

Perchloroindenone:* a Study of the Overcrowding

BY IVANKA MATUJAŠIĆ

Laboratory of Organic Chemistry and Biochemistry, Faculty of Science, University of Zagreb,
Strossmayerov trg 14, 41000 Zagreb, Yugoslavia

AND GABRIELE BOCELLI

Centro di Studio per la Strutturistica Diffraattometrica del CNR, Viale delle Scienze, 43100 Parma, Italy

(Received 30 August 1988; accepted 31 January 1989)

Abstract. C_9Cl_6O , $M_r = 336.82$, monoclinic, $P2_1/n$, $a = 17.508$ (3), $b = 5.715$ (3), $c = 11.294$ (2) Å, $\beta = 93.36$ (4)°, $V = 1128.1$ (7) Å³, $Z = 4$, $D_x = 1.98$ g cm⁻³, $\lambda(\text{Cu } K\alpha) = 1.5418$ Å, $\mu = 140.50$ cm⁻¹, $F(000) = 656$, room temperature, $R = 0.0615$ for 1713 observed unique reflections. The molecular structure is strongly influenced by the overcrowding; there are significant out-of-plane displacements especially in the five-membered ring. The mean C—Cl length in the aromatic ring is 1.714 (5) Å (uncorrected for thermal motion) and intramolecular Cl...Cl and O...Cl contacts are in the range 3.075 (3)–3.318 (2) Å.

Introduction. The structure determination of the title compound has been carried out in order to investigate overcrowding of the vicinal bulky substituents on the aromatic ring and also out-of-plane distortion of the molecule. A number of other molecules containing polyhalogenated aromatic rings have been studied in an attempt to determine whether or not molecular overcrowding can distort molecules that should otherwise be planar (*e.g.* Rudman, 1971; Byrn, Curtin & Paul, 1972; Herbstein, 1979; Fuchs, Lidor, Kruger & Lin, 1980; Marsh & Williams, 1981).

Experimental. Crystal grown by slow evaporation of methylene dichloride, colorless prismatic crystal of dimensions 0.42 × 0.71 × 0.96 mm, Siemens AED single-crystal diffractometer, Ni-filtered Cu $K\alpha$ radiation, cell parameters from least-squares fit of 27 reflections with 2θ values ranging from 30 to 50° accurately measured on the diffractometer, one check reflection measured every 50 counts without significant variation, profile analysis with Lehmann & Larsen (1974) procedure modified by Belletti, Ugozzoli, Cantoni & Pasquinelli (1979), $3 < \theta < 70^\circ$, Lp correction, absorption correction with Walker & Stuart (1983) procedure using *ABSORB* (Ugozzoli,

1986), maximum and minimum values of absorption coefficients in the polar angles φ and μ are 1.22 and 0.83 respectively, $-21 < h < 21$, $0 < k < 6$, $0 < l < 13$, 2467 reflections collected, 1821 observed at $2\sigma(I)$ level, 1743 independent ($R_{\text{int}} = 0.019$, direct methods with *MULTAN80* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980), full-matrix least-squares refinement with *SHELX76* (Sheldrick, 1976), all atoms anisotropic, ten reflections omitted in the last cycles, 145 parameters refined. Final $R = 0.062$ and $wR = 0.067$ with $w = 2.8562/[\sigma^2(F) + 0.00134F^2]$, $\sum w(\Delta F)^2$ minimized, $(\Delta/\sigma)_{\text{max}} = 0.07$ for all atoms, $\Delta\rho_{\text{max}} = 0.61$ e Å⁻³ (at 1.07 Å from Cl1), scattering factors of *SHELX76*, anomalous-dispersion factors taken from *International Tables for X-ray Crystallography* (1974), all calculations on an IBM AT personal computer using the *CRYRULER* package (Rizzoli, Sangermano, Calestani & Andreotti, 1987).

Discussion. The final atomic coordinates are listed in Table 1.† Fig. 1 shows the molecule with numbering of atoms and their deviations from the best molecular plane. Bond distances, angles and selected torsion angles are listed in Table 2.

In the absence of steric distortions all the atoms should lie on the same plane. Our data (Fig. 1) show that strong intramolecular overcrowding causes a significant deviation from planarity. The displacements of the substituted atoms are much greater than in tetrachlorophthalic anhydride: 0.08 (Rudman, 1971) and 0.028 Å (Wilkerson, Chodak & Strouse, 1975); in pentachlorobenzene: 0.04 Å (Marsh & Williams, 1981); and also in two derivatives of indenone: 0.08 (Fuchs *et al.*, 1980) and 0.03 Å (Watson & Nagl, 1987).

† Lists of structure factors, anisotropic thermal parameters and torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51923 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

* 2,3,4,5,6,7-Hexachloro-1-indenone.

Table 1. Atomic fractional coordinates ($\times 10^4$) and U_{eq} ($\times 10^4 \text{ \AA}^2$)
$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	U_{eq}
Cl1	448 (1)	6962 (3)	-2591 (1)	513 (5)
Cl2	316 (1)	2353 (3)	-822 (1)	491 (5)
Cl3	1525 (1)	-141 (2)	1075 (1)	406 (4)
Cl4	3221 (1)	-74 (2)	1955 (1)	401 (4)
Cl5	4328 (1)	3605 (3)	1011 (1)	455 (5)
Cl6	3721 (1)	7427 (2)	-789 (1)	392 (4)
O1	2132 (2)	8669 (6)	-1990 (3)	413 (13)
C1	1926 (3)	6900 (9)	-1524 (4)	303 (15)
C2	1145 (3)	5860 (9)	-1644 (4)	290 (15)
C3	1106 (3)	4021 (9)	-936 (4)	264 (15)
C4	1856 (3)	3600 (8)	-292 (3)	208 (12)
C5	2119 (3)	1945 (8)	520 (4)	242 (14)
C6	2888 (3)	1979 (8)	936 (4)	238 (14)
C7	3389 (3)	3639 (8)	530 (4)	265 (14)
C8	3113 (3)	5352 (8)	-283 (4)	250 (14)
C9	2362 (3)	5315 (8)	-666 (4)	236 (13)

Table 2. Bond distances (\AA), valence and selected torsion angles ($^\circ$)

Cl1—C2	1.694 (5)	C2—C3	1.323 (7)
Cl2—C3	1.691 (6)	C3—C4	1.482 (7)
Cl3—C5	1.723 (5)	C4—C5	1.376 (6)
Cl4—C6	1.719 (5)	C4—C9	1.402 (7)
Cl5—C7	1.700 (5)	C5—C6	1.399 (7)
Cl6—C8	1.713 (5)	C6—C7	1.387 (7)
O1—C1	1.204 (6)	C7—C8	1.406 (7)
O1—C2	1.490 (7)	C8—C9	1.360 (7)
O1—C9	1.500 (7)		
O1—C1—C9	129.3 (4)	Cl3—C5—C6	118.5 (3)
O1—C1—C2	126.3 (4)	Cl4—C6—C5	119.7 (3)
C2—C1—C9	104.3 (4)	C5—C6—C7	120.9 (4)
Cl1—C2—C1	122.2 (3)	Cl4—C6—C7	119.4 (3)
C1—C2—C3	110.0 (4)	Cl5—C7—C6	120.4 (3)
Cl1—C2—C3	127.9 (4)	C6—C7—C8	119.4 (4)
Cl2—C3—C2	124.4 (4)	Cl5—C7—C8	120.3 (3)
C2—C3—C4	110.4 (4)	Cl6—C8—C7	120.1 (4)
Cl2—C3—C4	125.2 (3)	C7—C8—C9	119.0 (4)
C3—C4—C9	107.3 (3)	Cl6—C8—C9	120.9 (3)
C3—C4—C5	133.6 (4)	C4—C9—C8	122.1 (4)
C5—C4—C9	119.2 (4)	C1—C9—C8	129.9 (4)
Cl3—C5—C4	122.1 (4)	Cl1—C9—C4	108.0 (4)
C4—C5—C6	119.4 (4)		
O1—C1—C2—C11	6.0 (8)	Cl4—C6—C7—Cl5	1.4 (6)
Cl1—C2—C3—Cl2	-0.7 (8)	Cl5—C7—C8—Cl6	-0.3 (6)
Cl3—C5—C6—Cl4	1.3 (6)		

The angles of the direction of bonds involving the O and Cl atoms with the mean ring planes range between 0.5 and 4.6° over the molecule. There is also a bending of the molecule along the C4—C9 bond with the dihedral angle between the best planes of the two rings equal to $2.4 (2)^\circ$.

The mean C—Cl length (where the C atoms belong to the aromatic ring) is $1.714 (5) \text{ \AA}$ and the corresponding mean value corrected for thermal vibration of $1.728 (5) \text{ \AA}$ can be compared well with the values of Herbstein (1979): $1.717 (8)$ and $1.721 (8) \text{ \AA}$ for perchlorinated aromatic hydrocarbons or with uncorrected values of $1.712 (2) \text{ \AA}$ in tetrachlorophthalic anhydride at 120 K (Wilkerson *et al.*, 1975) and 1.716 \AA in the tetrachlorophthalate

anion (Galloy, Putzeys, Germain & Van Meerssche, 1976). The other two C(sp^2)—Cl distances are $1.691 (6)$ and $1.694 (5) \text{ \AA}$. The localized double bond C2=C3 is $1.323 (7) \text{ \AA}$.

Herbstein (1979) reported an intramolecular non-bonded average Cl...Cl distance of 3.052 \AA for Cl atoms attached to the adjacent C atoms on an aromatic ring and Rudman (1971) one of 3.14 \AA . Our average value of the same distance is 3.096 \AA .

The molecules pack together in interpenetrating and parallel rows with each molecular plane lying along the row axis. One row is formed by molecules related to each other by a center of symmetry, while parallel rows in adjacent unit cells are related by a translation vector. This is shown in the packing diagram found in Fig. 2.

The intermolecular distances are in the normally expected range for nonbonded contacts; the Cl2...Cl3 distance is $3.458 (3)$ and the O1...C9 distance is $2.984 (6) \text{ \AA}$.

The authors express their gratitude to Dr H. Vančík for providing the crystals. IM thanks the

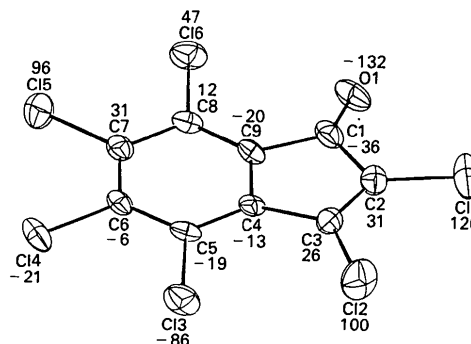


Fig. 1. ORTEP (Johnson, 1965) drawing of the molecule with numbering of atoms and deviations from the best molecular plane (all values are $\times 10^3 \text{ \AA}$). The thermal ellipsoids are at 50% probability.

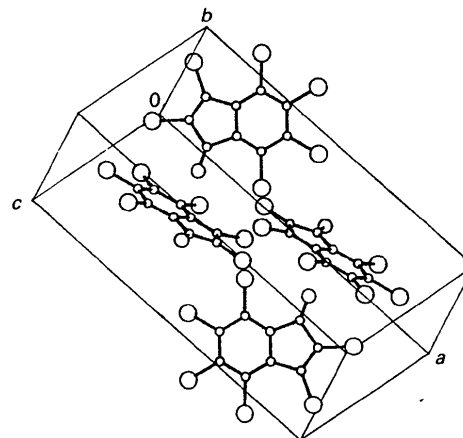


Fig. 2. Packing of the molecules.

Institute of Structural Chemistry, University of Parma, for a fellowship.

References

- BELLETTI, D., UGOZZOLI, F., CANTONI, A. & PASQUINELLI, G. (1979). *Gestione on line di Diffratometro a Cristallo Singolo Siemens AED con Sistema General Automation Jumbo 220*. Internal Report 1.3/79. Centro di Studio per la Strutturistica Diffraattometrica del CNR, Parma, Italy.
- BYRN, S. R., CURTIN, D. Y. & PAUL, I. C. (1972). *J. Am. Chem. Soc.* **94**, 890–898.
- FUCHS, B., LIDOR, R., KRUGER, C. & LIN, L.-K. (1980). *Nouv. J. Chim.* **4**, 361–363.
- GALLOY, J., PUTZEYS, J.-P., GERMAIN, G. & VAN MEERSSCHE, M. (1976). *Acta Cryst.* **B32**, 2718–2720.
- HERBSTEIN, F. H. (1979). *Acta Cryst.* **B35**, 1661–1670.
- International Tables for X-ray Crystallography* (1974). Vol. IV. p. 149. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
- JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.
- LEHMANN, M. S. & LARSEN, F. K. (1974). *Acta Cryst.* **A30**, 580–589.
- MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCO, J.-P. & WOOLFSON, M. M. (1980). *MULTAN80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univ. of York, England, and Louvain, Belgium.
- MARSH, P. & WILLIAMS, D. E. (1981). *Acta Cryst.* **B37**, 705–706.
- RIZZOLI, C., SANGERMANO, V., CALESTANI, G. & ANDRETTI, G. D. (1987). *J. Appl. Cryst.* **20**, 436–439.
- RUDMAN, R. (1971). *Acta Cryst.* **B37**, 262–269.
- SHELDRIK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.
- UGOZZOLI, F. (1986). *Comput. Chem.* **11**(2), 109–120.
- WALKER, M. & STUART, D. (1983). *Acta Cryst.* **A39**, 158–166.
- WATSON, W. H. & NAGL, A. (1987). *Acta Cryst.* **C43**, 2444–2445.
- WILKERSON, A. K., CHODAK, J. B. & STROUSE, C. E. (1975). *J. Am. Chem. Soc.* **97**, 3000–3004.

Acta Cryst. (1989). **C45**, 1546–1548

Structure of (2*S*,4*R*)-*cis*-4-Methyl-2-phthalimido- γ -butyrolactone

BY IVANKA MATIJAŠIĆ

Laboratory of Organic Chemistry, Faculty of Science, University of Zagreb, Strossmayerov trg 14, 41000 Zagreb, Yugoslavia

AND FRANCO UGOZZOLI, GABRIELE BOCELLI AND GIOVANNI D. ANDRETTI

Istituto di Strutturistica Chimica e Centro di Studio per la Strutturistica Diffraattometrica del CNR, Università di Parma, Viale delle Scienze, 43100 Parma, Italy

(Received 3 September 1988; accepted 3 February 1989)

Abstract. $C_{13}H_{11}NO_4$, $M_r = 245.23$, orthorhombic, $P2_12_12_1$, $a = 23.251$ (8), $b = 8.453$ (5), $c = 5.813$ (4) Å, $V = 1143$ (1) Å³, $Z = 4$, $D_x = 1.426$ g cm⁻³, Cu $K\alpha$, $\lambda = 1.5418$ Å, $\mu = 8.541$ cm⁻¹, $F(000) = 512$, room temperature, $R = 0.050$ for 2012 unique observed reflections [$I > 3\sigma(I)$]. The lactone ring has an envelope conformation with C3 deviating by 0.505 (2) Å from the least-squares plane formed by the remaining four ring atoms. The absolute configuration of two chiral C atoms was deduced as (2*S*, 4*R*). The phthalimido and methyl groups are in pseudo-equatorial positions, *cis* to each other.

Introduction. The structure of (2*S*,4*R*)-*cis*-4-methyl-2-phthalimido- γ -butyrolactone has been established as part of our investigation of the stereochemistry of different 2,4-disubstituted γ -butyrolactones (Matijašić, Bocelli, Ugozzoli & Sgarabotto, 1988).

Experimental. Colorless prismatic crystal recrystallized from benzene/ether solution, 0.24 × 0.45 ×

0.18 mm approximately. Data measured on a Siemens AED diffractometer, Ni-filtered Cu $K\alpha$ radiation, cell parameters from least-squares fit of 30 reflections accurately measured on the diffractometer in the range $38 < \theta < 43^\circ$, one check reflection measured every 50 counts without significant variation, profile analysis with Lehmann & Larsen (1974) procedure modified by Belletti, Ugozzoli, Cantoni & Pasquinelli (1979), $3 < \theta < 70^\circ$, Lp correction, absorption correction with Walker & Stuart (1983) procedure using *ABSORB* (Ugozzoli, 1986), maximum and minimum values of the absorption coefficients in the polar angles φ and μ are 1.19 and 0.84 respectively, $-28 < h < 28$, $0 < k < 10$, $0 < l < 7$, 2571 reflections collected, 2332 observed at $3\sigma(I)$ level, 2012 unique reflections ($R_{int} = 0.023$), direct methods with *MULTAN80* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980), full-matrix least-squares refinement with anisotropic thermal parameters for non-H atoms, H atoms located from difference Fourier map and refined