5)	
H(2)	657(2)	43(2)	388(4)	3.6(4)
H(3)	970(2)	237(2)	310(4)	3.4(4)
H(5)	519(3)	119(2)	14(4)	3.7(4)
H(6)	390(3)	203(2)	−364(4)	4.4(8)
H(8)	857(3)	479(2)	−466(4)	4.5(5)
H(9)	989(3)	387(2)	−72(4)	3.6(4)
H(10a)	339(3)	419(2)	−909(5)	5.7(6)
H(10b)	324(3)	277(2)	−821(5)	5.5(6)
H(10c)	294(3)	359(2)	−598(5)	5.8(6)

(*b*) Thermal parameters (× 10^4) for non-hydrogen atoms

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
O(1)	126(2)	90(1)	426(7)	25(1)	4(3)	30(2)
O(2)	155(2)	80(1)	384(6)	21(4)	16(3)	29(2)
O(3)	151(2)	84(1)	455(7)	43(1)	0(3)	42(2)
C(1)	137(3)	68(2)	272(7)	40(2)	17(4)	−13(2)
C(2)	130(3)	72(2)	304(8)	34(2)	−2(4)	−6(3)
C(3)	113(3)	70(2)	309(8)	33(2)	6(4)	−9(3)
C(4)	119(3)	59(1)	280(7)	31(2)	24(4)	−3(2)
C(5)	119(3)	64(2)	348(8)	19(2)	34(4)	19(3)
C(6)	105(3)	70(2)	384(9)	24(2)	2(4)	2(3)
C(7)	129(3)	62(1)	319(8)	39(2)	20(4)	2(3)
C(8)	124(3)	62(2)	436(9)	22(2)	44(4)	29(3)
C(9)	101(3)	67(2)	402(9)	21(2)	8(4)	−2(3)
C(10)	158(3)	96(2)	538(12)	53(2)	−48(5)	16(4)

TABLE 3

Bond distances and angles (not involving hydrogen) with their standard deviations * in parentheses

	(II)	(I)
(*a*) Distances (Å)		
O(1)–C(1)	1.279(4)	1.266(2)
O(2)–C(1)	1.259(4)	1.272(2)
C(1)–C(2)	1.470(4)	1.467(2)
C(2)–C(3)	1.322(4)	1.323(2)
C(3)–C(4)	1.467(4)	1.459(2)
C(4)–C(5)	1.391(4)	1.387(2)
C(5)–C(6)	1.384(4)	1.386(2)
C(6)–C(7)	1.372(6)	1.384(2)
C(7)–C(8)	1.381(5)	1.388(2)
C(8)–C(9)	1.390(4)	1.374(3)
C(9)–C(4)	1.395(4)	1.399(2)
C(7)–O(3)		1.395(2)
O(3)–C(10)		1.426(2)
(*b*) Angles (°)		
O(1)–C(1)–O(2)	122.7(3)	122.5(2)
O(1)–C(1)–C(2)	118.6(3)	120.2(2)
O(2)–C(1)–C(2)	118.7(3)	117.3(2)
C(1)–C(2)–C(3)	122.3(3)	122.4(2)
C(2)–C(3)–C(4)	126.2(3)	127.2(2)
C(3)–C(4)–C(5)	122.6(3)	123.1(2)
C(4)–C(5)–C(6)	120.5(3)	122.0(2)
C(5)–C(6)–C(7)	120.7(4)	119.3(2)
C(6)–C(7)–C(8)	119.7(4)	119.8(2)
C(7)–C(8)–C(9)	120.1(4)	120.3(2)
C(8)–C(9)–C(4)	120.5(3)	121.2(2)
C(9)–C(4)–C(5)	118.5(3)	117.5(2)
C(6)–C(7)–O(3)		124.7(2)
C(8)–C(7)–O(3)		115.5(2)
C(7)–O(3)–C(10)		117.7(2)

crystal structures of aromatic carboxylic acids.[3-6] The disposition of the hydrogen atoms in the hydrogen bonds is illustrated in Figure 3.

Aside from the anomalous C–O distances in the carboxy-groups, other bond distances and angles have their expected values, and there is very good agreement between the results for the two acids, the root-mean-square deviation for corresponding values of bond distances being 0.008 Å. The enlarged valence angle at C(3) in each and the asymmetry in exocyclic valence angles at C(7) in (I) were expected from previous studies.[3,4,7-12]

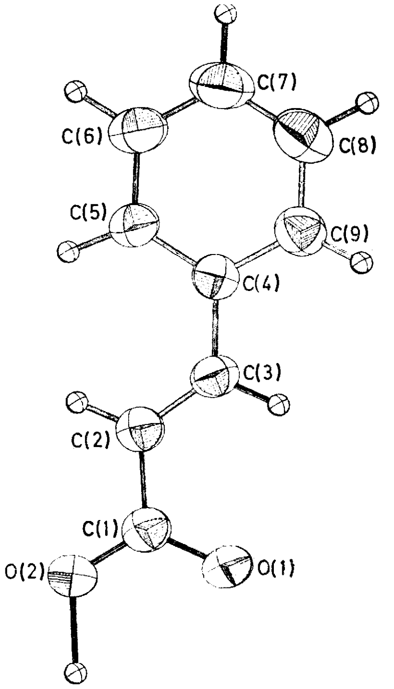

FIGURE 1 Thermal ellipsoid plot[9] for cinnamic acid (II) showing the numbering scheme adopted; hydrogen atoms are numbered according to the atom of attachment. Ellipsoids are drawn with 50% probability for C and O, and on an arbitrary scale for H

The overall molecular conformations may be defined in terms of three planar groups of atoms: (1) the phenyl ring; (2) the four-atom olefin group C(1)—(4), and (3) the four-atom carboxy-group centred on C(1). Information on these least-squares mean planes is given in Table 4. In (II), the dihedral angles between planes are: (1)–(2) 4.6, (2)–(3) 2.2, and (1)–(3) 6.8°. In (I), these

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[4] R. F. Bryan and L. F. Fallon, III., *J.C.S. Perkin II*, 1975, 1175

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[9] C. K. Johnson, Report ORNL 3794, 1965, Oak Ridge National Laboratory, Tennessee, U.S.A.

[10] G. Tieghi and M. Zocchi, *Cryst. Struct. Comm.*, 1972, **1**, 167.

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[12] R. F. Bryan, H. H. Mills, and J. C. Speakman, *J. Chem. Soc.*, 1963, 4351.

angles are 2.3, 1.6, and 3.0°, so that this acid is much more nearly planar overall than is (II). Indeed, the (1)–(2) dihedral angle in (I) is the smallest thus far recorded for a cinnamic acid derivative. These dihedral angles, and the enlargement of the valence angle at C(3), have commonly been attributed to 1,6-interactions involving H(2) and H(5), but a comparison of our results with those found for other cinnamates and cinnamides suggests that intermolecular forces predominate in determining the (1)–(2) dihedral angle, and that electronic forces dictate the valence angle at C(3). Consistent with intramolecular repulsions operating, a value of 4° has been found for the (1)–(2) angle in *NN*-dimethyl-*p*-bromocinnamide,[7] in methyl *p*-bromocinnamate,[8] and in methyl *m*-bromocinnamate.[8] However, in pentaerythritol tetracinnamate [10] the angles are 6, 10, 10, and 22°, in *p*-chlorocinnamide 14°,[11] in ammonium hydrogen dicinnamate 17°,[12] and in the alkaloid maytenine 30°.[13] Clearly, only a very small amount of this angular displacement is directly attributable to intramolecular H · · · H repulsions, and the angle is normally determined by intermolecular forces. The valence angle C(2)–C(3)–C(4) seems, moreover, to remain enlarged to the same extent even when the (1)–(2) dihedral angle is large. For the compounds of refs. 7—13 the angle ranges from 126.2 to 129.3° with no correlation obvious with the (1)–(2) angle. The H · · · H separation does vary with this torsion angle, however, so that the more-or-less constant enlargement is to be attributed either to electronic requirements or to a 1,3-steric repulsion between C(2) and C(4) arising from the shortness of the C(2)=C(3) bond. This latter effect does not predominate, however, as may be seen from the general identity of length of C(1)–C(2) and C(3)–C(4),

TABLE 4

Least-squares mean planes through selected groups of atoms as defined in the text

Coefficients are given for the equations in the form $aX + bY + cZ = d$ with X, Y, and Z in Å with respect to an orthogonal axial system related to the cell system by the matrix:

(II)	5.6440	0.0000	0.0000	(I)	8.3360	0.0000	0.0000
	0.0000	18.0110	0.0000		−4.4850	11.1584	0.0000
	−4.7081	0.0000	7.6926		−0.7807	0.4309	4.7592

Plane		a	b	c	d	$\Delta_{av.}$	$\Delta_{max.}$/Å × 10^3
(1):	(II)	−0.5387	−0.8336	0.1220	−1.4185	3	7
	(I)	−0.5383	0.5931	0.5987	−1.1895	2	3
(2):	(II)	−0.4710	−0.8699	0.1465	−1.3954	4	5
	(I)	−0.5651	0.5931	0.5736	−1.3403	10	10
(3):	(II)	−0.4396	−0.8831	0.1638	−1.3052	3	6
	(I)	−0.5588	0.6145	0.5569	−1.3200	1	2

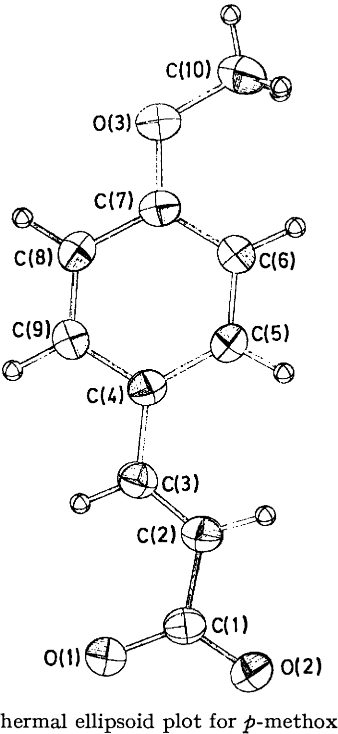

FIGURE 2 Thermal ellipsoid plot for *p*-methoxycinnamic acid (I)

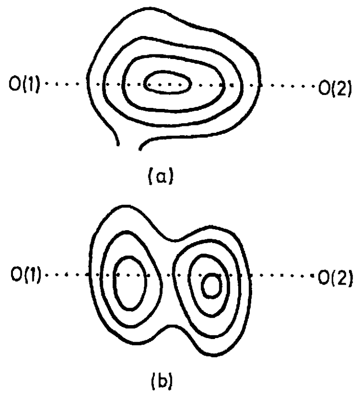

FIGURE 3 Difference electron-density in the carboxy-planes between the oxygen atoms. Contour levels are at 0.1 eÅ^{-3} from zero; (a) (II), (b) (I)

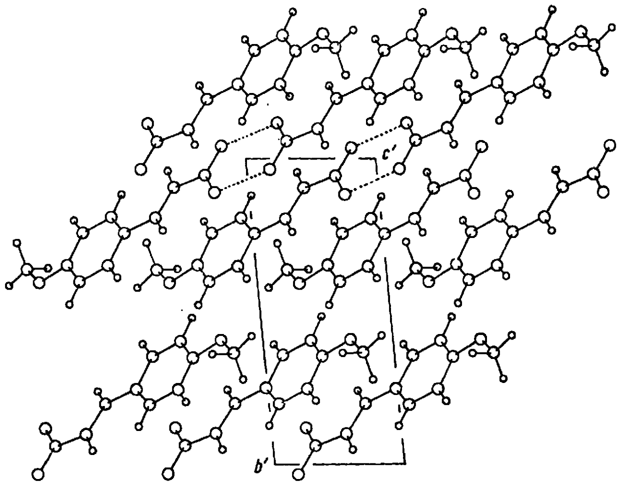

FIGURE 4 Projection down the *a* axis of the unit cell of the molecular arrangement in crystals of (I)

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[13] B. T. Blaylock and R. F. Bryan, unpublished results.

whereas the angle C(1)–C(2)–C(3) remains fairly constant around 122°.

Our main concern in this analysis, however, is not with the fine details of molecular geometry, but with the way in which the molecules pack in the crystals. Since the packing in each case is very different, and since in our view this determines whether or not a mesophase is produced, it is appropriate to consider each arrangement separately and in detail.

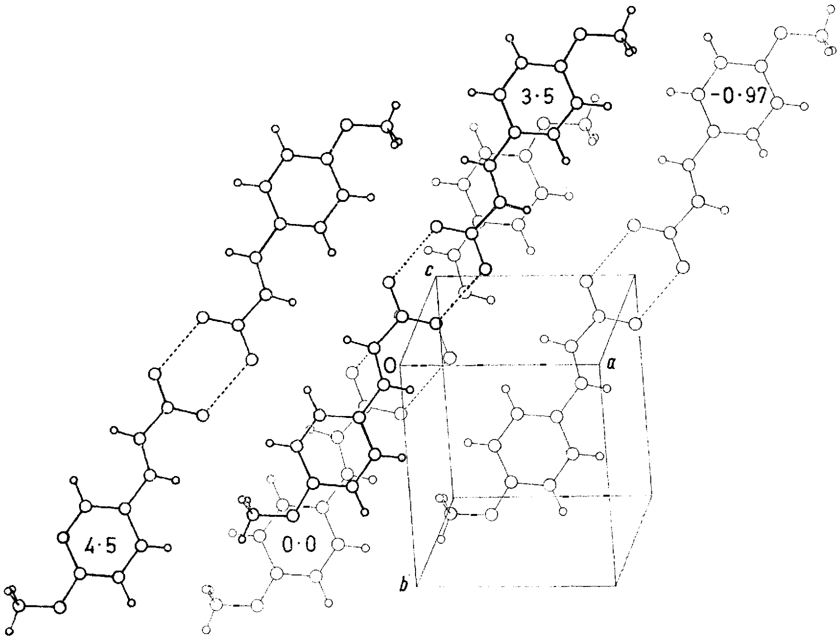

FIGURE 5 Projection on the molecular plane of stacks of (I) dimers. The height (Å) of each dimer above the reference plane is indicated. Hydrogen bonds are indicated by the broken lines

TABLE 5

Shorter intermolecular contacts (Å)

(*a*) For (II)

O(1) ··· H(6^{I})	2.65	H(6) ··· H(3^{II})	2.42
H(7) ··· C(9^{III})	2.90	H(5) ··· O(2^{IV})	2.58
C(1) ··· C(5^{V})	3.41	C(2) ··· C(4^{V})	3.64
C(2) ··· C(3^{V})	3.66	O(1) ··· C(1^{VI})	3.44
O(2) ··· C(1^{VI})	3.41	O(1) ··· O(2^{VI})	2.63

Roman numeral superscripts refer to the following equivalent positions relative to the reference molecule at x, y, z:

I $x - 1, y, z - 1$; II $1 + x, y, 1 + z$; III $x, \frac{1}{2} - y, \frac{1}{2} + z$; IV $2 - x, y, 1 + z$; V $1 - x, \bar{y}, 1 - z$; VI $1 - x, \bar{y}, \bar{z}$.

(*b*) For (I)

H(8) ··· H(8^{I})	2.30	H(10c) ··· H(3^{II})	2.55
H(8) ··· C(8^{I})	2.96	H(5) ··· O(2^{III})	2.65
H(10b) ··· O(2^{IV})	2.66	C(3) ··· C(8^{V})	3.53
C(1) ··· C(4^{V})	3.45	C(1) ··· C(3^{V})	3.57
O(1) ··· C(1^{VI})	3.33	O(1) ··· O(2^{VII})	2.61

I $2 - x, 1 - y, -z - 1$; II $x - 1, y, z - 1$; III $1 - x, \bar{y}, 1 - z$; IV $1 - x, \bar{y}, \bar{z}$; V $x, y, 1 + z$; VI $2 - x, \bar{y}, 1 - z$; VII $2 - x, \bar{y}, 2 - z$.

A view of the molecular arrangement in crystals of (I) is shown in Figure 4, and shorter intermolecular contacts are given in Table 5. There are no abnormally close contacts between molecules so that such dipolar attractions as may be important in the crystal structure operate across normal van der Waals separations. Figure 5 shows a projection of the structure on the plane of a single dimeric unit. As is implied by the space-group symmetry, the molecular planes are all parallel, as are the longitudinal axes of the dimers. The dimers are stacked, one atop another, in a stepped fashion. Within a stack there is a vertical displacement of *ca.* 3.5 Å between successive molecules, a longitudinal displacement of *ca.* 3.2 Å, and a lateral displacement of *ca.* 1.1 Å. The stepped stacks are repeated, parallel to one another, with a lateral displacement of *ca.* 5.5 Å, a longitudinal displacement of *ca.* 7.5 Å, and a vertical displacement of *ca.* 1.0 Å. When we consider this arrangement in detail, it is seen that it constitutes an ideal starting point for the generation of a mesophase.

The longitudinal displacement within a stack ensures a separation of the phenyl rings of successive molecules, placing these rings between the olefin group of one neighbour and the methoxy-oxygen of another. This arrangement avoids the direct overlap of phenyl rings characteristic of *p*-methoxy- and *p*-ethoxy-benzoic acids[3] [(III) and (IV)], and hence avoids the high melting points which inhibit mesophase formation in these two acids.[2] There is, however, a more important difference in the structures. While the transition temperature (170 °C) from the ordered solid to the nematic phase in (I) is lower than the m.p.s of (III) and (IV), it is nonetheless higher than the highest nematic-isotropic transition temperature noted for any alkoxybenzoic acid.[2]

In the three alkoxybenzoic acids whose crystal structures have been determined[3,4] the molecules are arranged head-to-tail with the hydrogen-bonded carboxy-group of one dimer flanked by the regions of van der Waals separation between the alkyl terminii of others. The existence of dimeric units is therefore necessary for imbricated overlap, and disruption of the hydrogen bonds destroys this. As may be seen from Figure 5, the environment of the carboxy-groups of a given dimer of (I) differs from that in the alkoxybenzoic acids. The longitudinal displacement within a stack in (I) sandwiches the carboxy-groups of one dimer between the stereochemically rigid olefin groups of neighbours above and below, and the displacements between stacks also flank the carboxy-linkages with phenyl and olefin groups of neighbours. In this arrangement, even if the hydrogen bonds rupture, imbricated overlap persists to a significant extent, and it is to this feature of the crystal structure that we attribute the enhanced thermal stability of the mesophase in (I).

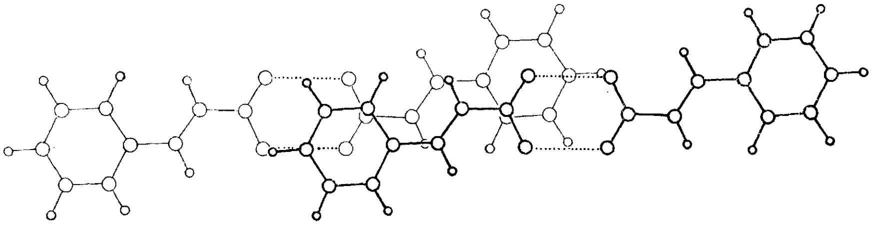

FIGURE 6 Projection on the molecular plane of a pair of centrosymmetrically related dimers of cinnamic acid, illustrating the packing within a single stack. The perpendicular separation between dimers is *ca.* 3.4 Å. Hydrogen bonds are indicated by dotted lines

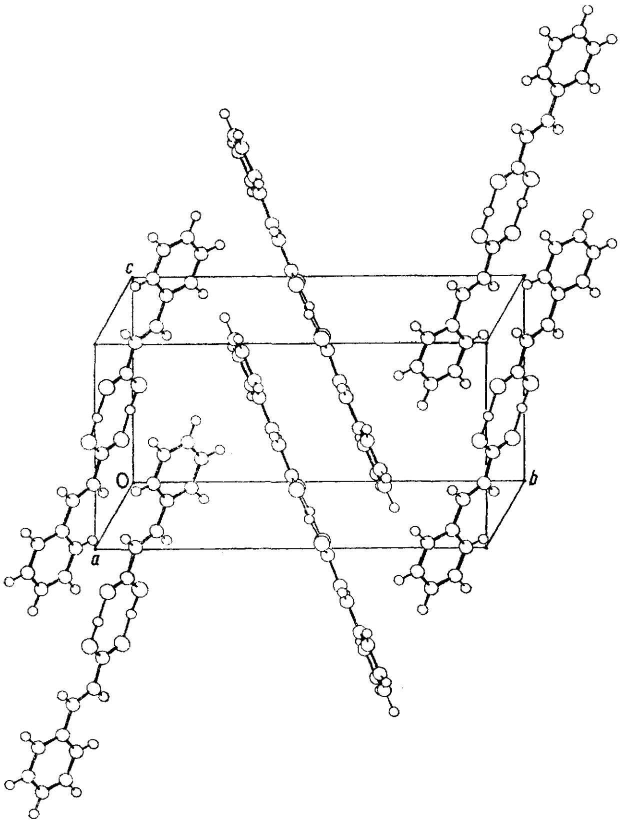

FIGURE 7 Projection down the *a* axis of the unit cell of the molecular arrangement in cinnamic acid. Note the relative dispositions of alternating stacks of dimers

The contrast between the molecular packing in (I) and (II) is instructive, and further emphasizes the critical role played by the molecular arrangement in the ordered crystal. As a hydrogen-bonded dimer, cinnamic acid has an overall length of 19 Å, or 21 Å if van der Waals radii are included, and has a breadth similar to that of (I). It is significantly longer, in this form, than many related covalent compounds showing nematic behaviour, and clearly has the molecular anisotropy which is a necessary, if not a sufficient, condition for such behaviour. We suggest that the reason for its failure to yield a mesophase lies in the way in which the molecules are arranged in the ordered crystal.

Figure 6 shows a projection on the molecular plane of a pair of centrosymmetrically related hydrogen-bonded dimers, corresponding to the stepped stacks of Figure 5. The obvious point of difference from (I) is the much larger longitudinal displacement of one dimer with respect to the other (*ca.* 8.2 Å). This results in a greatly reduced parallel overlap between the dimers, within a stack, and this reduced overlap does not allow complete sandwiching of the carboxy-groups of one dimer with covalently bonded regions of others. This diminished parallel overlap also leads to much weaker intermolecular attractions within a stack.

More important is the situation revealed by Figure 7, where it is seen that successive stacks are repeated in an alternating fashion laterally. The angle between the long axes of dimers in different stacks is 45°. Because no enhancement of order is to be expected with increasing temperature, this initial 45° orientation of the stacks must lead to random rearrangement of the dimer axes on melting either toward a parallel or a perpendicular relationship to one another: in other words to an isotropic melt.

EXPERIMENTAL

Cinnamic Acid (II)

Crystal Data.— $C_9H_8O_2$, $M = 148.16$. Monoclinic, $a = 5.644(1)$, $b = 18.011(6)$, $c = 9.019(3)$ Å, $\beta = 121.47(2)°$, $U = 781.9$ Å^3, $D_m = 1.248$, $Z = 4$, $D_c = 1.258$, $F(000) = 312$. Mo-K_α, $\lambda = 0.71\,069$ Å; μ(Mo-K_α) = 0.95 cm^{-1}. Space group $P2_1/c$.

Crystallographic Measurements.—Cell dimensions were found by a least-squares fit to the observed diffractometer values of $\pm 2\theta$ for 23 general reflections. The a and b axes of the cell, which is here given in the conventional setting $P2_1/c$, correspond to the c and b axes of the unit cell previously reported [14] for (II) in setting $P2_1/n$.

One quadrant of reciprocal space was surveyed to 2θ 51° and scattered intensity significantly above background $[I > 3\sigma(I)]$ measured by scintillation counting with pulse-height analysis at 899 of the 1 447 reciprocal lattice points surveyed. The θ—2θ scan method was used with a scan range of 3° in 2θ and a scan speed of 2° min^{-1}, and graphite-monochromated Mo-K_α radiation. Variations in intensity of two reference reflections chosen to monitor the experimental stability were very small and no absorption correction was applied.

Structure Analysis.—The phase problem was solved by direct methods (MULTAN) [15] by use of the 200 largest E values. Block-diagonal isotropic least-squares refinement of the parameters found from the E map gave R 0.16, and adoption of anisotropic thermal parameters gave R 0.10 at convergence. All hydrogen atoms were then located from a difference electron-density map and included in the refinement with isotropic thermal parameters. With a conventional weighting scheme [16] convergence was reached with R 0.059. Scattering functions were taken from ref. 17. With the exception of MULTAN, where the calculation was carried out on a CDC 6400 computer, all calculations were carried out with programs written in this laboratory for the XDS Sigma 2 computer, also used to control the diffractometer.*

p-*Methoxycinnamic Acid* (I)

Crystal Data.—$C_{10}H_{10}O_3$, $M = 178.18$. Triclinic, $a = 8.336(2)$, $b = 12.026(4)$, $c = 4.842(2)$ Å, $\alpha = 81.80(3)$, $\beta = 99.28(2)$, $\gamma = 111.90(3)°$, $U = 442.7$ Å^3, $D_m = 1.32$, $Z = 2$, $D_c = 1.336$, $F(000) = 188$. Mo-K_α radiation, $\lambda = 0.71069$ Å, $\mu(\text{Mo-}K_\alpha) = 1.05$ cm^{-1}. Space group $P\bar{1}$.

Crystallographic Measurements.—The same techniques were used as for (II) to measure the intensities of 1 675 independent non-zero reflections out of 2 543 locations surveyed within a single hemisphere, $2\theta \leqslant 60°$.

Structure Analysis.—The structure was determined by use of a locally modified version of the molecular-transform fitting routine ORTRAN.[18] The model used was a planar centrosymmetric hydrogen-bonded dimer excluding the terminal methyl group whose orientation was not known in advance. The solution of second highest figure of merit, corresponding to a molecule aligned with its long axis inclined at 45° to the short 4.8 Å axis of the unit cell, proved correct. The methyl carbon atom was located from a difference electron-density map, and refinement of the structural parameters by least-squares methods gave, at convergence, R 0.17 with isotropic and 0.087 with anisotropic thermal parameters. Hydrogen atoms were located from a difference electron-density map and included in the refinement with isotropic thermal parameters to yield R 0.048 at convergence when a Hughes-type weighting scheme was used.[19]

For both acids difference electron-density maps were calculated in the planes of the carboxy-groups to locate the hydrogen atoms. In each case, (Figure 3) there is convincing evidence of disorder in the position of these atoms.

We thank William C. Schmidt for modifications of the ORTRAN routine to fit the XDS Sigma 2 computer.

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* Observed and calculated structure factors for (I) and (II) are listed in Supplementary Publication No. SUP 21503 (20 pp., 1 microfiche.) For details see Notice to Authors No. 7, in *J.C.S. Perkin II*, 1974, Index issue.

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