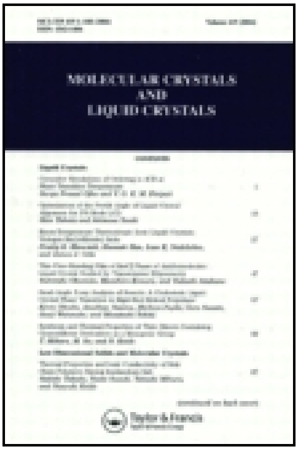

Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Crystal Structure Basis for the Absence of Thermal Mesomorphism in p-Hydroxy-trans-cinnamic Acid

R. F. Bryan [a] & P. G. Forcier [a]

[a] Chemistry Department, University of Virginia, Charlottesville, Virginia, 22901, USA

Version of record first published: 20 Apr 2011.

To cite this article: R. F. Bryan & P. G. Forcier (1980): Crystal Structure Basis for the Absence of Thermal Mesomorphism in p-Hydroxy-trans-cinnamic Acid, Molecular Crystals and Liquid Crystals, 60:3, 157-165

To link to this article: http://dx.doi.org/10.1080/00268948008072397

Mol. Cryst. Liq. Cryst., 1980, Vol. 60, pp. 157–166
0026-8941/80/6003-0157$04.50/0

Crystal Structure Basis for the Absence of Thermal Mesomorphism in *p*-Hydroxy-*trans*-cinnamic Acid

R. F. BRYAN and P. G. FORCIER
Chemistry Department, University of Virginia, Charlottesville, Virginia 22901, USA

(*Received August 3, 1979; in final form November 8, 1979*)

The molecular packing in *p*-hydroxy-cinnamic acid has been determined by single-crystal x-ray analysis in order to establish the role played by hydrogen bonding in inhibiting mesophase formation. The molecules exist in the crystal as centrosymmetric hydrogen-bonded dimers whose long axes are inclined at ± 84.7° to the crystal *b*-axis and lie almost in the (104) crystal planes. Rows of dimers lying parallel to *b* are linked into infinite sheets coincident with the (104) planes by head-to-tail hydrogen bonds involving the phenolic —OH groups. These sheets are interlocked by the alternating ring orientations of neighboring molecules in adjacent sheets.

Crystals belong to the monoclinic system, space group $P2_1/c$, with $a = 8.707(3)$, $b = 5.256(2)$, $c = 17.207(6)$ Å, $\beta = 99.67(2)°$, and $Z = 4$. The structure was solved by direct methods, and least-squares refinement gave $R = 0.057$ for 800 independent reflections whose intensities were measured by counter diffractometry.

INTRODUCTION

It is well known that many compounds which on the basis of their molecular anisotropy might be expected to form liquid crystals fail to do so when they contain substituents capable of taking part in intermolecular hydrogen bond formation.[1] There are at least two ways in which hydrogen bonding in the solid may act to inhibit mesophase formation. In the first case, an example of which is provided by the crystal structure of *p*-[(*p*-methoxybenzylidene) amino]phenol,[2] hydrogen bonding may lead to a molecular arrangement in the solid in which the local three-dimensional parallelism of molecules which is an apparent precondition for mesomorphism is absent. Thus, in the phenol, hydrogen bonding between the terminal hydoxy group and the central nitrogen atom of adjacent molecules leads to infinite molecular chains in which the long axes of linked molecules alternate at 70 and 110°

to one another leading to an overall packing mode incapable of transition to a mesophase.[3]

In the second case the molecular arrangement might still be spatially compatible with transition to a mesophase but the hydrogen bonding acts to stabilize the crystal structure to a temperature in excess of the upper limit of thermal stability of the potential mesophase. Such an example is provided by the crystal structure of *p*-hydroxy-*trans*-cinnamic acid (POCA) described here.

EXPERIMENTAL

Crystals for the X-ray study were grown by recrystallization of a commercial sample (Aldrich Chemical Co.) from ethanol. The solid decomposes at 216° without melting.

Crystal data $C_9H_8O_3$, mol. wt. 164.2. Monoclinic, $a = 8.707(3)$, $b = 5.256(2)$, $c = 17.207(6)$ Å, $\beta = 99.67(2)°$, cell volume = 776.3 Å^3, $D_{obs} = 1.40$, $Z = 4$, $D_{cal} = 1.405$ g cm^{-3}. Cu Kα radiation, $\lambda = 1.5418$ Å, $\mu = 9$ cm^{-1}. Space group $P2_1/c$.

The space group was uniquely determined from the conditions governing diffraction: $h0l$ with $l = 2n$ only, and $0k0$ with $k = 2n$ only as observed on 25° precession photographs taken with Mo Kα radiation. The unit cell dimensions were derived from a least-squares fit of the observed diffractometer values of $\pm 2\theta$ for 20 strong general reflections measured for a carefully centered crystal. The density was determined by flotation in aqueous potassium iodide solution.

Intensity measurements were made, using monochromatic Cu Kα radiation, from a single crystal 0.3 × 0.2 × 0.3 mm mounted with a^* parallel to the ϕ-axis on a Picker four circle diffractometer operated under the control of an XDS Sigma 2 computer. A single quadrant of reciprocal space was examined ($2\theta < 120°$) using the θ–2θ scan technique with a scan range of 2° and a scan speed of 2° min^{-1} in 2θ. Scintillation counting was used with pulse-height analysis. A total of 1147 independent reciprocal lattice points accessible to the system was surveyed and intensity significantly above background [$I > 3\sigma(I)$] was recorded at 800 of them. The intensities of two reference reflections were monitored after every 50 measurements to check the stability of the experimental conditions. Their intensities showed a 1.7% r-m-s deviation about their mean values with no systematic trends apparent. Intensities were reduced to structure amplitudes and normalized structure amplitudes were calculated in the usual way. No correction was made for absorption.

The structure was solved by use of the program *MULTAN*,[4] and the parameters refined by the block-diagonal least-squares method using the

800 significant reflections. Hydrogen atoms were located from a three-dimensional difference electron-density map and their positional parameters included in the refinement. Anisotropic thermal parameters were adopted for C and O, isotropic values for H. Scattering factors were taken from Ref. 5. Convergence was reached with the average shift to error ratio 0.08 and the maximum ratio 0.55. For the 800 reflections used the final conventional weighted and unweighted residuals were 0.057 and 0.050. For the complete set of 1147 measurements the unweighted residual was 0.070.†

Except for the programs *MULTAN* and *ORTEP*,[6] for which a CDC Cyber 172 computer was used, all computations were carried out with programs written in this laboratory for the XDS Sigma 2 computer.

RESULTS AND DISCUSSION

Atomic parameters defining the crystal structure are given, together with their estimated standard deviations, in Table I. The molecules are present in the crystal as centrosymmetric hydrogen-bonded dimers, the centers of the dimers coinciding with the space group centers of symmetry at 0, 0, 0 and 0, $\frac{1}{2}$, $\frac{1}{2}$ An *ORTEP* diagram of one such dimer, showing the numbering scheme adopted, is shown in Figure 1. Bond lengths and angles, with their associated e.s.d's, are given in Table II.

The O···O separation in the O—H···O hydrogen bonds linking the monomeric units into dimers is 2.632 Å. This value is not significantly different from the 2.630 Å found for this separation in α-*trans*-cinnamic acid,[7] and lies between the values of 2.614 Å found for *p*-methoxycinnamic acid[7] and 2.645 Å found for *p*-ethoxycinnamic acid.[8] The two C—O bond distances in the carboxy group, 1.274(5) and 1.258(4) Å, are not significantly different from one another, and the electron density associated with the carboxy hydrogen atom is located almost midway between the two hydrogen-bonded oxygen atoms. Both facts indicate the presence of a static or dynamic disordering of the carboxy group of a type common in crystals of aromatic carboxylic acids.[9]

Other bond distances and angles in the molecule have values typical of those found in the crystal structures of other cinnamic acids.[7,8,10] Characteristic features include the opening of the angle C(2)—C(3)—C(4) to 127.8(3)° and of C(3)—C(4)—C(5) to 122.4(3)°.[7] The mean C—C bond length in the phenyl ring is 1.385 Å, and only C(4)—C(5) deviates significantly (2.5σ) from that value. Observed C—H bond distances range from 0.91(3) Å to 1.01(3) Å, with a mean value of 0.96 Å. The carboxy O—H

---

† Lists of observed and calculated structure amplitudes have been provided to the editor and are available upon request from the authors.

TABLE I

Atomic parameters defining the crystal structure with their e.s.d's

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O(1)	1615(5)	1779(5)	−121(1)	51(1)	54(2)	64(2)	−10(1)	28(1)	15(1)
O(2)	716(3)	−1891(5)	−674(1)	51(1)	58(2)	60(2)	−18(1)	26(1)	−12(1)
O(3)	9626(3)	1732(5)	−2241(1)	46(1)	53(2)	65(2)	−3(1)	33(1)	1(1)
C(1)	1704(4)	−126(7)	−570(2)	38(2)	51(2)	41(2)	−4(2)	9(2)	2(2)
C(2)	3037(4)	−279(7)	−992(2)	42(2)	54(2)	43(2)	0(2)	16(2)	−3(2)
C(3)	4166(4)	1434(7)	−903(2)	41(2)	46(2)	37(2)	−1(2)	13(2)	3(2)
C(4)	5566(3)	1467(6)	−1275(2)	39(2)	37(2)	36(2)	2(2)	13(2)	1(2)
C(5)	5852(4)	−381(7)	−1816(2)	40(2)	41(2)	45(2)	−4(2)	14(2)	−5(2)
C(6)	7195(4)	−321(7)	−2146(2)	46(2)	41(2)	44(2)	2(2)	19(2)	−2(2)
C(7)	8265(3)	1602(7)	−1931(2)	37(2)	38(2)	41(2)	0(2)	15(2)	6(2)
C(8)	8015(4)	3460(7)	−1402(2)	43(2)	44(2)	52(2)	−9(2)	17(2)	−7(2)
C(9)	6658(4)	3371(7)	−1080(2)	50(2)	43(2)	44(2)	−6(2)	19(2)	−7(2)
H(01)	339(4)	169(7)	23(2)	9.7(13)					
H(03)	972(6)	−6(12)	−255(3)	16.3(18)					
H(2)	314(4)	−177(6)	−127(2)	5.9(9)					
H(3)	404(3)	280±6)	−57(2)	6.3(9)					
H(5)	511(3)	−180(6)	−195(2)	3.8(7)					
H(6)	745(3)	−168(6)	−251(2)	4.7(8)					
H(8)	878(3)	463(6)	−125(2)	4.7(8)					
H(9)	652(3)	472(6)	−71(2)	4.9(8)					

Positional parameters are given as fractions of the unit cell edges ($\times 10^4$ for O and C, $\times 10^3$ for H). Mean-square amplitudes of vibration ($\text{Å}^2 \times 10^3$) are given for O and C as U_{ij} to conform to the expression for the exponent in the form $[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}\text{hk}a^*b^* \cos\gamma^* + 2U_{13}hla^*c^* \cos\beta^* + 2U_{23}klb^*c^* \cos\alpha^*)]$, and for H as B values.

distances are 1.29(4) and 1.36(4) Å, reflecting the disorder in that group previously mentioned, and O(3)—H is 1.09(6) Å.

As is characteristic of other *para*-substituted cinnamic acids whose crystal structures have been determined,[7,8] the solid-state conformation of this acid is closely planar, but is more accurately defined in terms of three rigorously planar units. These are: (1) the four-atom carboxy group centered on C(1); (2) the four-atom olefinic group C(1), C(2), C(3), and C(4); and (3) the phenyl ring. Information on these and other least-squares mean planes of interest is given in Table III. The interplanar angles are: 1.5° between planes (1) and (2); 4.7° between planes (1) and (3); and 2.6° between planes (2) and (3). The carboxy planes of the two monomeric units of the dimer, though parallel by crystallographic requirement, are stepped relative to one another by 0.11 Å.

Our principal concern, however, is with the way in which the molecules are packed in the crystal, and how inter-dimer hydrogen bonding stabilizes the solid phase. Two views of the moelcular packing are given in Figures 2 and 3.

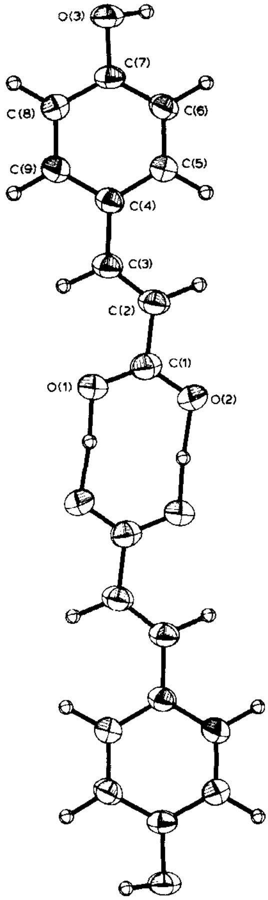

FIGURE 1 *ORTEP* drawing of a dimer of the acid as found in the crystal, and showing the numbering scheme adopted for C and O. Hydrogen atoms are numbered to correspond to the atom of attachment. Thermal ellipsoids for C and O are drawn to the 50% probability level as boundary surface and H atoms are represented by spheres of arbitrary radius.

The long axis of a dimer may conveniently be defined as the axis O(3)$\cdots$O(3′) through the phenolic oxygen atoms. These axes lie very close to the crystal (104) planes, as may be seen from Figure 2, and they make an angle of ±84.7° with the crystal b-axis. A director axis for the crystal may therefore be defined parallel to the [$\bar{4}$01] direction. The molecular planes make an angle of ±57.3° with the plane $y = 0$, the plane of projection in Figure 2. The dimers are linked into infinite sheets, extending parallel to (104), by hydrogen bonds (O$\cdots$O = 2.885 Å) involving the phenolic —OH groups.

TABLE II

Bond distances and bond angles with their e.s.d's.

Bond	Å	Bond	Å
C(1)—O(1)	1.274(4)	C(4)—C(9)	1.382(4)
C(1)—O(2)	1.258(4)	C(5)—C(6)	1.383(4)
C(1)—C(2)	1.471(4)	C(6)—C(7)	1.382(4)
C(2)—C(3)	1.323(4)	C(7)—C(8)	1.377(4)
C(3)—C(4)	1.470(4)	C(8)—C(9)	1.388(4)
C(4)—C(5)	1.396(4)	C(7)—O(3)	1.380(3)

Angle	Deg.	Angle	Deg.
O(1)—C(1)—O(2)	123.8(3)	C(4)—C(5)—C(6)	121.0(3)
O(1)—C(1)—C(2)	118.4(3)	C(5)—C(6)—C(7)	119.0(3)
O(2)—C(1)—C(2)	117.8(3)	C(6)—C(7)—C(8)	121.4(3)
C(1)—C(2)—C(3)	122.6(3)	C(6)—C(7)—O(3)	121.1(3)
C(2)—C(3)—C(4)	127.8(3)	C(8)—C(7)—O(3)	117.5(3)
C(3)—C(4)—C(5)	122.4(3)	C(7)—C(8)—C(9)	118.7(3)
C(3)—C(4)—C(9)	119.3(3)	C(8)—C(9)—C(4)	121.6(3)
C(5)—C(4)—C(9)	118.3(3)		

The hydrogen bonding propagates along the space-group 2_1-axes parallel to the crystal *b*-axis. A view of one such sheet is shown in Figure 3. Within a given row of dimers, parallel to *b*, the inclination of the molecular planes to the (104) sheet plane is uniform, but the inclination alternates (±34.5°) from row to row. This alternation in the orientation of the molecular planes within a sheet also provides an additional stability to the structure by providing an interlocking effect as the sheets are stacked atop one another. Adjacent molecules in successive sheets have a parallel orientation where they are related by the space-group centers of symmetry, but are not parallel where they are related by the space-group two-fold screw axes.

TABLE III

Least-squares mean planes for selected groups of atoms.

Plane	*a*	*b*	*c*	*d*	Δ_{ave}	Δ_{max}
I	0.39738	−0.50202	0.76815	−0.05419	0.000	0.000
II	0.37914	−0.53257	0.75672	−0.07804	0.007	0.008
III	0.34482	−0.56240	0.75154	−0.26404	0.002	0.003
IV	0.34322	−0.56247	0.75222	−0.27570	0.002	0.004
V	0.36701	−0.54009	0.75737	−0.10618	0.033	0.077

Coefficients are given for the equations in the form: $aX + bY + cZ = d$ with $X = x + z.\cos\beta$, $Y = y$, and $Z = z.\sin\beta$. Average and mean deviations of atoms from the plane are given in Å. Planes: I, carboxy group + C(2); II, olefinic group C(1)-C(4); III, phenyl ring; IV, phenyl ring + O(3); V, complete molecule.

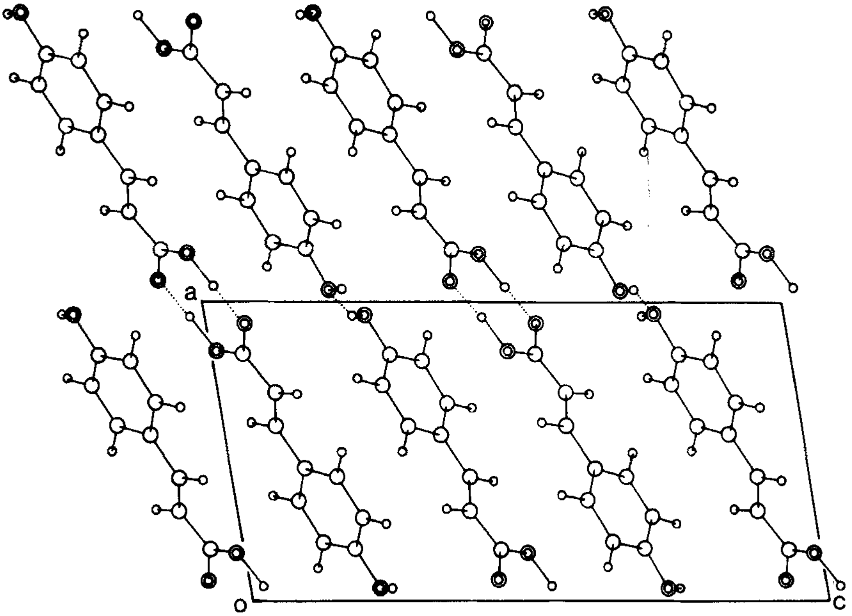

FIGURE 2 Projection of the crystal structure down *b*. The reference molecule for which coordinates are given is immediately to the left and above the origin.

Intermolecular approach distances have been calculated and a complete list of shorter contacts is available from the authors upon request. Because hydrogen atom positions determined by X-ray diffraction are subject both to substantial experimental error and to systematic error due to the non-coincidence of the nuclear center and the center of the electron density, hydrogen atoms attached to carbon were placed, for the calculation of intermolecular contacts, in idealized positions with C—H = 1.08 Å along the bisector of the appropriate C—C—C bond angle. These positions are given in Table IV.

Excluding hydrogen-bonded contacts, the crystal structure is a very open one with only a very small number of the intermolecular approach distances corresponding to limiting van der Waals contacts. The only C···C contact <3.60 Å is that of 3.42 Å ($2r$ + 0.02 Å) between C(1) and C(9) of molecules in adjacent sheets related by a center of symmetry. The shortest C···O contact is 3.28 Å ($r_1 + r_2$ + 0.18 Å) and is between C(1) and O(3) of molecules in adjacent sheets related by a 2_1-axis. O(1) is 2.66 Å ($r_1 + r_2$ + 0.06 Å) from H(9) of a molecule in an adjacent stack, and C(5) is only 2.78 Å ($r_1 + r_2$ − 0.12 Å) from H(5) of a stacked neighbor. Other contacts, including all intrasheet contacts, are comfortably in excess of the sum of the van der Waals radii (r) of the atoms involved.

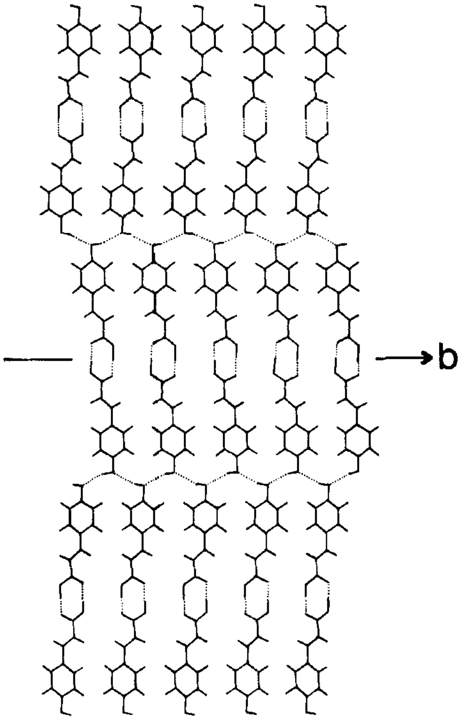

FIGURE 3 Projection of the structure onto the (104) plane showing a single hydrogen-bonded sheet element.

TABLE IV

Idealized hydrogen positions used in calculation of intermolecular approaches

Atom	*x*	*y*	*z*
H(2)	3096	−1851	−1390
H(3)	4044	2994	−509
H(5)	5012	−1881	−1979
H(6)	7405	−1756	−2565
H(8)	8859	−4956	−1241
H(9)	6449	4825	−666

Coordinates are given as fractions of the unit cell edges × $10.^4$

In conclusion, although the near parallel arrangement of molecular dimers in the crystal is compatible with potential mesophase formation, such behavior is inhibited by the high thermal stability of the crystal structure. This thermal stability arises primarily from the hydrogen-bonded sheet character of the structure but is aided by the altèrnation in orientation of the ring planes from sheet to sheet. Whereas a sheet structure with only weak van der Waals interactions between sheets might still form a mesophase in which sheets or sheet fragments moved relative to one another, such motion is restricted here by the interlocking of the non-parallel segments of neighboring sheets. The combination of these two factors leads to a solid phase structure which persists to a temperature at which decomposition sets in.

Acknowledgement

This work was supported, in part, by a grant, DMR 78-19884, from the National Science Foundation.

References

1. G. W. Gray, *Molecular Structure and the Properties of Liquid Crystals*, Academic Press, London (1962).
2. R. F. Bryan, P. Forcier, and R. W. Miller, *J. Chem. Soc. Perkin Trans. II*, 368 (1978).
3. R. F. Bryan, *Proc. Organic Crystal Chemistry Symposium*, Poznan–Dymaczewo, 103 (1978).
4. G. Germain, P. Main, and M. M. Woolfson, *Acta Crystallogr.*, **A27**, 368 (1971).
5. D. T. Cromer and J. T. Waber, *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, (1974); R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).
6. C. K. Johnson, ORTEP–II: *A Fortran Thermal-Ellipsoid Plot Program for Crystal Structure Illustrations*, ORNL–5138, Oak Ridge National Laboratory, Oak Ridge, (1976).
7. R. F. Bryan and D. P. Freyberg, *J. Chem. Soc. Perkin Trans. II*, 1835 (1975).
8. R. F. Bryan, P. Forcier, and P. Hartley, unpublished results.
9. P. J. Wheatley, *J. Chem. Soc.*, 6036 (1964); S. Hayashi and J. Umemura, *J. Chem. Phys.*, **60**, 2630 (1974); R. F. Bryan and J. J. Jenkins, *J. Chem. Soc. Perkin Trans. II*, 1171 (1975); R. F. Bryan and L. Fallon, III, *ibid.*, 1175 (1975).
10. D. Rabinovoch, *J. Chem. Soc.* (*A*), 2361 (1969); R. F. Bryan, H. H. Mills, and J. C. Speakman, *ibid.*, 4351 (1963); G. Tieghi and M. Zocchi, *Crystal Structure Commun.*, **1**, 167 (1972).