

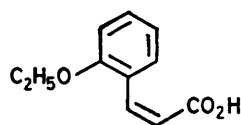
Probable Absence of Lattice Control of *cis-trans*-Isomerization in 2-Ethoxy-*cis*-cinnamic Acid

By Robert F. Bryan* and Paul Hartley, Department of Chemistry, University of Virginia, Charlottesville, Virginia 22901, U.S.A.

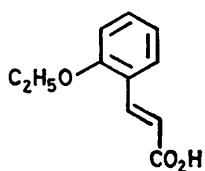
The crystal structure of the title compound has been determined from 1 380 reflections measured by diffractometer. Crystals are orthorhombic, space group *Pbca*, with $a = 10.811(3)$, $b = 12.137(3)$, $c = 15.233(4)$ Å, $Z = 8$. The structure was solved by direct methods and refined by least-squares to give R 0.041. The acid is present in the crystal in a non-planar conformation and forms centrosymmetric hydrogen-bonded dimers (O—H \cdots O, 2.651 Å). The plane of the double bond, C(1)—C(β)—C(α)—C(7), is inclined to the plane of the phenyl ring at 59.4°, and to that of the carboxy-group at 12.3°. There is a limiting intramolecular contact between the carbonyl oxygen O(1) and C(6) of the phenyl ring. It has been postulated that the solid-state *cis-trans* isomerization of such cinnamic acids is lattice controlled, through interactions between $>C=C<$ bonds in neighbouring molecules in close contact (4.0—4.4 Å). It is shown that this crystal, where isomerization is known to occur, contains no such suitable contacts.

BREGMAN *et al.*¹ have interpreted the solid-state photochemistry of substituted *cis*-cinnamic acids as resulting from lattice-controlled isomerization to the *trans*-acid which, after a recrystallization step, is either trapped in a light-stable structure or reacts to give the dimer(s) characteristic of its crystal structure(s).

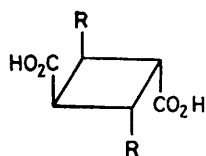
Following prolonged irradiation with a mercury lamp, and subsequent solvent extraction, 2-ethoxy-*cis*-cinnamic acid (I) yields the light-stable γ -form of the *trans*-acid (II) and the 2,2'-diethoxy-derivatives of α -truxillic (III) and β -truxinic (IV) acids, which can be accounted for as the photodimers of the α - and β -polymorphs of (II), respectively.¹



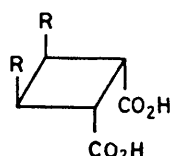
(I)



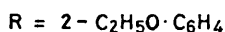
(II)



(III)



(IV)

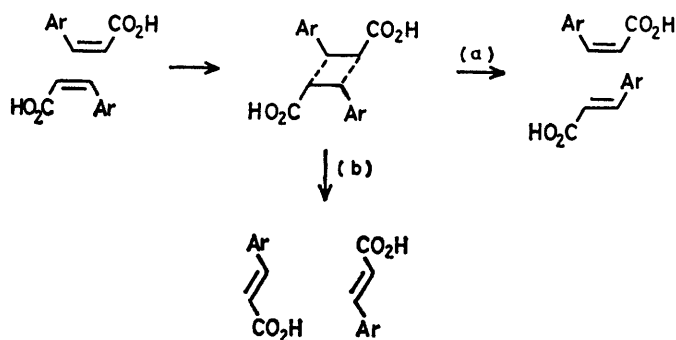


Bregman *et al.*¹ suggested that lattice control of isomerization was exerted through a mechanism such as that shown below, which requires interaction of an excited $>C=C<$ group in one molecule with a nearest neighbour $>C=C<$ group *ca.* 4.0—4.4 Å † distant.

We have determined the crystal structure of the *cis*-isomer (I) examined by these workers, and find that the

† 1 Å = 10^{-10} m.

closest approach of an atom in the double bond of a given molecule to an atom in the double bond of a neighbouring molecule in the crystal is 5.18 Å, and that there are, in fact, no suitable contacts between molecules in the crystal such as would be needed to support the proposed mechanism.



RESULTS AND DISCUSSION

A projection onto the phenyl plane of a dimer of the acid, in the conformation present in the crystal, and showing the numbering scheme adopted, is shown in Figure 1. Table 1 gives the final atomic co-ordinates and equivalent isotropic thermal parameters. Bond lengths and angles are given in Table 2, and Table 3 contains the equations of selected least-squares mean planes. Figure 2 shows a view of the molecular packing, seen in partial projection down c .

The acid is present in the crystal as centrosymmetric hydrogen-bonded dimers with O—H \cdots O 2.651 Å. The *cis*-configuration is, of necessity, non-planar, and the observed structure shows strain in the expanded bond angles: C(1)—C(9)—C(8), 129.8(2); C(9)—C(8)—C(7), 126.3(2); and C(8)—C(7)—O(1), 124.2(2)°. ‡ The plane of the double bond, C(7)—C(8)—C(9)—C(1), is inclined at 59.4° to the plane of the phenyl ring and at 12.3° to that of the carboxy-group. The degree of twist about

‡ 1° = ($\pi/180$) rad.

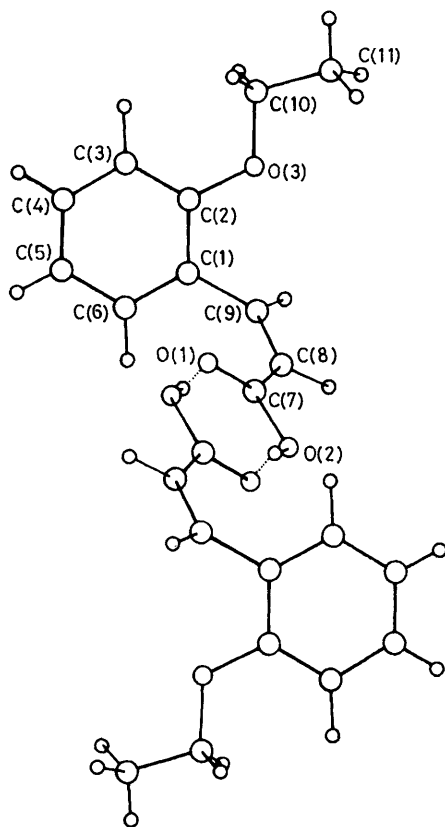


FIGURE 1 Projection of a dimer of the acid onto the plane of the phenyl group

C(8)-C(7) and C(9)-C(1) is controlled by the limiting intramolecular contact of 3.10 Å between the carbonyl oxygen O(1) and C(6) of the ring. Avoidance of lone-pair interactions presumably dictates this preference for the orientation of the acrylic acid residue over that which would place O(1) adjacent to the ether oxygen O(3).

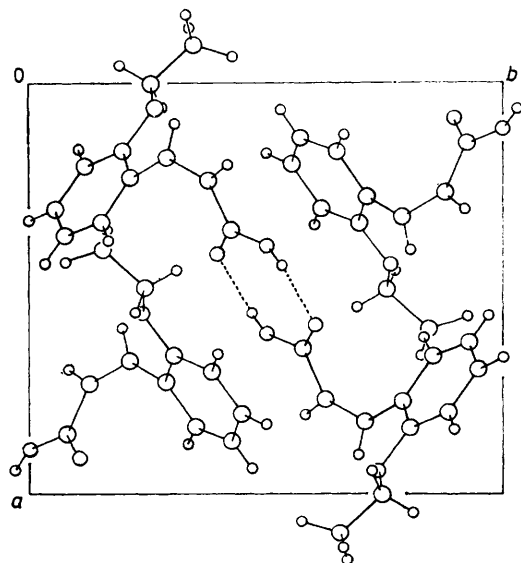


FIGURE 2 Projection of half the unit cell contents down *c*

TABLE 1

Fractional co-ordinates ($\times 10^4$, $H \times 10^3$) and equivalent isotropic *B* values (Å²). Hydrogen atoms have been labelled to correspond to the atom of attachment.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>
O(1)	-875(1)	1 040(1)	330(1)	5.35
O(2)	-1 111(1)	33(1)	-888(1)	5.76
O(3)	-4 420(1)	2 388(1)	1 394(1)	5.52
C(1)	-2 746(2)	2 868(2)	505(1)	4.25
C(2)	-3 411(2)	3 052(1)	1 276(1)	4.50
C(3)	-3 037(2)	3 851(2)	1 860(1)	5.69
C(4)	-1 977(2)	4 467(2)	1 683(2)	6.21
C(5)	-1 306(2)	4 285(2)	946(2)	5.75
C(6)	-1 679(2)	3 494(2)	363(1)	5.10
C(7)	-1 469(2)	789(1)	-326(1)	4.44
C(8)	-2 676(2)	1 266(2)	-557(1)	4.68
C(9)	-3 228(2)	2 108(2)	-159(1)	4.74
C(10)	-5 033(2)	2 443(2)	2 233(1)	6.79
C(11)	-5 982(3)	1 572(2)	2 260(2)	7.93
H(O2)	-54(3)	-26(2)	-66(2)	13.1(8)
H(3)	-344(2)	395(2)	246(1)	7.5(5)
H(4)	-175(2)	503(2)	208(2)	10.2(7)
H(5)	-59(2)	471(2)	88(1)	6.7(5)
H(6)	-127(2)	335(1)	-207(1)	5.8(4)
H(8)	-312(2)	83(1)	-102(1)	5.2(4)
H(9)	-404(2)	225(2)	-37(1)	7.4(5)
H(10a)	-447(2)	225(2)	272(1)	8.7(6)
H(10b)	-540(2)	313(2)	226(1)	8.0(5)
H(11a)	-631(2)	164(2)	286(1)	10.5(7)
H(11b)	-670(3)	170(2)	184(2)	12.4(8)
H(11c)	-566(3)	84(2)	211(2)	11.8(8)

TABLE 2

Bond lengths (Å) and bond angles (°)

C(1)-C(2)	1.394(2)	C(7)-O(1)	1.226(2)
C(1)-C(6)	1.398(2)	C(7)-O(2)	1.313(2)
C(2)-C(3)	1.376(2)	C(7)-C(8)	1.471(2)
C(3)-C(4)	1.394(3)	C(8)-C(9)	1.330(2)
C(4)-C(5)	1.354(2)	C(2)-O(3)	1.368(2)
C(5)-C(6)	1.369(2)	C(10)-O(3)	1.441(2)
C(1)-C(9)	1.464(2)	C(10)-C(11)	1.474(3)
O(1)-C(7)-O(2)	123.4(2)	C(2)-C(1)-C(6)	118.0(2)
O(1)-C(7)-C(8)	124.2(2)	C(9)-C(1)-C(2)	119.9(2)
O(2)-C(7)-C(8)	112.4(2)	C(9)-C(1)-C(6)	121.9(2)
C(7)-C(8)-C(9)	126.3(2)	C(1)-C(2)-C(3)	120.3(2)
C(8)-C(9)-C(1)	129.8(2)	C(1)-C(2)-O(3)	115.3(2)
C(2)-O(3)-C(10)	117.1(2)	C(3)-C(2)-O(3)	124.4(2)
O(3)-C(10)-C(11)	108.1(2)	C(2)-C(3)-C(4)	119.7(2)
C(3)-C(4)-C(5)	120.8(2)	C(4)-C(5)-C(6)	119.6(2)
C(5)-C(6)-C(1)	121.5(2)		

TABLE 3

Selected least-squares planes,* distances (Å) of atoms from planes being given in square brackets

Plane (i): Phenyl ring

$$0.551\ 37X - 0.680\ 48Y + 0.482\ 63Z = -3.624\ 71$$

[C(1) 0.010, other ring atoms <0.007]

Plane (ii): C(7), C(8), C(9), C(1)

$$-0.411\ 54X - 0.586\ 38Y + 0.697\ 70Z = -0.267\ 98$$

[C(1) 0.015, C(9) -0.035, C(8) 0.034, C(7) -0.014]

Plane (iii): O(1), O(2), C(7), C(8)

$$-0.467\ 15X - 0.707\ 19Y + 0.530\ 71Z = -0.188\ 15$$

[O(1) -0.004, O(2) -0.003, C(7) 0.010, C(8) -0.003]

Plane (iv): O(3), C(10), C(11)

$$0.670\ 62X - 0.636\ 12Y + 0.381\ 61Z = -4.237\ 99$$

* *X*, *Y*, and *Z* are in Å with respect to the cell axial system.

The plane of the ethoxy-group is inclined at 9.3° to the plane of the phenyl ring and at 68.7° to that of the double bond.

The most interesting finding, however, is that the crystal contains no approaches between the $>C=C<$ groups of neighbouring molecules of the type required to support the proposed mechanism of lattice control of *cis-trans*-isomerization. Table 4 shows the approaches

TABLE 4

Closest approaches (\AA) between atoms of the double bonds in neighbouring molecules *

C(8) \cdots C(9)	5.18	$[-\frac{1}{2} - x, y - \frac{1}{2}, z]$
C(9) \cdots C(8)	5.18	$[-\frac{1}{2} - x, \frac{1}{2} + y, z]$
C(9) \cdots C(8)	5.31	$[x - \frac{1}{2}, \frac{1}{2} - y, -z]$
C(8) \cdots C(9)	5.31	$[\frac{1}{2} + x, \frac{1}{2} - y, -z]$
C(9) \cdots C(9)	5.51	$[\frac{1}{2} + x, \frac{1}{2} - y, -z]$ and $[x - \frac{1}{2}, \frac{1}{2} - y, -z]$

* Contacts are between the first atom in the reference molecule and the second atom in the symmetry related position indicated.

$<6.0 \text{ \AA}$ between atoms of the double bond in the reference molecule, and the double-bond atoms of neighbours. The shortest such approach is 5.18 \AA , characteristic of the separations found in photostable *trans*-cinnamic acids.² In no case do the two atoms of a given double bond come closer than 6.0 \AA to both of the corresponding atoms of a neighbour. The conclusion seems inescapable that lattice control of isomerization is unlikely in this case.

EXPERIMENTAL

Crystals of the *cis*-isomer, suitable for X-ray study, were obtained as the sole product on recrystallization, from ethanol, of a commercial sample of the acid (Pfaltz and Bauer, Inc.) which was of unspecified configuration, and most probably a mixture of isomers.

Crystal Data.— $C_{11}H_{12}O_3$, $M = 192.2$. Orthorhombic tabular, $a = 10.811(3)$, $b = 12.137(3)$, $c = 15.223(4) \text{ \AA}$, $U = 1997.5 \text{ \AA}^3$, $D_m = 1.27(1)$ (floatation), $Z = 8$, $D_c = 1.278$, $F(000) = 816$. Systematic absences: $0kl$, k odd; $h0l$, l odd; $hk0$, h odd; space group *Pbca*. Cu- K_α radiation (graphite monochromator), $\lambda = 1.5418 \text{ \AA}$, $\mu(\text{Cu-}K_\alpha) = 7.7 \text{ cm}^{-1}$; single-crystal diffractometry. The unit cell found

* 1 min = 60 s.

† For details see Notice to Authors No. 7, in *J. Chem. Soc., Perkin Trans. 2*, 1980, Index issue.

corresponds to that reported for the acid in ref. 1, confirming the identity of the polymorph examined in each case.

Intensity Data.—These were measured for a single crystal $0.5 \times 0.5 \times 0.15 \text{ mm}$ with a Nicolet P3m diffractometer. The θ — 2θ scan method was used with scan ranges of 1.2° in 2θ below and above the $K_{\alpha 1}$ and $K_{\alpha 2}$ maxima, and with scan speeds ranging from 1.0 to $29.3^\circ \text{ min}^{-1}$, * as determined by a 2 s pre-scan. The reflections in a single octant of reciprocal space were measured ($2\theta \leq 122^\circ$), yielding intensity data with $I > 2\sigma(I)$ at 1 380 of the 1 521 (90.7%) locations accessible to the instrument. No absorption corrections were made and structure amplitudes and normalized structure amplitudes were derived in the usual ways.

Structure Determination and Refinement.—Correct phases were found by routine application of the program MULTAN, in its 1974 version.³ An interesting curiosity is that MULTAN in its 1980 version does not yield a correct solution (on routine application) for this simple centrosymmetric structure. Block-diagonal least-squares refinement (3×3 and 6×6 matrices) minimizing the function $\sum w(|F_o| - |F_c|)^2$ gave R 0.041 and R_w 0.037 at convergence, for the 1 380 reflections used. The weighting scheme had $w = 1.2/[\sigma^2(F) + 0.0001F^2]$, $\sigma(F)$ being the uncertainty in the observed structure amplitude based on counting statistics only. For the full set of 1 521 data R was 0.051. The maximum shift : error ratio in the final cycle of refinement was 0.40 and the mean ratio was 0.07. Anisotropic thermal parameters were used for O and C, and individual isotropic B values were refined for H. The scattering curves used were taken from ref. 4. Observed and calculated structure amplitudes, and anisotropic thermal parameters, are given as Supplementary Publication No. SUP 23200 (13 pp.).†

This work was supported by a grant, DMR-78-19884, from the National Science Foundation, U.S.A.

[1/1124 Received, 15th July, 1981]

REFERENCES

- 1 J. Bregman, K. Osaki, G. M. J. Schmidt, and F. I. Sonntag, *J. Chem. Soc.*, 1964, 2021.
- 2 G. M. J. Schmidt, *J. Chem. Soc.*, 1964, 2014.
- 3 G. Germain, P. Main, and M. M. Woolfson, *Acta Crystallogr.*, 1971, **A27**, 368.
- 4 D. T. Cromer and J. T. Waber, 'International Tables for X-ray Crystallography,' Kynoch Press, Birmingham, 1975, vol. 4; R. F. Stewart, E. R. Davidson, and W. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.