

Un angle endocyclique des phényles diffère peut-être significativement de 120°: c'est l'angle C_o-C(7)-C_o dont le sommet est le carbone C(7) lié à l'azote N(6). Il vaut 118,3 (3)° dans le composé (I) et 117,5 (4)° dans le composé (II). De telles déformations dans le cycle benzénique par rapport à la géométrie hexagonale idéale ont été mises au compte du pouvoir électro-captateur du groupement attaché au benzène (Domenicano, Vaciego & Coulson, 1975).

JPD et MH marquent leur gratitude respectivement au Fonds National (Belge) de la Recherche Scientifique et à l'Institut pour l'Encouragement de la Recherche Scientifique dans l'Industrie et l'Agriculture pour les mandat et bourse dont ils ont bénéficié. Le diffractomètre a été acquis grâce à une subvention du Fonds de la Recherche Fondamentale Collective.

Références

DOMENICANO, A., VACIEGO, A. & COULSON, C. A. (1975). *Acta Cryst.* B31, 221-234.

Acta Cryst. (1981). B37, 1299-1301

3-Coumaric Acid*

BY S. RAGHUNATHAN AND VASANTHA PATTABHI

Department of Crystallography and Biophysics, University of Madras, Guindy Campus, Madras-600025, India

(Received 12 November 1980; accepted 5 January 1981)

Abstract. C₉H₈O₃, monoclinic, $P2_1/n$, $a = 5.402$ (3), $b = 18.693$ (11), $c = 7.973$ (4) Å, $\beta = 98.28$ (2)°, $V = 796.8$ Å³, $Z = 4$, $D_m = 1.395$, $D_c = 1.388$ Mg m⁻³, $M_r = 164.2$. $R = 0.072$ for 1236 reflections. O-H...O hydrogen bonds link the molecules to form dimers. The interplanar angle between the phenyl ring and the carboxyl group is 6.5 (8)°.

Introduction. The spatial relationship between the ring and the side chain is an important factor in the activity of auxin molecules. After a study of structure and activity, it was suggested (Veldstra, 1944) that, for an auxin molecule to be active, the ring and the carboxyl group should lie in different planes. The crystal structure of 3-coumaric acid (3-hydroxy-*trans*-cinnamic acid) was investigated as part of the project on the structure and function of plant hormones. Cinnamic acid exists in *cis* and *trans* forms. *cis*-Cinnamic acid demonstrates good auxin activity and its *trans* isomer does not.

GERMAIN, G., DECLERCQ, J. P., TOUILLAUX, R., VAN MEERSSCHE, M. & HENRIET, M. (1979). *Acta Cryst.* B35, 3068-3070.

MAIN, P., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J. P. & WOOLFSON, M. M. (1978). *MULTAN 78. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. de York, Angleterre, et Louvain, Belgique.

MAIN, P., LESSINGER, L., WOOLFSON, M. M., GERMAIN, G. & DECLERCQ, J. P. (1977). *MULTAN 77. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. de York, Angleterre, et Louvain, Belgique.

MOTHERWELL, S. & CLEGG, W. (1978). *PLUTO*. Univ. de Cambridge, Angleterre.

SHELDRIK, G. M. (1976). *SHELX 76. Program for Crystal Structure Determination*. Univ. de Cambridge, Angleterre.

STEWART, J. M., KRUGER, G. J., AMMON, H. L., DICKINSON, C. & HALL, S. R. (1972). *XRAY 1972*. The XRAY system - version of June 1972. Tech. Rep. TR-192, Computer Science Center, Univ. de Maryland.

Crystals were obtained by evaporation from a mixture of chloroform, hexane and ether. The cell parameters were refined by least squares (Main & Woolfson, 1963) from 24 reflections. Intensities for 1236 reflections with $2\theta \leq 130^\circ$ were measured with a $\theta/2\theta$ scan, Ni-filtered Cu K α radiation ($\lambda = 1.5418$ Å) and a 2° min⁻¹ scan speed. The scan range was 2° and the background was measured on either side of the peak for 10 s. The data were corrected for Lorentz and polarization factors but not for absorption. Each reflection was assigned a weight (σ_F) by calculating the reciprocal of the variance of observation (Stout & Jensen, 1968).

The structure was solved by symbolic addition (Karle & Karle, 1963). 158 reflections with $|E| \geq 1.5$ were used to generate triplets and phase propagation was carried out by hand with the \sum_2 formula (Hauptman & Karle, 1953). An *E* map revealed all 12 non-H atoms ($R = 0.45$). Block-diagonal least-squares refinement of these atoms (Shiono, 1968), with isotropic temperature factors, reduced *R* to 0.17. A difference synthesis computed at this stage revealed all

* Contribution No. 544.

Table 1. Fractional positional parameters ($\times 10^4$) and equivalent isotropic temperature factors for the non-H atoms with e.s.d.'s in parentheses

$$B_{eq} = \frac{1}{3} \sum_{i=1}^3 \sum_{j=1}^3 (a_i \cdot a_j) \beta_{ij} \quad \sigma(B_{eq}) = \frac{1}{3} \sum_{i=1}^3 \sum_{j=1}^3 (a_i \cdot a_j) \sigma(\beta_{ij})$$

	x	y	z	B (Å ²)
O(3)	1396 (5)	3646 (2)	10168 (3)	2.96 (11)
O(2)	-2535 (5)	4530 (1)	821 (3)	2.98 (11)
O(1)	-5472 (4)	4977 (1)	2209 (3)	3.13 (9)
C(1)	-3392 (6)	4621 (2)	2147 (4)	2.70 (7)
C(2)	-2222 (6)	4354 (2)	3813 (4)	2.89 (11)
C(3)	-134 (6)	3978 (2)	3979 (4)	3.09 (8)
C(4)	1243 (6)	3679 (2)	5545 (4)	3.69 (12)
C(5)	546 (6)	3817 (2)	7140 (4)	3.67 (12)
C(6)	1939 (7)	3527 (2)	8572 (4)	3.00 (11)
C(7)	3989 (7)	3094 (2)	8458 (4)	3.10 (15)
C(8)	4660 (7)	2956 (2)	6876 (5)	3.71 (10)
C(9)	3321 (6)	3253 (2)	5428 (4)	3.72 (11)

Table 2. Fractional positional ($\times 10^3$) and isotropic thermal parameters of the H atoms, with e.s.d.'s in parentheses

	x	y	z	B (Å ²)
H(C2)	-293 (6)	444 (2)	479 (4)	1.7
H(C3)	43 (7)	385 (2)	309 (4)	2.9
H(C5)	-104 (6)	414 (2)	718 (4)	4.4
H(C7)	511 (6)	287 (2)	960 (5)	2.6
H(C8)	592 (6)	266 (2)	667 (4)	2.3
H(C9)	395 (7)	310 (2)	430 (4)	3.1
H(O1)	-637 (6)	511 (2)	97 (4)	7.2
H(O3)	-9 (7)	389 (2)	1019 (4)	6.2

* The average e.s.d. in B is 1.1 Å².

eight H atoms which were assigned the isotropic temperature factors of the atoms to which they were bonded. Full-matrix least-squares refinement was carried out (Gantzel, Sparks & Trueblood, 1961) with isotropic temperature factors for H, anisotropic temperature factors for the non-H atoms and weight $w = 1/\sigma_F^2$ for each reflection giving a final R of 0.072.

Scattering factors for C, O and H were taken from *International Tables for X-ray Crystallography* (1962). The final positional parameters are listed in Tables 1 and 2.*

Discussion. The bond lengths and angles are shown in Fig. 1. The average e.s.d.'s in the bond lengths and angles not involving H atoms are 0.004 Å and 0.2° respectively. The average bond length in the benzene ring is 1.388 (5) Å. C(1)—C(2) and C(3)—C(4) exhibit partial double-bond character with lengths 1.473 (4),

* Lists of structure factors and anisotropic thermal parameters of the non-H atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35890 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

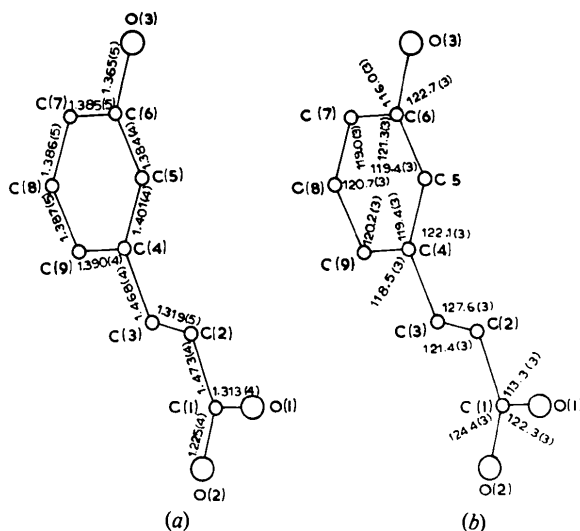


Fig. 1. (a) Bond lengths (Å) and (b) angles (°) with e.s.d.'s in parentheses.

1.468 (4) Å. To minimize steric interaction, C(4)—C(3)—C(2) expands (Zabel, Watson, Cassels & Langs, 1980) to 127.6 (3)° consistent with those in *p*-coumaric acid (126.1°) (Utsumi, Fujii, Irie, Furusaki & Nitta, 1970) and 2-coumaric acid [126.1 (3)°] (Raghunathan & Pattabhi, 1979).

Least-squares planes are given in Table 3. The angle between the two planes is 6.5 (8)°. This is comparable to the angle between the ring and the carboxyl group planes in other related structures such as *p*-coumaric acid (5°) (Utsumi *et al.*, 1970), 2-coumaric acid (4.8°) (Raghunathan & Pattabhi, 1979) and β -chloro-*trans*-cinnamic acid (11.7°) (Fillipakis, Leiserowitz, Rabinovich & Schmidt, 1972) but differs significantly from that in β -chloro-*cis*-cinnamic acid (65.4°) and β -methyl-*cis*-cinnamic acid (83°) (Fillipakis *et al.*, 1972).

C(4) is *trans* to C(1) with torsion angle C(1)—C(2)—C(3)—C(4) = 179.4 (3)°. Table 4 lists the corresponding torsion angle and the interplanar angle observed in other plant hormones. The table shows that

Table 3. Equations of least-squares planes and atomic deviations (Å)

(i) Phenyl ring

Plane through C(4), C(5), C(6), C(7), C(8), C(9)

$$0.5836x + 0.8066y + 0.0930z = 5.9782$$

C(4)	0.003 (3)	C(7)	0.001 (4)
C(5)	0.004 (3)	C(8)	0.007 (4)
C(6)	-0.006 (3)	C(9)	-0.009 (3)

(ii) Carboxyl group

Plane through O(1), O(2), C(1), C(2)

$$0.5040x + 0.8495y + 0.1554z = 6.5570$$

O(1)	-0.001 (3)	C(1)	0.003 (3)
O(2)	-0.001 (2)	C(2)	-0.001 (3)

Table 4. Torsion angle and the interplanar angle observed in some plant hormones ($^{\circ}$)

Molecule	Torsion angle*	Angle between planes†
3-Coumaric acid ^a	179.4	6.5
2-Coumaric acid ^b	-179.2	4.8
4-Coumaric acid ^c	179.0	5.0
2-Naphthoxyacetic acid ^d	176.5	4.2
2-Chlorophenoxyacetic acid ^e	-173.2	6.8
2,4,5-Trichlorophenoxyacetic acid ^f	-174.6	4.1
2,4-Dichlorophenoxyacetic acid ^g	-80.5	85.2
2,4,5-Trichlorophenoxypropanoic acid ^h	-71.3	77.8
2-(4-Chloro-2-methylphenoxy)propanoic acid ⁱ	78.6	85.5
2,4,6-Trichlorophenoxyacetic acid ^j	-152.3	32.0
2,5-Dichlorophenoxyacetic acid ^k	-72.4	81.2

References: (a) Present study, (b) Raghunathan & Pattabhi (1979), (c) Utsumi *et al.* (1970), (d) Pattabhi, Raghunathan & Chacko (1978), (e) Chandrasekhar & Pattabhi (1977), (f) Smith, Kennard & White (1976b), (g) Smith, Kennard & White (1976a), (h) Smith, Kennard, White & Hodgson (1977), (i) Smith, Kennard, White & Hodgson (1980), (j) Smith, Kennard & White (1977), (k) Smith, Whitnall & Kennard (1976).

* Torsion angle about the bond connecting the benzene ring and the carboxyl group.

† Angle between the benzene ring and carboxyl group.

the interplanar angle is always close to 0° when this torsion angle is *trans*, probably due to steric interactions. On the other hand the carboxyl group takes a perpendicular conformation when this angle is close to *gauche*.

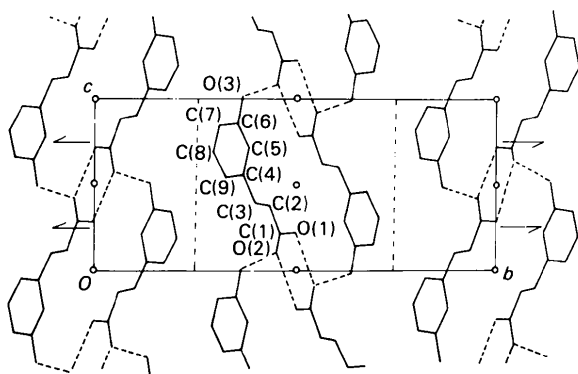


Fig. 2. The crystal structure of 3-coumaric acid viewed down [100]. Hydrogen bonds are shown by broken lines.

Table 5. Hydrogen-bond lengths (\AA) and angles ($^{\circ}$)

D-H...A	D-H	D...A	H...A	D-H...A
O(1)-H(O1)...O(2) ⁱ	1.06 (7)	2.65 (1)	1.60 (7)	169.3 (2.1)
O(3)-H(O3)...O(2) ⁱⁱ	0.94 (7)	2.80 (1)	1.89 (7)	163.0 (2.1)

Symmetry code: (i) $-1-x, 1-y, -z$; (ii) $x, y, 1+z$.

The packing of the molecules is illustrated in Fig. 2 as viewed down *a*. The molecules translated along *c* are cross-linked by O-H...O hydrogen bonds [2.80 (1) \AA] involving the terminal carboxyl O(2) and the central hydroxyl O(3) to form an infinite zig-zag chain. These chains are linked by O-H...O hydrogen bonds [2.65 (1) \AA] around the centre of symmetry forming dimers involving O(1) and O(2) of the carboxyl group. The hydrogen bonds help the chains to form a set of parallel sheets which are held together by van der Waals forces. The hydrogen-bonding scheme is given in Table 5.

One of us (SR) thanks the University Grants Commission and the CSIR, India, for financial assistance.

References

- CHANDRASEKHAR, K. & PATTABHI, V. (1977). *Acta Cryst.* B33, 1257-1260.
- FILLIPAKIS, S. E., LEISEROWITZ, L., RABINOVICH, D. & SCHMIDT, G. M. J. (1972). *J. Chem. Soc. Perkin Trans. 2*, pp. 1750-1758.
- GANTZEL, P. K., SPARKS, R. A. & TRUEBLOOD, K. N. (1961). Program UCLALS 1, Univ. of California.
- HAUPTMAN, H. & KARLE, J. (1953). *The Solution of the Phase Problem. I. The Centrosymmetric Crystal*, ACA Monograph No. 3. Pittsburgh: Polycrystal Book Service.
- International Tables for X-ray Crystallography* (1962). Vol. III. Birmingham: Kynoch Press.
- KARLE, J. & KARLE, I. L. (1963). *Acta Cryst.* 16, 969-975.
- MAIN, P. & WOOLFSON, M. M. (1963). *Acta Cryst.* 16, 731-733.
- PATTABHI, V., RAGHUNATHAN, S. & CHACKO, K. K. (1978). *Acta Cryst.* B34, 3118-3120.
- RAGHUNATHAN, S. & PATTABHI, V. (1979). *Acta Cryst.* B35, 214-215.
- SHIONO, R. (1968). Block-diagonal least-squares program for the IBM 1130. Department of Crystallography, Univ. of Pittsburgh.
- SMITH, G., KENNARD, C. H. L. & WHITE, A. H. (1976a). *J. Chem. Soc. Perkin Trans. 2*, pp. 791-792.
- SMITH, G., KENNARD, C. H. L. & WHITE, A. H. (1976b). *Aust. J. Chem.* 29, 2727-2730.
- SMITH, G., KENNARD, C. H. L. & WHITE, A. H. (1977). *Cryst. Struct. Commun.* 6, 49-52.
- SMITH, G., KENNARD, C. H. L., WHITE, A. H. & HODGSON, P. G. (1977). *Acta Cryst.* B33, 2922-2924.
- SMITH, G., KENNARD, C. H. L., WHITE, A. H. & HODGSON, P. G. (1980). *Acta Cryst.* B36, 992-994.
- SMITH, G., WHITNALL, J. & KENNARD, C. H. L. (1976). *Cryst. Struct. Commun.* 5, 749-752.
- STOUT, G. H. & JENSEN, L. H. (1968). *X-ray Structure Determination*. New York: Macmillan.
- UTSUMI, H., FUJII, K., IRIE, H., FURUSAKI, A. & NITTA, I. (1970). *Nippon Kagaku Zasshi (J. Chem. Soc. Jpn)*, 91, 439-443.
- VELDSTRA, H. (1944). *Enzymologia*, 11, 97-163.
- ZABEL, V., WATSON, W. H., CASSELS, B. K. & LANGS, D. A. (1980). *Cryst. Struct. Commun.* 9, 461-467.