

In the solid state, the *trans-trans* and *trans-gauche* configurations for the C<sub>α</sub>-C<sub>β</sub> and C<sub>β</sub>-C<sub>γ</sub> bonds of the dimethylaminopropyl substituent have been observed (Corey, Corey & Glick, 1976). The dimethylaminopropyl groups of the two independent molecules in the recently published structure of (+)-*cis*-9-(3-dimethylaminopropyl)-10-methyl-2-(trifluoromethyl)-9,10-dihydroanthracene (Chu & Chung, 1976) have the *trans-trans* configuration, as is observed in this structure.

The distance between the chloride ion and the quarternary ammonium center is 3.016 (3) Å; the Cl to H distance in the hydrogen bond is 1.98 (4) Å and the N-H...Cl angle is 178 (3)°. The closest intermolecular nonbonded distance between non-H atoms is 3.641 (4) Å between Cl(22) and C(20)', related by translation in the y direction.

JYC and ERC acknowledge the support of NIH research grant No. R01NS10903 from the National Institute of Neurological Diseases and Stroke.

#### References

- BORDNER, J., STANFORD, R. H. JR & ZIEGER, H. E. (1973). *Acta Cryst.* **B29**, 313-318.
- BRENNAN, T., PUTKEY, E. F. & SUNDARALINGAM, M. (1971). *J. Chem. Soc. (D)*, pp. 1490-1491.
- BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). *ORFLS*. Oak Ridge National Laboratory Report ORNL-TM-305.
- BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1964). *ORFFE*. Oak Ridge National Laboratory Report ORNL-TM-306.
- CHU, S. S. C. & CHUNG, B. (1973). *Acta Cryst.* **B29**, 2253-2259.
- CHU, S. S. C. & CHUNG, B. (1974). *Acta Cryst.* **B30**, 1616-1618.
- CHU, S. S. C. & CHUNG, B. (1976). *Acta Cryst.* **B32**, 836-842.
- CHU, S. S. C. & MANGION, M. (1975). *Acta Cryst.* **B31**, 2134-2136.
- COREY, E. R., COREY, J. Y. & GLICK, M. D. (1976). *Acta Cryst.* **B32**, 2025-2031.
- D'YACHENKO, O. A., ATOVMIAN, L. O. & SOBELEVA, S. V. (1975). *Zh. Strukt. Khim.* **16**, 505-508; *Chem. Abs.* **83**, 200520i.
- D'YACHENKO, O. A., ATOVMIAN, L. O. & SOBOLEVA, S. V. (1976). *Zh. Strukt. Khim.* **16**, 191-193; *Chem. Abs.* **84**, 179557w.
- D'YACHENKO, O. A., ATOVMIAN, L. O., SOBOLEVA, S. V., MARKOVA, T. YU., KOMALENKOVA, N. G., SHAMSHIN, L. N. & CHERNYSHEV, E. A. (1974). *Zh. Strukt. Khim.* **15**, 170-171; *Chem. Abs.* **80**, 125760f.
- FERRIER, W. G. & IBALL, J. (1954). *Chem. Ind.* pp. 1296-1297.
- HOSOYA, S. (1958). *Chem. Ind.* pp. 980-981.
- HOSOYA, S. (1966). *Acta Cryst.* **21**, 21-26.
- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press.
- JOHNSON, C. K. (1965). *ORTEP*. Oak Ridge National Laboratory Report ORNL-3794.
- LONG, R. E. (1965). *The Crystal and Molecular Structures of 7,7,8,8-Tetracyanoquinodimethane and Cyclopropane-carboxamide and a Program for Phase Determination*, Thesis, Appendix III, Univ. of California, Los Angeles.
- MIYAKE, S., TOGAWA, S. & HOSOYA, S. (1964). *Acta Cryst.* **17**, 1083-1084.
- PATON, W. F., COREY, E. R., COREY, J. Y. & GLICK, M. D. (1977). *Acta Cryst.* **B33**, 226-228.
- SAYRE, R. (1952). *Acta Cryst.* **5**, 60-65.
- SCHMONSEES, W. (1974). *X-ray Structural Studies of Cobalt and Mercury Transition Metal Complexes*, Thesis, Ch. 1 and Appendix I, Wayne State Univ.
- SOBOLEVA, S. V., D'YACHENKO, O. A. & ATOVMIAN, L. O. (1974). *Izv. Akad. Nauk SSSR, Ser. Khim.* p. 1443; *Chem. Abs.* **81**, 112290y.
- STANFORD, R. H. JR (1973). *Acta Cryst.* **B29**, 2849-2855.
- ZALKIN, A. (1974). *HFINDR: A Fortran Program for the Calculation of Idealized Hydrogen Positions*.

*Acta Cryst.* (1977). **B33**, 1257-1260

## 2-Chlorophenoxyacetic Acid

BY K. CHANDRASEKHAR AND VASANTHA PATTABHI

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

(Received 1 November 1976; accepted 27 November 1976)

**Abstract.** C<sub>8</sub>H<sub>7</sub>O<sub>3</sub>Cl, *M<sub>r</sub>* = 186.5, monoclinic, space group *P2*<sub>1</sub>, *a* = 7.602 (6), *b* = 22.164 (17), *c* = 5.328 (4) Å, β = 114.26 (3)°, *V* = 818.1 Å<sup>3</sup>, *Z* = 4,

*D*<sub>o</sub> = 1.523, *D*<sub>c</sub> = 1.514 g cm<sup>-3</sup>. There are two molecules in the asymmetric unit. Strong hydrogen bonds of the O...H-O type are observed.

**Introduction.** The title compound, a plant-growth hormone, is soluble in warm water, and crystals suitable

\* Contribution No. 446.

for X-ray analysis were obtained by slow evaporation. Cell constants were measured by a least-squares fit of 31  $\theta$  values measured on a Picker four-circle diffractometer. Photographs showed systematic absences indicating space group  $P2_1$  or  $P2_1/m$ ; the latter was eliminated by statistical tests. A suitable crystal was selected and intensities were collected photographically with the multiple-film equi-inclination Weissenberg technique and Ni-filtered Cu  $K\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ). There was a paucity of high-angle data even after long exposures. Intensities of 922 reflexions were estimated visually by comparison with a standard set of spots prepared from the same crystal. They were corrected for Lorentz, polarization and spot-shape factors (Phillips, 1954). No absorption corrections were applied ( $\mu t = 0.74$ ). The  $hkl$  ( $l = 0$  to 4) reflexions were brought to a common scale by cross-correlation with  $hkl$  ( $h = 0, 2$ ) reflexions.

The positions of the Cl atoms were obtained from a Patterson map ( $R = 0.52$ ). The full structure was determined from a Fourier synthesis in which only reflexions having  $|F_{Cl}| \geq \frac{1}{2}|F_o|$  were used. Structure-factor calculations with all 24 non-hydrogen atoms gave an  $R$  of 0.26. Block-diagonal least-squares refinement (Shiono, 1968) with isotropic temperature factors and unit weights for all observed reflexions reduced  $R$  to 0.19. Full-matrix refinement with isotropic temperature fac-

Table 1. Fractional positional parameters ( $\times 10^4$ ) of non-hydrogen atoms, with *e.s.d.*'s in parentheses

	<i>x</i>	<i>y</i>	<i>z</i>
Molecule A			
Cl(1)	9944 (6)	3158 (0)	3300 (9)
C(1)	6478 (22)	2659 (7)	3004 (30)
C(2)	7447 (20)	3061 (7)	1828 (28)
C(3)	6509 (28)	3389 (9)	-370 (38)
C(4)	4550 (27)	3330 (8)	-1338 (37)
C(5)	3546 (30)	2929 (9)	-333 (40)
C(6)	4485 (23)	2619 (8)	1897 (32)
O(1)	7585 (15)	2355 (6)	5229 (19)
C(7)	6559 (23)	1959 (7)	6405 (25)
C(8)	7946 (24)	1734 (7)	8904 (28)
O(2)	7225 (17)	1352 (6)	10122 (24)
O(3)	9690 (18)	1874 (6)	9744 (19)
Molecule B			
Cl(2)	-799 (6)	-276 (3)	1185 (8)
C(9)	2601 (23)	224 (7)	1481 (31)
C(10)	1599 (26)	-164 (8)	2534 (35)
C(11)	2567 (29)	-472 (9)	4850 (39)
C(12)	4607 (26)	-405 (9)	5984 (34)
C(13)	5559 (27)	-16 (9)	4804 (37)
C(14)	4584 (27)	303 (9)	2464 (39)
O(4)	1550 (17)	540 (6)	-732 (22)
C(15)	2510 (21)	941 (9)	-1919 (31)
C(16)	1100 (25)	1157 (8)	-4431 (31)
O(5)	1899 (15)	1538 (6)	-5652 (22)
O(6)	-613 (16)	993 (6)	-5250 (19)

Table 2. Fractional positional parameters ( $\times 10^4$ ) and isotropic thermal parameters ( $\text{\AA}^2$ ) for the hydrogen atoms

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>
H(1)	7166	3666	-1500	6.14
H(2)	4000	3639	-3166	6.75
H(3)	2083	2916	-2000	6.21
H(4)	3835	2278	2805	5.46
H(5)	5333	2222	6666	4.94
H(6)	6223	1611	5056	4.94
H(7)	8011	1000	11833	6.25
H(8)	1834	-653	5653	6.68
H(9)	5000	-500	8333	6.01
H(10)	7120	50	5981	6.67
H(11)	5347	585	1667	6.13
H(12)	3000	1322	-667	5.46
H(13)	3833	722	-2140	5.46
H(14)	1333	1832	7666	5.91

tors and the weighting scheme of Cruickshank, Bujosa, Lovell & Truter (1961),  $w = (a + |F_o| + b|F_o|^2)^{-1}$  with  $a = 1.4$ ,  $b = 0.033$ , and the program of Gantzel, Sparks & Trueblood (1961) yielded an  $R$  of 0.167. The H atoms were fixed from geometrical considerations and evidence for them was found in a difference map. They were given the isotropic temperature factors of the atoms to which they are attached. Full-matrix refinement with isotropic temperature factors for the ring atoms and anisotropic temperature factors for the remainder, yielded a final  $R$  of 0.100.

The positions of the H atoms were not refined. Scattering factors were taken from *International Tables for X-ray Crystallography* (1962) and anomalous dispersion corrections [ $\Delta f' = 0.348$ ,  $\Delta f'' = -0.702$  (Cromer & Liberman, 1970)] were applied for Cl. The final positional parameters of the non-hydrogen atoms are listed in Table 1.\* Table 2 gives the positions of the H atoms.

**Discussion.** The bond lengths and angles are shown in Fig. 1. They are similar (within the  $3\sigma$  limit) to those reported for 2,4-dichlorophenoxyacetic acid (Gopalakrishnan & Rao, 1973; Smith, Kennard & White, 1976). The only major difference is for C(7)-C(8) and C(15)-C(16) which we find to be 1.41  $\text{\AA}$ , while Smith *et al.* (1976) report 1.52  $\text{\AA}$ . The average bond length in the ring system is 1.380  $\text{\AA}$  and the average bond angle 119.9°.

The equations of the least-squares planes: 1 through C(1) to C(6); 2 through C(9) to C(14); 3 through C(7),

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32325 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

C(8), O(2), O(3); 4 through C(15), C(16), O(5), O(6), are

$$1: 0.3213X + 0.7430Y - 0.5870Z = 10.9927$$

$$2: 0.3339X + 0.7607Y - 0.5565Z = -0.2065$$

$$3: 0.4059X + 0.7646Y - 0.5005Z = 11.6669$$

$$4: 0.4189X - 0.7705Y - 0.4804Z = -0.1840$$

where  $X$ ,  $Y$  and  $Z$  are referred to  $\mathbf{a}$ ,  $\mathbf{b}$  and  $\mathbf{c}^*$ .

The angle between planes 1 and 3 is  $7.0^\circ$  and that between 2 and 4 is  $6.6^\circ$ . This is comparable to the angle between the ring system and the carboxyl group planes in *trans*- $\beta$ -2-furylacrylic acid ( $5.7^\circ$ ) (Fillippakis & Schmidt, 1967), but differs significantly from that observed in other plant hormones like 2,4-dichlorophenoxyacetic acid ( $85.2^\circ$ ) (Smith *et al.*, 1976), 3-indolylacetic acid ( $90^\circ$ ) (Karle, Britts & Gum, 1964) and  $\alpha$ -naphthaleneacetic acid ( $97^\circ$ ) (S. S. Rajan, personal communication).

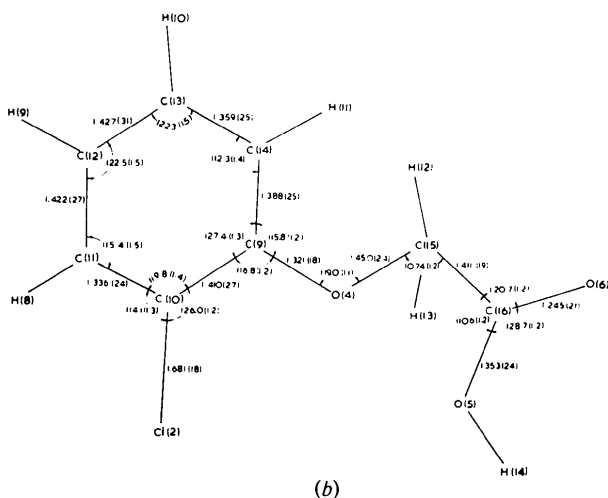
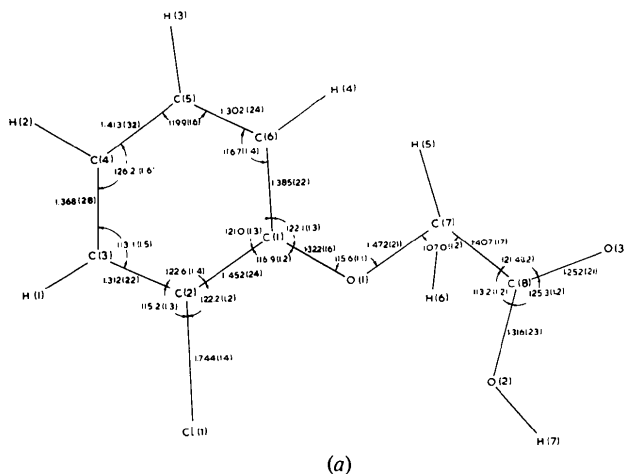


Fig. 1. Bond lengths and angles in 2-chlorophenoxyacetic acid, with e.s.d.'s in parentheses. (a) Molecule A, (b) molecule B.

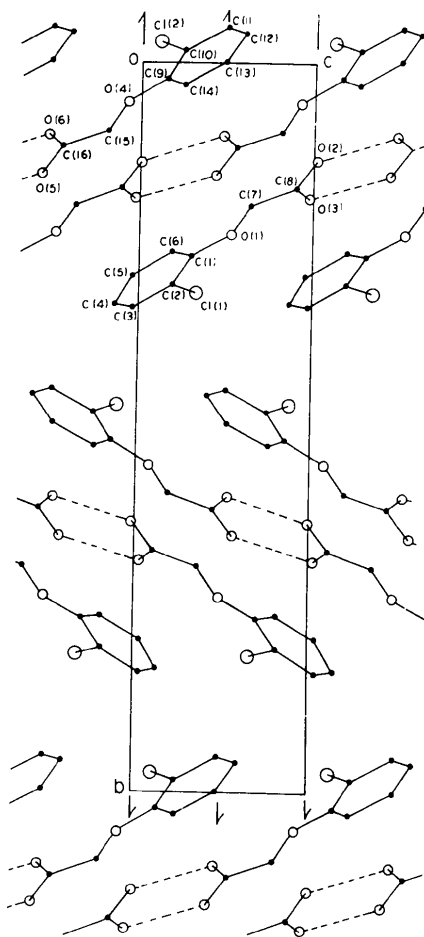


Fig. 2. Projection of the structure down  $\mathbf{a}$ . Hydrogen bonds are shown by broken lines.

Fig. 2 shows the mode of packing of the molecules, viewed down  $\mathbf{a}$ . The two molecules in the asymmetric unit form a dimer, the structure being stabilized by a network of strong hydrogen bonds of the  $\text{O}-\text{H}\cdots\text{O}$  type. The angles  $\text{O}(2)-\text{H}(7)\cdots\text{O}(6)$  and  $\text{O}(3)\cdots\text{H}(14)-\text{O}(5)$  are, respectively,  $138.9$  and  $138.6^\circ$ , while  $\text{O}(2)\cdots\text{O}(6)$  ( $2.467$ ) and  $\text{O}(3)\cdots\text{O}(5)$  ( $2.451$  Å) are about  $0.35$  Å shorter than the  $\text{O}\cdots\text{O}$  van der Waals distance of  $2.8$  Å. Short symmetric bonds seem to be the rule in many acid salts of carboxylic acids (Table 5.4, Hamilton & Ibers, 1968) and it is probable that the  $\text{O}-\text{H}\cdots\text{O}$  bond in the present compound is symmetric. A definitive answer to that question must await a neutron diffraction study.

The authors thank Professor R. Srinivasan for helpful discussions and encouragement. One of the authors (KC) acknowledges financial assistance from the University Grants Commission, New Delhi, India, in the form of a Research Fellowship.

## References

- CROMER, D. T. & LIBERMAN, D. (1970). Los Alamos Scientific Laboratory, Univ. of California Report, LA-4403 UC-34.
- CRUICKSHANK, D. W. J., BUJOSA, A., LOVELL, F. M. & TRUTER, M. R. (1961). In *Computing Methods and the Phase Problem in Crystal Structure Analysis*, edited by R. PEPINSKY & J. M. ROBERTSON. New York: Pergamon Press.
- FILIPPAKIS, S. E. & SCHMIDT, G. M. J. (1967). *J. Chem. Soc. (B)*, pp. 229–234.
- GANTZEL, P. K., SPARKS, R. A. & TRUEBLOOD, K. N. (1961). Univ. of California program UCLALS 1.
- GOPALAKRISHNAN, T. & RAO, L. M. (1973). *Ind. J. Pure Appl. Phys.* **11**, 360–361.
- HAMILTON, W. C. & IBERS, J. A. (1968). *Hydrogen Bonding in Solids*. New York: Benjamin.
- International Tables for X-ray Crystallography* (1962). Vol. III. Birmingham: Kynoch Press.
- KARLE, I. L., BRITTS, K. & GUM, P. (1964). *Acta Cryst.* **17**, 496–500.
- PHILLIPS, D. C. (1954). *Acta Cryst.* **7**, 746–751.
- SHONO, 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. (1976). *J. Chem. Soc. Perkin II*, pp. 791–792.

*Acta Cryst.* (1977). **B33**, 1260–1263

### Tetra-*O*-methyldehydrocaffeic Acid Dilactones, (+) and (–) Isomers

BY HIKARU NAKAMURA AND YOICHI IITAKA

*Faculty of Pharmaceutical Sciences, University of Tokyo, Hongo, Tokyo 113, Japan*

AND YOSHIKI KUMADA, TOMIO TAKEUCHI AND HAMAO UMEZAWA

*Institute of Microbial Chemistry, Kamiosaki, Shinagawa-ku, Tokyo 141, Japan*

(Received 22 October 1976; accepted 29 November 1976)

**Abstract.**  $C_{22}H_{22}O_8$ ,  $M_r = 414.4$ . Orthorhombic,  $P2_12_1$ ,  $a = 10.343$  (3),  $b = 34.014$  (10),  $c = 5.597$  (2) Å,  $Z = 4$ ,  $D_x = 1.398$  g cm<sup>-3</sup>. The absolute configuration was determined for the (+) and (–) compounds from the anomalous dispersion effect of O atoms for Cu  $K\alpha$  radiation.

**Introduction.** Dehydrocaffeic acid dilactone was isolated, with caffeic acid, from a mushroom culture as a result of the inhibitory activity against catechol-*O*-methyltransferase. Both (+) and (–) compounds were produced by the mushroom and they exhibit nearly the same power of inhibition to catechol-*O*-methyltransferase, dopamine  $\beta$ -hydroxylase and dopa decarboxylase (Kumada, Naganawa, Iinuma, Matsuzaki, Takeuchi & Umezawa, 1976).

The crystals were grown from acetone solution as colourless prisms. The crystal,  $0.35 \times 0.27 \times 0.05$  mm, used for the present analysis was the (–) compound. The lattice constants and intensity data were obtained by a Philips four-circle X-ray diffractometer with graphite-monochromated Cu  $K\alpha$  radiation. Intensities of 1879 of 2476 possible reflexions were measured as having  $I_o \geq 2\sigma(I_o)$ , within the  $2\theta$  range of 6–156°, by the  $\theta$ – $2\theta$  scanning method. The scans were repeated twice when the total counts during a single scan were

less than  $10^4$ . The scan speed was  $2\theta = 4^\circ$  min<sup>-1</sup> and the background was measured at each end of the scan for 10 s. The intensities were corrected for Lorentz and polarization effects but not for absorption. The structure was solved by the direct method with *MULTAN* (Main, Woolfson & Germain, 1971). Starting with 10 reflexions, including three origin-defining and three known phases obtained by the  $\Sigma_1$  relations, the phases of 305 structure factors with  $E \geq 1.3$  were assigned, but first attempts to arrive at the correct solution were unsuccessful. Reassignment of the starting set by eliminating the five strongest reflexions yielded a reasonable  $E$  map in which 28 of the 30 heavy atoms could be located. The structure determination was completed by the Fourier method and the refinement was carried out by the block-diagonal least-squares method with *HBL5* (Okaya & Ashida, 1967). Unit weight was applied for each reflexion. The final  $R$  value was 0.043 including all the H atoms with isotropic temperature factors. The final atomic parameters are given in Table 1.\*

\* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32334 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.