

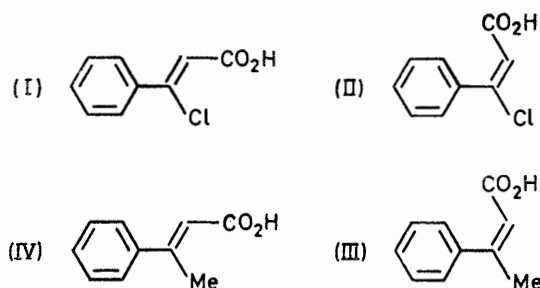
Molecular Packing Modes. Part IV.† Crystal and Molecular Structures of Three Cinnamic Acids

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The crystal structures of β -methyl-*cis*-. (III), β -chloro-*cis*-. (II), and β -chloro-*trans*-cinnamic. (I), acids have been determined from three-dimensional counter data by Patterson and Fourier methods. (I): $a = 19.588$, $b = 5.374$, $c = 16.683$ Å, $\beta = 103.62^\circ$, $Z = 8$, space group $A2/a$, R 0.054 (1873 reflections); (II): $a = 5.797$, $b = 24.247$, $c = 7.240$ Å; $\beta = 121.56^\circ$, $Z = 4$, space group $P2_1/c$, R 0.046 (1917 reflections); (III): $a = 7.504$, $b = 7.442$, $c = 17.056$ Å, $\beta = 107.00^\circ$, $Z = 4$, space group $P2_1/c$, R 0.066 (1987 reflections). The σ values of the experimental bond lengths are <0.01 Å, except for the C-H bonds where they are 0.03 Å.

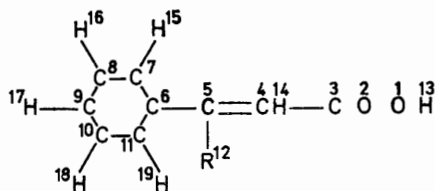
The electron-density distribution in the planes of the paired carboxy-groups and the lengths of the C-O bonds suggests that the packing of these groups is disordered in the two *cis*-cinnamic acids but not in β -chloro-*trans*-cinnamic acid.

THE structure analyses of the three cinnamic acids (I)—(III) were originally undertaken in order to provide further information on the mechanism and crystal-



structure dependence of *cis-trans* interconversion in the solid state.¹ At the same time a comparison of the bond characteristics, in particular of the C-C-C system, of pairs of geometrical isomers in the cinnamic acids was considered interesting as well as an analysis of the hydrogen-bonding pattern of the acid function.

EXPERIMENTAL



Numbering of atoms employed in the structure analyses

Preparation of Materials.—Chloro-derivatives. The mixture of the two chloro-acids obtained by the action of concentrated hydrochloric acid on phenylpropionic acid² was separated *via* their barium salts.³

Methyl derivatives. The *trans*-acid was obtained by the Reformatzky reaction of acetophenone with methyl bromoacetate, followed by dehydration and hydrolysis. Irradiation of the *trans*-acid in alkaline solution (quartz vessel) with a medium-pressure quartz burner led to partial isomerisation;⁴ the *cis*-acid was precipitated at pH 2 after removal of the *trans*-isomer at pH 7.¹

Crystal Data.—(i) β -Chloro-*trans*-cinnamic acid, (I).

† Part III, L. Leiserowitz and G. M. J. Schmidt, *J. Chem. Soc. (A)*, 1969, 2372.

¹ J. Bergman, K. Osaki, G. M. J. Schmidt, and F. I. Sonntag, *J. Chem. Soc.*, 1964, 2021.

$C_9H_7ClO_2$, $M = 182.5$, m.p. 143–144 °C. Monoclinic, $a = 19.588(1)$, $b = 5.374(1)$, $c = 16.683(1)$ Å, $\beta = 103.62(1)^\circ$, $U = 1699.2$ Å³, $Z = 8$, $D_c = 1.427$, $F(000) = 752$. Space group $A2/a$ or Aa (the former established as correct by the present analysis) from systematic absences: $h0l$ for h and l odd, hkl for $h + l$ odd. $Cu-K\alpha$ radiation, $\lambda = 1.5405$ Å; $\mu(Cu-K\alpha) = 36$ cm⁻¹.

(ii) β -Chloro-*cis*-cinnamic acid, (II), $C_9H_7ClO_2$, m.p. 132–133 °C. Monoclinic, $a = 5.797(1)$, $b = 24.247(1)$, $c = 7.240(1)$ Å, $\beta = 121.56(1)^\circ$, $U = 867.0$ Å³, $Z = 4$, $D_c = 1.367$, $F(000) = 376$. Space group $P2_1/c$ from systematic absences: $h0l$ for l odd, $0k0$ for k odd. $\mu(Cu-K\alpha) = 35$ cm⁻¹.

(iii) β -Methyl-*cis*-cinnamic acid, (III), $C_{10}H_{10}O_2$, $M = 162.2$, m.p. 131.0–131.5 °C. Monoclinic, $a = 7.504(1)$, $b = 7.442(1)$, $c = 17.056(1)$ Å, $\beta = 107.00(1)^\circ$, $U = 910.9$ Å³, $Z = 4$, $D_c = 1.182$, $F(000) = 344$. Space group $P2_1/c$ from systematic absences: $h0l$ for l odd, $0k0$ for k odd. $\mu(Cu-K\alpha) = 6.7$ cm⁻¹.

(iv) β -Methyl-*trans*-cinnamic acid, (IV), $C_{10}H_{10}O_2$, m.p. 97.5–98.0 °C. Triclinic, $a = 12.98$, $b = 18.52$, $c = 7.55$ Å, $\alpha = 98.5$, $\beta = 105.7$, $\gamma = 100.1^\circ$, $U = 842.8$ Å³, $Z = 8$, $D_c = 1.27$. Space group $P1$ or $P\bar{1}$.

β -Chloro-*trans*-cinnamic acid (I) was crystallised by slow evaporation of ethanol solutions as monoclinic laths elongated along [010], showing {100}, {001}, and {21 $\bar{1}$ }. Crystals of β -chloro-*cis*-cinnamic acid (II) were obtained by slow evaporation ethyl acetate solutions showing {100}, {010}, and {001}. Needles of β -methyl-*cis*-cinnamic acid (III), elongated along [100], showing {010}, {001}, and {20 $\bar{1}$ }, were obtained by slow evaporation of methyl acetate solutions. β -Methyl-*trans*-cinnamic acid (IV) was crystallised from slowly cooled light petroleum (b.p. 60–80 °C) solutions.

Cell constants were determined from zero- and n -level Weissenberg and precession photographs, accurate cell dimension being derived by a least-squares procedure based on high-angle spectra measured on the General Electric goniostat with $Cu-K\alpha$ radiation.

The three-dimensional data for the three acids were collected on a General Electric goniostat by the stationary-counter, stationary-crystal technique. During the periods of measurement the monitored intensities gradually fell off by 12 (I), 15 (II), and 20% (III). The weighting factors $w(hkl)$ were derived by the procedure previously described;⁵ reflections were regarded as unobserved $2\sigma(I - B) >$

² R. Stoermer and P. Heymann, *Ber.*, 1913, **46**, 1249.

³ T. C. James, *J. Chem. Soc.*, 1911, **99**, 1620.

⁴ R. Stoermer, F. Grimm, and E. Laage, *Ber.*, 1917, **50**, 959.

⁵ S. E. Filippakis, L. Leiserowitz, and G. M. J. Schmidt, *J. Chem. Soc. (B)*, 1967, 305.

($I - B$), where I is the measured intensity and B the associated background. The dimensions of the three crystal specimens were: (I) 0, 0.07, 0.27, 0.08, 0, 0.38, 0, 0.40 mm, measured normal to the faces 100, $\bar{1}00$, 001, $00\bar{1}$, $\bar{2}11$, $2\bar{1}\bar{1}$, $2\bar{1}\bar{1}$, $\bar{2}11$; (II) 0, 0.28, 0, 0.15, 0, 0.25 mm, measured normal to the faces $00\bar{1}$, 001, $0\bar{1}0$, 010 , $\bar{1}00$, 100; and (III) 0.06, 0, 0.26, 0, 0.35, 0, measured normal to the faces $00\bar{1}$, 001, $0\bar{1}0$, 010 , $20\bar{1}$, $\bar{2}01$. Absorption corrections were applied according to our standard procedure.⁶ The number of Gaussian grid points^{7,8} used in the computation of the absorption factors were 1440 (I), 1200 (II), and 1000 (III).

Solution and Refinement of the Structures.—(i) β -Chloro-*trans*-cinnamic acid, (I). 1873 Independent reflections were recorded of which 266 were unobserved. The intensities ranged from 70,000 -1 counts s^{-1} counted for a preset period of 10s. The sharpened three-dimensional Patterson function was computed with coefficients $F^2(hkl)/f_{Cl}^2$. The $^sP(\chi O_z)$ section exhibited a very strong peak at 1.7 Å from the origin; on the assumption that this peak corresponded to the $C \cdots Cl$ vector parallel to the ac plane all co-ordinates could be deduced from the Patterson sections. The trial parameters were smoothly refined isotropically till R' was 0.15 [$R' = \Sigma w(k^2 F_o^2 - |F_c|^2)^2 / \Sigma w k^4 |F_o^4|$]. At this stage all hydrogen atoms were inserted in chemically reasonable positions; the hydroxy-hydrogen was attached to the oxygen of the longer C-O bond. Refinement was continued with anisotropic temperature factors for all but the hydrogen atoms until the (undamped) shifts had become $< 0.02\sigma$. Secondary extinction corrections⁵ were then applied; further least-squares cycles left the positional parameters of all atoms unchanged, but produced shifts in the temperature parameters. The final agreement factors were R' 0.021 and R 0.056 (all reflections) and 0.054 (observed reflections only).

(ii) β -Chloro-*cis*-cinnamic acid, (II). 1917 Independent reflections were recorded of which 320 were unobserved. The intensities ranged from 25,000 -1 counts s^{-1} counted for a preset period of 10 s. Trial co-ordinates were taken from the structure of the isomorphous β -bromo-*cis*-cinnamic acid and refined as described for (I) except that in view of the equality of the C-O bond lengths (1.261 and 1.259 Å) the hydroxy-hydrogen was not inserted into the model.

After several least-squares cycles secondary-extinction corrections were applied, and refinement was continued until the parameter shifts had become negligible.

(iii) β -Methyl-*cis*-cinnamic acid, (III).—1987 Reflections were measured of which 799 were unobserved. The structure was solved by our SEARCH procedure⁹ with a molecular model constructed from the previously solved β -chloro-*cis*-cinnamic acid. Refinement of the SEARCH model with anisotropic temperature factors of all but the hydrogen atoms proceeded smoothly until R' and R were 0.017 and 0.073 (all reflections) and 0.064 (observed only). Secondary extinction corrections were applied to measurements on the original crystal; several further least-squares cycles introduced no changes in positional parameters but did affect the thermal parameters [R' 0.017; R 0.071 (0.063)]. Throughout this refinement procedure the hydrogen atoms of the carboxy-group had been omitted in view

⁶ P. Coppens, L. Leiserowitz, and D. Rabinovich, *Acta Cryst.*, **1965**, **18**, 1035.

⁷ W. R. Busing and H. A. Levy, *Acta Cryst.*, **1957**, **10**, 180.

⁸ S. E. Filippakis, L. Leiserowitz, and G. M. J. Schmidt, *J. Chem. Soc. (B)*, **1967**, 290.

⁹ D. Rabinovich and G. M. J. Schmidt, *Nature*, **1966**, **211**, 1391.

TABLE I
Atomic co-ordinates and standard deviations (Å)
referred to axes a , b , c

(a) β -Chloro- <i>trans</i> -cinnamic acid			
Atom	x	y	z
C(3)	0.6562(27)	1.3776(24)	-1.0274(23)
C(4)	1.1320(26)	2.3807(25)	-1.8787(23)
C(5)	2.1502(23)	3.2572(23)	-1.4841(21)
C(6)	2.6238(22)	4.1880(22)	-2.4288(20)
C(7)	3.5324(27)	5.2200(27)	-1.9285(24)
C(8)	3.9819(30)	6.0711(29)	-2.8276(28)
C(9)	3.5086(29)	5.9064(28)	-4.2214(27)
C(10)	2.5939(30)	4.8865(29)	-4.7452(26)
C(11)	2.1683(29)	4.0198(28)	-3.8513(23)
Cl(12)	3.0338(11)	3.3720(11)	0.2240(7)
O(1)	1.0555(22)	1.2655(20)	0.2160(17)
O(2)	-0.2842(22)	0.5760(20)	-1.7902(18)
H(13)	-0.545(34)	-0.092(36)	-1.211(32)
H(14)	0.696(34)	2.351(32)	-2.878(31)
H(15)	3.816(31)	5.325(32)	-0.952(28)
H(16)	4.593(36)	6.784(35)	-2.515(30)
H(17)	3.785(36)	6.513(33)	-4.932(30)
H(18)	2.242(31)	4.770(33)	-5.706(30)
H(19)	1.496(35)	3.309(34)	-4.264(32)
(b) β -Chloro- <i>cis</i> -cinnamic acid			
Atom	x	y	z
C(3)	-1.9422(28)	0.8148(22)	2.5941(25)
C(4)	-1.2651(29)	1.3788(24)	1.7250(26)
C(5)	-0.3362(24)	2.4537(22)	2.1564(24)
C(6)	0.1402(22)	3.3815(19)	3.4694(23)
C(7)	1.7106(26)	3.5301(23)	4.6341(27)
C(8)	2.1336(28)	4.4173(26)	5.8557(28)
C(9)	1.0159(31)	5.1758(24)	5.9109(29)
C(10)	-0.5329(30)	5.0493(24)	4.7487(31)
C(11)	-0.9775(25)	4.1564(23)	3.5337(28)
Cl(12)	0.3901(7)	2.8816(8)	0.9573(7)
O(1)	-2.9676(25)	-0.0826(19)	1.8882(23)
O(2)	-1.4864(25)	1.1914(18)	3.9696(20)
$h^1(13)$ *	-3.329(96)	-0.347(91)	2.464(92)
$h^2(13)$ *	-1.942(80)	0.809(80)	4.470(77)
H(14)	-1.548(24)	0.893(26)	0.739(29)
H(15)	2.479(29)	2.958(25)	4.553(30)
H(16)	3.256(33)	4.534(29)	6.694(32)
H(17)	1.364(32)	5.774(28)	6.778(31)
H(18)	-1.356(32)	5.576(30)	4.810(30)
H(19)	-2.051(33)	4.061(28)	2.755(30)
(c) β -Methyl- <i>cis</i> -cinnamic acid			
Atom	x	y	z
C(3)	-1.7317(24)	0.9698(23)	-0.6077(23)
C(4)	-3.0536(25)	1.7013(23)	-0.9360(23)
C(5)	-3.4106(22)	2.7308(21)	-1.8387(22)
C(6)	-2.5220(22)	3.3226(19)	-2.6415(22)
C(7)	-2.7274(28)	2.9585(23)	-4.0127(25)
C(8)	-1.9279(34)	3.5404(29)	-4.7789(31)
C(9)	-0.9331(32)	4.4803(28)	-4.1847(38)
C(10)	-0.7516(31)	4.8603(29)	-2.8325(38)
C(11)	-1.5330(28)	4.2882(25)	-2.0652(30)
C(12)	-4.8168(32)	3.3787(35)	-2.0895(39)
O(1)	-1.6160(23)	0.0203(20)	0.2703(20)
O(2)	-0.7693(23)	1.2528(20)	-1.1284(21)
$h^1(13)$ *	-0.811(80)	-0.366(57)	0.495(62)
$h^2(13)$ *	-0.166(67)	0.850(50)	-0.861(55)
H(14)	-3.712(25)	1.365(21)	-0.458(23)
H(15)	-3.513(26)	2.327(23)	-4.466(27)
H(16)	-2.076(29)	3.268(25)	-5.713(30)
H(17)	-0.361(29)	4.857(24)	-4.761(29)
H(18)	-0.017(34)	5.563(29)	-2.370(33)
H(19)	-1.385(29)	4.558(23)	-1.057(29)
H(20)	-5.290(31)	3.340(25)	-3.165(34)
H(21)	-4.687(30)	4.289(29)	-1.818(31)
H(22)	-5.360(32)	2.934(26)	-1.543(30)

* For definition of h^1 and h^2 see Discussion section.

of the lengths of the two C—O bonds (1.259–1.281 Å). With the further refinement of the electron-density in the carboxy-group described in the Discussion section, these values change to 1.253 and 1.275 Å.

The positional and thermal parameters of the three

The mean σ value of the C—C, C—O, and C—Cl bond lengths are 0.004, 0.004, and 0.003 Å, and of all C—H bonds is 0.03 Å. The mean σ value of angles between heavy atoms is 0.3°, that of angles involving one hydrogen, 2°. As an independent check of σ for bond lengths we compute the 'bond

TABLE 2

Observed thermal parameters u_{ij} and U and standard deviations (Å²) referred to axes a, b, c

(a) β -Chloro-*trans*-cinnamic acid

Atom	u_{11}	u_{22}	u_{33}	u_{12}	u_{23}	u_{13}
C(3)	0.0685(13)	0.0555(14)	0.0551(12)	−0.0097(10)	0.0063(10)	0.0198(10)
C(4)	0.0676(13)	0.0592(14)	0.0495(11)	−0.0083(11)	0.0115(10)	0.0136(10)
C(5)	0.0574(11)	0.0561(13)	0.0455(10)	−0.0022(9)	0.0065(8)	0.0159(8)
C(6)	0.0542(10)	0.0494(11)	0.0499(10)	−0.0011(9)	0.0064(8)	0.0179(9)
C(7)	0.0696(13)	0.0632(15)	0.0533(12)	−0.0102(12)	0.0023(10)	0.0188(10)
C(8)	0.0788(16)	0.0604(16)	0.0712(15)	−0.0182(13)	0.0034(12)	0.0259(13)
C(9)	0.0789(16)	0.0611(15)	0.0678(14)	−0.0030(12)	0.0160(12)	0.0321(13)
C(10)	0.0814(16)	0.0787(18)	0.0527(13)	−0.0102(14)	0.0121(11)	0.0222(12)
C(11)	0.0751(15)	0.0675(15)	0.0518(12)	−0.0167(12)	0.0050(10)	0.0189(11)
Cl(12)	0.1344(8)	0.1474(9)	0.0443(4)	−0.0825(7)	0.0214(4)	0.0004(4)
O(1)	0.0991(14)	0.0805(13)	0.0531(9)	−0.0357(12)	0.0141(8)	0.0139(9)
O(2)	0.0926(13)	0.0763(13)	0.0553(9)	−0.0329(11)	0.0098(8)	0.0140(9)

Atom	U	Atom	U	Atom	U	Atom	U
H(13)	0.086(12)	H(15)	0.042(7)	H(17)	0.058(9)	H(19)	0.060(9)
H(14)	0.052(8)	H(16)	0.046(8)	H(18)	0.050(8)		

(b) β -Chloro-*cis*-cinnamic acid

Atom	u_{11}	u_{22}	u_{33}	u_{12}	u_{23}	u_{13}
C(3)	0.0753(14)	0.0513(11)	0.0549(11)	−0.0137(10)	−0.0087(9)	0.0337(10)
C(4)	0.0779(14)	0.0595(12)	0.0563(11)	−0.0110(10)	−0.0083(9)	0.0370(11)
C(5)	0.0563(11)	0.0582(11)	0.0557(10)	−0.0015(9)	0.0036(9)	0.0313(9)
C(6)	0.0496(9)	0.0430(9)	0.0555(10)	−0.0029(7)	0.0043(8)	0.0281(8)
C(7)	0.0525(11)	0.0552(11)	0.0692(12)	0.0028(9)	−0.0028(10)	0.0292(10)
C(8)	0.0612(13)	0.0670(14)	0.0620(12)	−0.0024(10)	−0.0059(10)	0.0233(10)
C(9)	0.0789(15)	0.0552(12)	0.0670(13)	−0.0071(11)	−0.0082(10)	0.0410(11)
C(10)	0.0702(14)	0.0551(11)	0.0825(15)	0.0044(10)	0.0010(11)	0.0483(12)
C(11)	0.0493(10)	0.0564(11)	0.0704(12)	−0.0012(9)	0.0027(10)	0.0302(10)
Cl(12)	0.0714(4)	0.0928(5)	0.0664(4)	−0.0130(3)	−0.0021(3)	0.0450(3)
O(1)	0.1048(14)	0.0669(10)	0.0736(11)	−0.0377(10)	−0.0219(8)	0.0534(10)
O(2)	0.1112(14)	0.0635(10)	0.0612(9)	−0.0297(9)	−0.0124(7)	0.0502(10)

Atom	U	Atom	U	Atom	U	Atom	U
$h^1(13)$	0.077(25)	H(14)	0.036(6)	H(16)	0.052(7)	H(18)	0.052(7)
$h^2(13)$	0.048(17)	H(15)	0.040(7)	H(17)	0.049(7)	H(19)	0.049(7)

(c) β -Methyl-*cis*-cinnamic acid

Atom	u_{11}	u_{22}	u_{33}	u_{12}	u_{23}	u_{13}
C(3)	0.0843(15)	0.0898(14)	0.0711(12)	−0.0182(12)	0.0070(11)	0.0294(11)
C(4)	0.0787(14)	0.0912(14)	0.0768(14)	−0.0127(12)	0.0008(11)	0.0290(11)
C(5)	0.0763(13)	0.0814(13)	0.0718(12)	−0.0107(10)	−0.0117(11)	0.0227(10)
C(6)	0.0722(12)	0.0689(11)	0.0747(13)	0.0010(9)	0.0004(9)	0.0231(10)
C(7)	0.0994(17)	0.0860(15)	0.0803(15)	0.0004(12)	−0.0047(12)	0.0344(13)
C(8)	0.1201(21)	0.1031(18)	0.0867(18)	0.0246(16)	0.0101(15)	0.0480(16)
C(9)	0.0976(19)	0.0962(18)	0.1284(24)	0.0170(14)	0.0344(17)	0.0558(18)
C(10)	0.1029(20)	0.1075(19)	0.1274(24)	−0.0269(16)	0.0066(17)	0.0402(18)
C(11)	0.0994(17)	0.1029(17)	0.0900(17)	−0.0299(13)	−0.0061(14)	0.0292(14)
C(12)	0.0901(18)	0.1042(21)	0.1161(24)	0.0023(15)	−0.0033(17)	0.0418(17)
O(1)	0.0938(13)	0.1158(13)	0.1030(13)	0.0013(11)	0.0390(11)	0.0413(10)
O(2)	0.0860(13)	0.1163(14)	0.1176(14)	0.0063(11)	0.0447(11)	0.0452(11)

Atom	U	Atom	U	Atom	U	Atom	U
$h^1(13)$	0.074(19)	H(15)	0.076(8)	H(18)	0.114(10)	H(21)	0.090(10)
$h^2(13)$	0.035(16)	H(16)	0.089(9)	H(19)	0.083(8)	H(22)	0.093(9)
H(14)	0.067(7)	H(17)	0.090(8)	H(20)	0.096(9)		

compounds are listed in Tables 1 and 2. hF_o and F_o are listed in Supplementary Publication No. SUP 20324 (60 pp., 2 microfiches).^{*} Scattering factor curves were taken from ref. 10 for carbon and oxygen, from ref. 11 for hydrogen, and from ref. 12 for chlorine.

^{*} For details see Notice to Authors No. 7 in *J. Chem. Soc. (A)*, 1970, Issue No. 20.

scatter' of chemically equivalent C—C bonds, $\sigma(r)$, as 0.005 Å. Experimental bond lengths and angles are shown

¹⁰ J. Berghius, IJ. M. Haanappel, M. Potters, B. O. Loopstra, C. H. MacGillavry, and A. L. Veenendaal, *Acta Cryst.*, 1955, **8**, 478.

¹¹ R. McWeeny, *Acta Cryst.*, 1951, **4**, 513.

¹² B. Dawson, *Acta Cryst.*, 1960, **13**, 403.

in Figures 1 and 2. The equations of certain best planes and the distances of atoms from these planes, are given in Table 3.

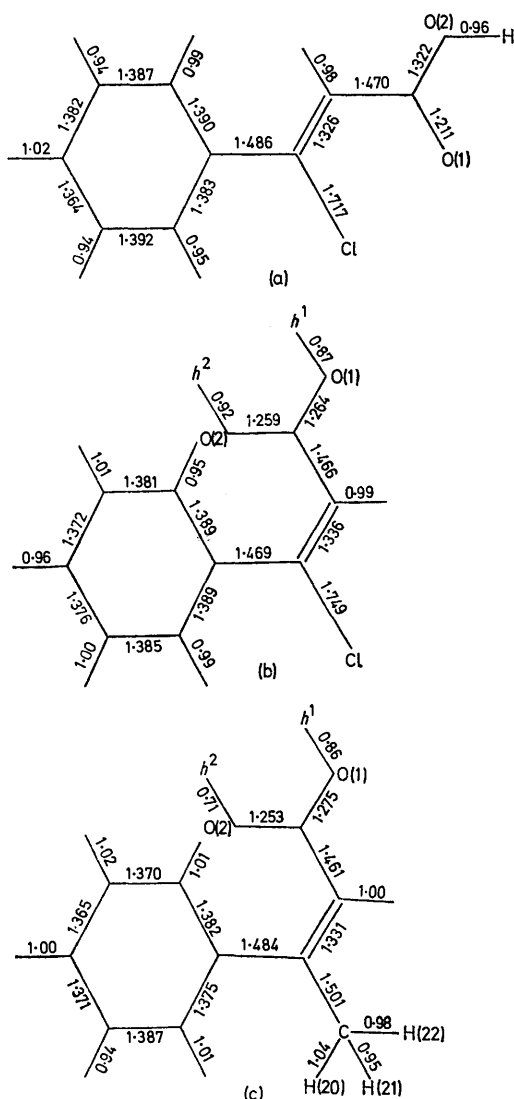


FIGURE 1 Experimental bond lengths: (a) β -chloro-*trans*-, (b) β -chloro-*cis*-, and (c) β -methyl-*cis*-cinnamic acid

DISCUSSION

Bond Lengths and Angles.—Since the bond lengths could not be corrected for thermal vibrations we consider that the σ values do not provide a fine yardstick for their comparison. Table 4 shows that comparable C-C bond lengths are essentially identical in the three structures. On the other hand, the differences in the C-Cl bonds of (I) and (II) and in the C-O bonds of (I) are certainly significant. That the three C(5)-C(6) bonds are almost equal in the three acids despite angles of twist around this bond of 11.7 (I), 65.4 (II), and 83.3°

¹³ O. Bastiansen, L. Hedberg, and K. Hedberg, *J. Chem. Phys.*, 1957, **27**, 1311.

¹⁴ D. P. Shoemaker, H. Kindler, W. G. Sly, and R. C. Srivastava, *J. Amer. Chem. Soc.*, 1965, **87**, 482.

(III) is not altogether surprising: the length of the sp^2 - sp^2 bond appears to be relatively insensitive to the angle of twist as is shown by a comparison of the C-C bond lengths in planar butadienes (zero torsion angle) and in non-planar cyclo-octatetraenes (torsion angle of 60°). In the former we have found ⁵ a value of 1.452 Å based on four structure analyses, as against 1.462 and 1.470 Å in cyclo-octatetraene ¹³ and its carboxylic acid.¹⁴

The length of the C-Cl bond in vinyl chloride ¹⁵ has a value (1.726 Å) close to that in (I) (1.717 Å). The bond angles around the carbon atom bonded to chlorine of vinyl chloride (Figure 3) agree far better with those of the *trans*- than of the *cis*-acid; hence the non-equality

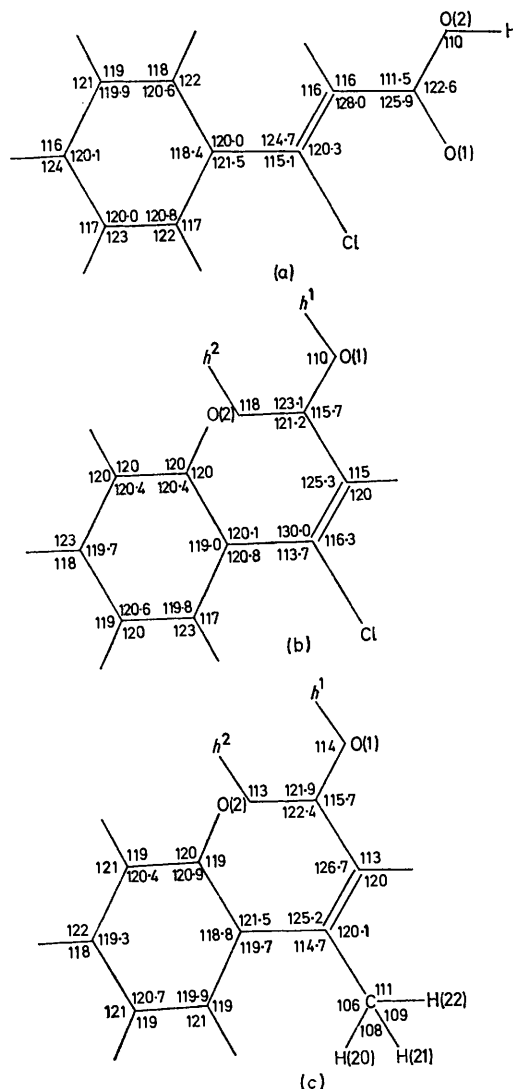


FIGURE 2 Experimental bond angles: (a) β -chloro-*trans*-, (b) β -chloro-*cis*-, and (c) β -methyl-*cis*-cinnamic acid [H(20)-C(12)-H(22) 113, C(5)-C(12)-H(21) 109°]

of the C-Cl bond lengths in the two acids may be related to differences in the bond angles around C(5), an effect

¹⁵ D. Kivelson, E. B. Wilson, and D. R. Lide, *J. Chem. Phys.*, 1960, **32**, 205.

TABLE 3

Equations of planes in the form $Ax + By + Cz + D = 0$ where x, y, z are fractional co-ordinates; distances (10^3 \AA) of relevant atoms from the planes, are given in square brackets

(a) β -Chloro-*trans*-cinnamic acid

Plane (A):

$$C(3), C(4), \quad -15.1719x + 3.3461y + 5.0566z - 0.0366 = 0$$

O(1), O(2)

$$[C(3) \ 2, C(4) \ -1, O(1) \ -1, O(2) \ -1, C(5) \ -124, C(6) \ -197, Cl(12) \ -219, H(13) \ -40]$$

Plane (B):

$$C(3)-(6) \quad -14.0740x + 3.6269y + 5.7385z - 0.1253 = 0$$

$$[C(3) \ -20, C(4) \ 22, C(5) \ 18, C(6) \ -19, O(1) \ 45, O(2) \ -148, Cl(12) \ 48, H(14) \ -30]$$

Plane (C):

$$C(6)-(11) \quad -15.5570x + 3.2651y + 3.1997z + 0.0085 = 0$$

$$[C(6) \ 4, C(7) \ 5, C(8) \ -7, C(9) \ 1, C(10) \ 7, C(11) \ -10, C(3) \ 127, C(4) \ 196, C(5) \ -5, Cl(12) \ -309, O(1) \ -19, O(2) \ 241, H(14) \ 330, H(15) \ 30, H(16) \ 0, H(17) \ 10, H(18) \ 30, H(19) \ 10]$$

(b) β -Chloro-*cis*-cinnamic acid

Plane (A):

$$C(3), C(4), \quad 3.5031x - 17.0765y + 0.0076z + 1.7363 = 0$$

O(1), O(2)

$$[C(3) \ -9, C(4) \ 3, O(1) \ 3, O(2) \ 3, C(5) \ -19, C(6) \ -557, h^1(13) \ -30, h^2(13) \ 0]$$

Plane (B):

$$C(3)-(6) \quad 3.5783x - 13.5315y + 1.0811z + 1.2741 = 0$$

$$[C(3) \ 8, C(4) \ -19, C(5) \ 19, C(6) \ -8, O(1) \ -230, O(2) \ 284, Cl(12) \ 50, C(7) \ 52, C(11) \ -1121, H(14) \ -70]$$

Plane (C):

$$C(6)-(11) \quad -2.6216x - 17.3975y + 4.9817z + 0.1090 = 0$$

$$[C(6) \ 7, C(7) \ -9, C(8) \ 4, C(9) \ 3, C(10) \ -5, C(11) \ 0, C(3) \ 2188, C(4) \ 879, C(5) \ -16, Cl(12) \ -1476, H(15) \ 0, H(16) \ -10, H(17) \ 10, H(18) \ 30, H(19) \ 20]$$

(c) β -Methyl-*cis*-cinnamic acid

Plane (A):

$$C(3)-(6), \quad -1.3160x - 4.7323y - 11.3850z - 0.0920 = 0$$

C(12), O(1),
O(2)

$$[C(3) \ 1, C(4) \ 5, C(5) \ -3, C(6) \ 1, C(12) \ -1, O(1) \ -2, O(2) \ -1, C(7) \ 1184, C(11) \ -1171, H(20) \ 820, H(21) \ -780, H(22) \ 10, h^1(13) \ -50, h^2(13) \ -30]$$

Plane (B):

$$C(6)-(11) \quad 4.7040x - 5.3414y + 1.8201z + 4.2559 = 0$$

$$[C(6) \ 9, C(7) \ -5, C(8) \ -4, C(9) \ 9, C(10) \ -6, C(11) \ -3, C(3) \ 2410, C(4) \ 1018, C(5) \ -38, C(12) \ -1411, H(15) \ -90, H(16) \ 0, H(17) \ 40, H(18) \ 0, H(19) \ 0]$$

TABLE 4

Comparison of experimental bond lengths (\AA)

	(I)	(II)	(III)
Mean C-C(ring)	1.383	1.382	1.375
C(5)-C(6)	1.486	1.469	1.484
C(4)-C(5)	1.326	1.336	1.331
C(3)-C(4)	1.470	1.466	1.461
C(3)-O(1)	1.211	1.264	1.275
C(3)-O(2)	1.322	1.259	1.253
C(5)-Cl(12)	1.717	1.749	
C(5)-C(12)			1.501

¹⁶ D. R. Lide and D. Christensen, *J. Chem. Phys.*, 1961, **35**, 1374.

¹⁷ L. S. Bartell and R. A. Bonham, *J. Chem. Phys.*, 1960, **32**, 824.

which probably stems from their dissimilar intramolecular environments.

In this connection the comparison of the bond lengths C(12)-C(5)=C(4) in the β -methyl acid with those of propylene¹⁶ and isobutene¹⁷ is interesting: the C=C values of 1.331, 1.336, and 1.334 \AA are identical, as are the CH₃-C lengths of 1.501, 1.501, and 1.505 \AA .

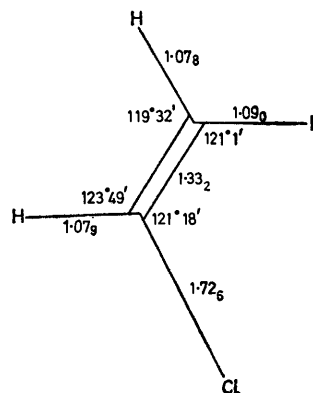


FIGURE 3 Vinyl chloride: bond lengths and angles (from ref. 15)

Intramolecular Non-bonded Interactions.—Comparable non-bonded 1,3-interactions in the three acids (Table 5) show reasonably small scatter, and hence determine to a large degree the conformational details.¹⁸ Thus, the

TABLE 5

Comparison of intramolecular 1,3-non-bonded distances (\AA)

	(I)	(II)	(III)	Mean
C(3) \cdots C(5)	2.52	2.49	2.50	
C(4) \cdots C(6)	2.49	2.54	2.50	
C(5) \cdots C(7)	2.50	2.49	2.47	
C(5) \cdots C(11)	2.49	2.48	2.50	2.50 \pm 0.04
O(1) \cdots O(2)	2.22	2.22	2.21	2.22
O(1) \cdots C(4)	2.31	2.31	2.33	
O(2) \cdots C(4)	2.39	2.38	2.40	2.35 \pm 0.05
C(Me) \cdots C(4)			2.45	
C(Me) \cdots C(6)			2.52	
Cl \cdots C(4)	2.65	2.63		
Cl \cdots C(6)	2.71	2.70		2.67 \pm 0.04

If we assign 'non-bonded radii' of $\frac{1}{2}(2.50 \text{ \AA})$ to carbon and of $\frac{1}{2}(2.22 \text{ \AA})$ to oxygen we arrive at the 'calculated' C \cdots O distance of 2.36 \AA , the mean of the experimental values.

shape of the almost planar system O(1),O(2),C(3)-(6),Cl in the *trans*-acid appears to be determined by the contacts Cl \cdots C(6), Cl \cdots C(4), and Cl \cdots O(1) since these distances reproduce the values observed in *o*-chlorobenzoic acid¹⁹ (Figure 4). The twist of 11.7° around the C(5)-C(6) bond is probably controlled by the Cl \cdots H(15) (2.51 \AA), Cl \cdots C(7) (2.97 \AA), and H(14) \cdots H(19) (2.02 \AA) contacts.

The twist around C(5)-C(6) in the *cis*-acid (65.4°) is

¹⁸ L. S. Bartell, *Tetrahedron*, 1962, **17**, 177.

¹⁹ G. Ferguson and G. A. Sim, *Acta Cryst.*, 1961, **14**, 1262.

probably due to the $O(2) \cdots H(19)$ and $O(2) \cdots C(11)$ interactions.

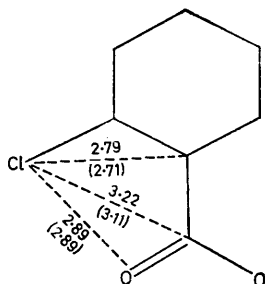


FIGURE 4 *o*-Chlorobenzoic acid. Some intramolecular contacts (from ref. 19). Corresponding distances in β -chloro-*trans*-cinnamic acid in parentheses

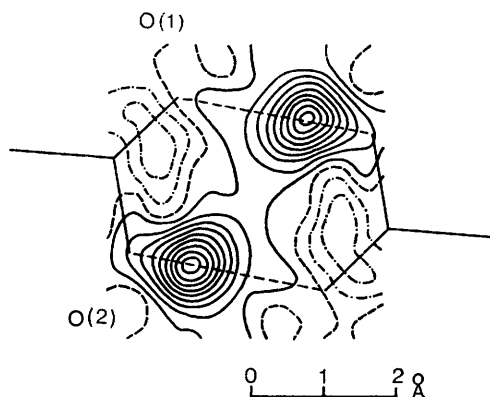


FIGURE 5 β -Chloro-*trans*-cinnamic acid. Electron-density difference-Fourier section in the plane of the carboxy-dimer, contoured at intervals of $0.05 \text{ e}\text{\AA}^{-3}$; zero contours are dashed and negative contours dash-dotted

In the methyl-*cis*-acid (III) the twist around $C(5)-C(6)$ is still larger, (83.3°) and the angle $C(4)-C(5)-C(6)$ smaller, than in the chloro-analogue. In this configuration

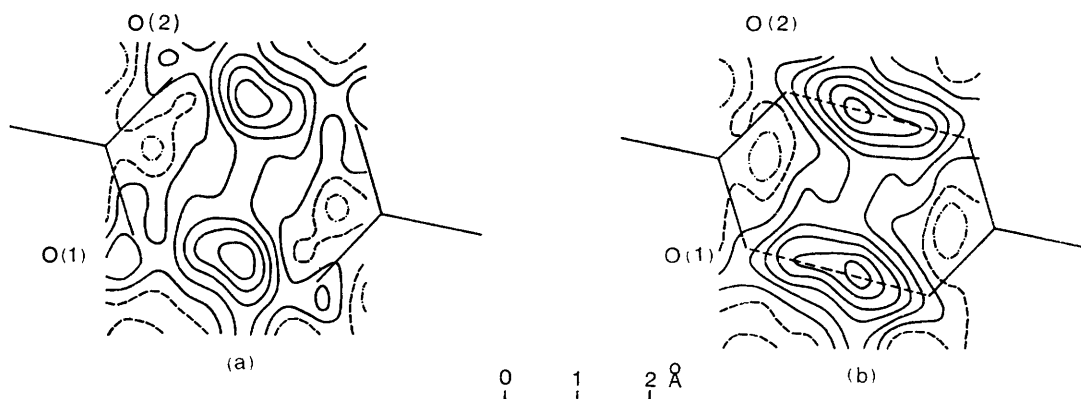


FIGURE 6 β -Chloro-*cis*-cinnamic acid; electron-density difference-Fourier section in the plane of the carboxy-dimer (a) before and (b) after insertion of two 'half' electrons, contoured as for Figure 5

$O(1), O(2), C(3)-(6)$ is planar whereas in the chloro-acid (II) the plane of the carboxy-groups makes an angle of 9° with that of the plane of $C(3)-(6)$. The *cis*-conform-

²⁰ L. Leiserowitz and G. M. J. Schmidt, *Acta Cryst.*, 1965, **18**, 1058.

ation of the exocyclic $C=C$ and $C=O$ groups in the *trans*-acid (I) follows the established pattern.²⁰

Structure of the Carboxy-group.—The refinement of (I) had proceeded normally with all hydrogen atoms included in chemically reasonable positions, in particular with $H(13)$ attached to the longer $C-O$ bond along the intermolecular $O \cdots O$ vector. The carboxy-group had $C-O$ bond lengths of 1.211 \AA [$O(1)$] and 1.322 \AA [$O(2)$] with a hydrogen-bonded distance $O-H \cdots O$ of 2.66 \AA . A difference-Fourier synthesis based on F_o computed with all atoms except the hydroxy-hydrogen (Figure 5) clearly showed the peak ($0.5 \text{ e}\text{\AA}^{-3}$) of this hydrogen. The position of the hydroxy-hydrogen was therefore reasonably well defined with $O-H$ 0.96 \AA , and $C(3)-O(2)-H(13)$ 110° ; the temperature factor of the hydrogen atom was 0.086 \AA^2 . The deviation of the hydrogen from the plane of $O(1), O(2), C(3), C(4)$ was 0.04 \AA ; the carboxy-groups forming the hydrogen bridge were not coplanar, the displacement between them being 0.074 \AA .

On the other hand, the two $C-O$ bonds of (II) and (III) were equal in length (1.261 and 1.259 \AA) or nearly so (1.259 and 1.282 \AA). In order to locate the hydroxy-hydrogens in these two compounds difference-Fourier syntheses $\delta(xyz)$ (Figures 6a, 7a) in the planes of the carboxy-groups were computed: these maps showed peaks of maximum height $0.3 \text{ e}\text{\AA}^{-3}$, extending along the $O \cdots O$ line. Since hydrogen atoms could not be assigned to either $O(1)$ or $O(2)$ two 'half-electrons' were inserted along the $O \cdots O$ line at 1 \AA from each oxygen, and their positional and thermal parameters refined. In the chloro-*cis*-acid (II) the two 'half-electrons' were eventually located at 0.87 and 0.92 \AA respectively from their nearest oxygen atoms, with temperature factors of 0.077 and 0.048 \AA^2 . R' and R which before the insertion of those 'half-electrons' had been 0.020 and 0.047 (observed only) and 0.050 (all reflections) were reduced to

0.016 and 0.042 (0.046). The two $C-O$ bond lengths were then 1.264 and 1.259 \AA . The positional parameters of the other heavy atoms were unaffected by this treatment; the changes in u_{ij} did not exceed 3σ of these parameters. A new difference-Fourier synthesis $\delta(xyz)$

in the plane of the carboxy-group based on all atoms except the two 'half-electrons' h^1, h^2 showed two better-resolved peaks of height 0.25 and 0.30 $e\text{\AA}^{-3}$ in the $O \cdots O$

110 and 118°. The distances of $h^1(13)$ and $h^2(13)$ from the plane of C(3), C(4), O(1), O(2) are 0.03 and 0.01 Å. The carboxylic-acid pair is coplanar to within 0.02 Å.

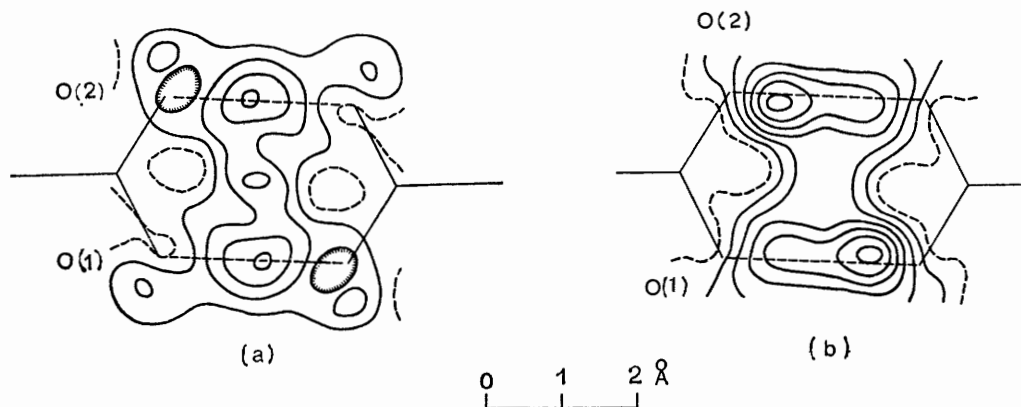


FIGURE 7 β -Methyl-*cis*-cinnamic acid: electron-density difference-Fourier section in the plane of the carboxy-dimer (a) before and (b) after insertion of two 'half' electrons, contoured as before

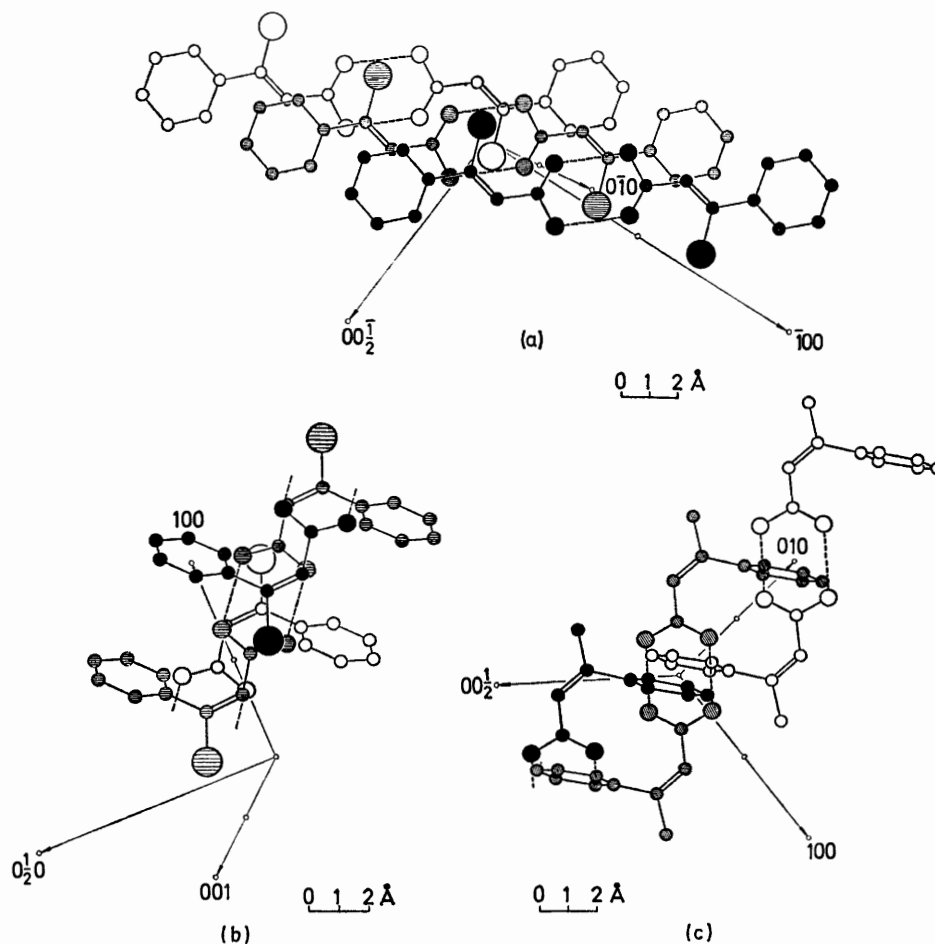


FIGURE 8 Molecular packing arrangements seen perpendicular to the plane of the carboxy-group: (a) β -chloro-*trans*-, (b) β -chloro-*cis*-, and (c) β -methyl-*cis*-cinnamic acid

region (Figure 6b). The peak of lower density corresponded to the 'half-electron' having the higher temperature factor.

The angles $C(3)-O(1)-h^1(13)$ and $C(3)-O(2)-h^2(13)$ are

For the β -methyl-*cis*-acid (III), as before, two 'half-electrons' were inserted and least-squares refinement was continued until R' and R were reduced from 0.017 and 0.063 (0.071) to 0.014 and 0.057 (0.066). The C-O bond

lengths were then 1.253 and 1.275 Å whilst the positional parameters of all other atoms remained unchanged. The difference-Fourier map based on the last refinement cycle without the contribution of the two 'half-electrons' (Figure 7b) shows peaks of heights 0.24 and 0.32 eÅ⁻³, at 0.86 and 0.71 Å respectively from their nearest oxygen atoms, with temperature factors of 0.074 and 0.035 Å². The angles C(3)-O(1)-h¹(13) and C(3)-O(2)-h²(13) are 114 and 113°. The distance of h¹ and h² from the plane of O(1), O(2), C(3), C(4) are 0.05 and 0.03 Å; the carboxy-dimer is non-planar, the perpendicular distance between the planes of the two carboxy-groups being 0.184 Å.

In order to test the significance of an iteration procedure based on two 'half-electrons' the same treatment was applied to the carboxy-group of the β-chloro-*trans*-acid. Replacement of the hydroxy-hydrogen by two 'half-electrons' 1.0 Å from each oxygen atom along the O...O vectors with temperature factors of 0.086 Å² led after one iteration to $u = 0.197$ Å² of the 'half-electron' attached to the C=O and to 0.002 Å² of the other 'half-electron'; the positional parameters of the oxygen atoms remained unchanged. Thus, the least-squares refinement removed the electron density near the doubly-bonded oxygen and sharpened up the 'half-electron' in the neighbourhood of the 'proton' position.

Thus, we have two examples of organic acids in which

TABLE 6

Intermolecular contacts (Å) bounded at the sums of van der Waals radii²¹ plus 0.5 Å

(a) β-Chloro- <i>trans</i> -cinnamic acid			
<i>A</i> (000)*	<i>D</i> (011)		<i>D</i> (001)
C(8) ... H(17)	3.17	C(8) ... C(9)	3.86
C(9) ... C(9)	3.85	C(8) ... C(10)	3.80
C(9) ... H(16)	3.19	C(9) ... C(9)	3.85
C(9) ... H(17)	3.19		
C(10) ... H(16)	3.18		
		<i>C</i> (000)	
		C(7) ... Cl(12)	3.74
		C(7) ... H(15)	3.27
		Cl(12) ... C(12)	3.86
		Cl(12) ... H(15)	3.46
		H(15) ... H(15)	2.48
		<i>B̄</i> (011)	
		C(4) ... C(10)	3.77
		C(4) ... C(18)	3.38
		C(10) ... H(14)	3.28
		C(11) ... H(14)	3.36
		<i>A</i> (010)	
		C(8) ... C(11)	3.80
		C(9) ... C(11)	3.78
		<i>Ā</i> (010)	
		O(1) ... C(3)	3.43
		O(1) ... C(4)	3.52
		C(3) ... C(4)	3.76
		C(3) ... Cl(12)	4.02
		<i>A</i> (000)	
		O(1) ... O(1)	3.25
		O(1) ... O(2)	2.66
		O(1) ... H(13)	1.69
		<i>B̄</i> (001)	
		O(2) ... C(11)	3.46
		O(2) ... H(19)	2.61
		H(13) ... H(18)	2.75

TABLE 6 (Continued)

(b) β-Chloro-*cis*-cinnamic acid

<i>A</i> (000) †	<i>A</i> (101)	<i>A</i> (001)	
C(5) ... H(16)	3.20	C(8) ... Cl(12)	3.89
Cl(12) ... H(16)	2.97	C(9) ... Cl(12)	3.52
		C(10) ... Cl(12)	3.76
		<i>B</i> (101)	
		C(10) ... H(16)	3.11
		<i>A</i> (100)	
		O(1) ... Cl(12)	3.64
		O(2) ... H(15)	2.81
		C(3) ... Cl(12)	3.61
		C(10) ... H(15)	3.40
		C(11) ... Cl(12)	3.99
		C(11) ... H(15)	3.22
		<i>Ā</i> (100)	
		O(1) ... C(4)	3.36
		O(1) ... H(14)	2.38
		C(3) ... H(14)	3.35
		H(14) ... H(14)	2.89
		<i>Ā</i> (101)	
		O(1) ... O(1)	3.39
		O(1) ... O(2)	2.62
		O(1) ... C(3)	3.38
		O(2) ... C(3)	3.42
		C(3) ... C(3)	3.82
		<i>B̄</i> (001)	
		C(6) ... H(17)	3.27
		C(7) ... H(17)	3.11
		C(8) ... H(17)	3.05
		C(9) ... H(17)	3.15
		C(10) ... H(17)	3.29
		C(11) ... H(17)	3.35
		C(11) ... H(18)	3.22
		<i>B̄</i> (100)	
		C(8) ... C(10)	3.87
		C(8) ... H(18)	3.21
		C(9) ... H(18)	3.31
		H(16) ... H(18)	2.51
		H(17) ... H(18)	2.74
		<i>A</i> (101)	
		C(8) ... Cl(12)	3.78
		<i>B̄</i> (001)	
		C(6) ... H(17)	3.27

(c) β-Methyl-*cis*-cinnamic acid

<i>A</i> (000) †	<i>B</i> (111)	<i>B</i> (011)	
C(4) ... C(8)	3.68	C(8) ... H(17)	3.27
C(4) ... H(16)	3.34	C(8) ... H(18)	3.18
C(5) ... C(8)	3.79	H(16) ... H(18)	2.68
C(12) ... H(17)	3.31		
H(16) ... H(21)	2.90		
		<i>B̄</i> (001)	
		C(8) ... O(1)	3.59
		<i>B</i> (101)	
		C(6) ... H(15)	3.22
		C(7) ... H(15)	3.33
		C(9) ... C(12)	3.57
		C(9) ... H(20)	2.97
		C(8) ... H(15)	3.33
		C(10) ... H(20)	3.35
		C(11) ... H(15)	3.20
		H(17) ... H(20)	2.83
		<i>Ā</i> (100)	
		C(4) ... O(1)	3.55
		O(1) ... H(14)	2.63
		H(14) ... H(14)	2.89
		<i>Ā</i> (110)	
		C(4) ... C(12)	3.79
		C(4) ... H(21)	3.09
		H(14) ... H(21)	2.83
		<i>A</i> (100)	
		C(9) ... C(12)	3.79
		C(9) ... H(20)	3.22
		C(10) ... C(12)	3.62

* Co-ordinates of equivalent positions:

<i>A</i> x, y, z	<i>C</i> $\frac{1}{2} - x, y, \bar{z}$
<i>Ā</i> $\bar{x}, \bar{y}, \bar{z}$	<i>C̄</i> $\frac{1}{2} + x, \bar{y}, x$
<i>B</i> $x, \frac{1}{2} + y, \frac{1}{2} + z$	<i>D</i> $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$
<i>C̄</i> $\bar{x}, \frac{1}{2} - y, \frac{1}{2} - z$	<i>D̄</i> $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$

† Co-ordinates of equivalent positions:

<i>A</i> x, y, z	<i>B</i> $\bar{x}, \frac{1}{2} + y, \frac{1}{2} - z$
<i>Ā</i> $\bar{x}, \bar{y}, \bar{z}$	<i>B̄</i> $x, \frac{1}{2} - y, \frac{1}{2} + z$

A(*pqr*) denotes fractional co-ordinates $p + x, q + y, r + z$.

the C-O bond lengths of the carboxy-groups are essentially equal (1.26 ± 0.01), as are the O...O contacts of 2.63 ± 0.01 Å. We suggest that the equality of the two C-O bond lengths can be accounted for by packing disorder of the carboxy-group pair.

Packing Arrangement.—Molecules of the chloro-*trans*-acid (I) are steeply inclined to the *ac* plane such that the interplanar distance between molecules related by the *b* axis is 3.48 Å. The packing diagram along the normal to the molecular plane (Figure 8a) shows that the hydrogen-bonded dimers at (000) and (010) are sandwiched between antiparallel C-Cl bonds. The C=O groups are packed antiparallel across centres of symmetry. No short translation contact of benzene rings exists between the molecular dimers along the *b* axis; instead, molecular overlap occurs between the ethylene system and part of the benzene ring.

The crystal structure of the *cis*-acid (II) also displays carboxy-acid dimers which are sandwiched between C-Cl bonds (Figure 8b). The crystal structure of (III) shows hydrogen-bonded dimers which are sandwiched between antiparallel benzene rings (Figure 8c). No abnormally short intermolecular distances have been observed; a list of van der Waals contacts is given in Table 6.²¹

The implications of these packing arrangements for the mechanism of photoisomerisation in the solid state will be discussed elsewhere.

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²¹ L. Pauling, 'The Nature of the Chemical Bond,' 3rd edn., Cornell University Press, Ithaca, New York, 1960, p. 260.