

The Structure of a Disordered Chlorobenzene Adduct of 3,3',5,5',6-Pentachloro-2'-hydroxysalicylanilide*

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Abstract. $C_{13}H_6Cl_5NO_3 \cdot \frac{1}{2}(C_6H_5Cl)$, triclinic, $P\bar{1}$, $a = 7.110$ (3), $b = 9.767$ (3), $c = 14.079$ (2) Å, $\alpha = 93.80$ (2), $\beta = 94.13$ (4), $\gamma = 65.23$ (2)°, $U = 884.7$ (5) Å³, $D_m = 1.71$, $D_c = 1.72$ Mg m⁻³, $Z = 2$, $\mu(\text{Mo } K\alpha) = 0.83$ mm⁻¹, $R = 0.091$, 1766 observed reflections. The molecular conformation and hydrogen-bonding are similar to those of the unsolvated α and β polymorphs. The average chlorobenzene molecule is generated by centrosymmetric superposition of two molecules with half-weight atoms.

Introduction. The crystal structures of two unsolvated polymorphs (α and β forms) of 3,3',5,5',6-pentachloro-2'-hydroxysalicylanilide, otherwise known as oxyclozanide, have been determined as part of a study of some structurally related flukicides (Sindt & Mackay, 1979). A further crystalline form, grown from chlorobenzene, was differentiated from the other two by its infrared spectrum. This was believed to be another polymorph and was found to have a greater aqueous solubility than either the α or β polymorph (information supplied by ICI Australia). In view of the differing solubilities reported for the three crystalline forms, the crystal structure determination of the title compound was undertaken.

Pale-yellow triclinic crystals were grown from chlorobenzene. The cell parameters were determined by least squares from 2θ values measured for 25 strong reflections; the density was determined by flotation in a xylene/bromoform mixture. Intensities were measured with Mo $K\alpha$ radiation (graphite crystal monochromator) on a Rigaku-AFC four-circle diffractometer with a crystal ca $0.27 \times 0.20 \times 0.09$ mm. The intensities were recorded by an ω - 2θ scan of 4° min⁻¹ and 10 s stationary background counts. Indications of radiation damage were apparent; during data collection the intensities of three reference reflections, monitored every 50 reflections, decreased to 60% of their original value. The data were scaled accordingly. Of 2320 non-equivalent terms measured to a 2θ maximum of 45°, 1766 with $|F_o| > 2\sigma|F_o|$ were used for the structure

refinement. The intensities were corrected for Lorentz and polarization factors but not for absorption. The scattering factors for Cl, O, N and C were from Cromer & Mann (1968), for H from Stewart, Davidson & Simpson (1965). Anomalous-dispersion corrections, f' and f'' , were made for all atoms (Cromer & Liberman, 1970).

The structure was solved by direct methods with *SHELX76* (Sheldrick, 1976). On the assumption that the space group was the centrosymmetric $P\bar{1}$, phases for 241 terms with $|E| > 1.1$ were derived. Peaks on the resultant E map could be assembled to correspond to the sites of 12 benzene-ring C atoms and four Cl atoms; peaks on successive difference maps corresponded to the remaining non-hydrogen atoms. Refinement of this model in $P\bar{1}$ was unsuccessful. However, further refinement in the non-centrosymmetric space group $P1$ indicated that the structure was centrosymmetric, and that the molecular sites initially derived required translation in the unit cell along the three axial directions. Following refinement with anisotropic thermal parameters for the Cl atoms and isotropic for O, N and C atoms, a difference map indicated a chlorobenzene molecule, with half-weight atoms, situated at a center of symmetry. In the final full-matrix least-squares refinements, the non-hydrogen atoms in the oxyclozanide molecule were given anisotropic thermal parameters; the H atoms, located on difference maps, were given the same isotropic thermal parameters as the carrier atoms, and their positional coordinates were not refined. The C and Cl atoms of the chlorobenzene were given a refined isotropic thermal parameter, $U = 0.149$ Å²; their coordinates, derived from difference maps and a knowledge of the expected molecular geometry, were not refined. A final $R = \sum ||F_o| - |F_c|| / \sum |F_o| = 0.091$ was attained for the 1766 observed terms.† The refinements were made with *SHELX76* (Sheldrick, 1976), the function

* Flukicides. III. Part I: Sindt & Mackay (1978). Part II: Sindt & Mackay (1979).

† Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34559 (20 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Final atomic coordinates with e.s.d.'s in parentheses

The H atom coordinates and those of the chlorobenzene have been multiplied by 10^3 . All other values are $\times 10^4$.

	x	y	z
Cl(1)	2345 (6)	11098 (3)	2612 (2)
Cl(2)	6480 (6)	5763 (4)	853 (2)
Cl(3)	7578 (5)	4167 (3)	2761 (2)
Cl(4)	11780 (5)	164 (3)	6440 (2)
Cl(5)	7732 (6)	5285 (4)	8504 (2)
O(1)	3471 (13)	9445 (8)	4322 (5)
O(2)	5014 (13)	7228 (8)	5292 (5)
O(3)	10092 (12)	2242 (8)	4781 (5)
N	7547 (13)	5060 (9)	4812 (5)
C(1)	5489 (15)	6976 (10)	3637 (7)
C(2)	4264 (17)	8534 (11)	3554 (8)
C(3)	3790 (16)	9157 (11)	2674 (7)
C(4)	4487 (19)	8325 (13)	1868 (8)
C(5)	5667 (18)	6774 (12)	1910 (7)
C(6)	6155 (18)	6114 (11)	2777 (8)
C(7)	5993 (17)	6420 (11)	4631 (7)
C(1')	8204 (16)	4393 (11)	5705 (7)
C(2')	9569 (15)	2847 (11)	5657 (7)
C(3')	10250 (17)	2077 (11)	6507 (7)
C(4')	9674 (17)	2814 (12)	7390 (7)
C(5')	8393 (17)	4337 (12)	7402 (7)
C(6')	7699 (18)	5138 (12)	6589 (7)
H(O1)	425	912	500
H(O3)	1127	109	475
H(N)	830	423	437
H(4)	436	878	126
H(4')	1043	219	806
H(6')	638	630	670
Cl(a)	711	1051	1085
C(1a)	909	1016	1027
C(2a)	1024	1113	1020
C(3a)	1181	1085	962
C(4a)	1289	949	915
C(5a)	1193	846	927
C(6a)	1014	882	980

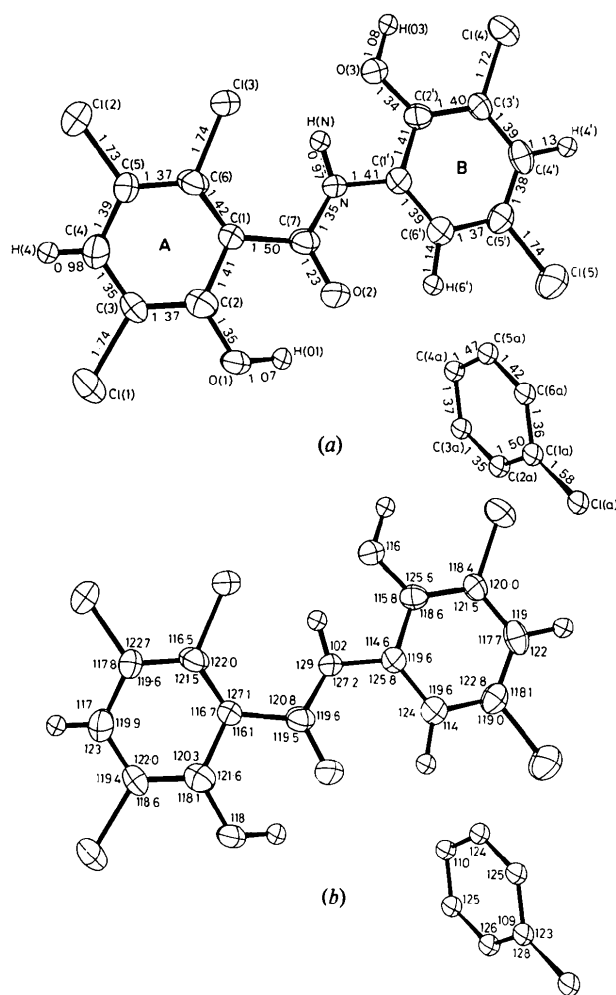


Fig. 1. Perspective view of the structure with thermal ellipsoids scaled to 50% probability showing (a) bond lengths, e.s.d.'s are 0.01 Å; (b) bond angles, e.s.d.'s range from 0.8 to 1.1°. The diagram was prepared with ORTEP (Johnson, 1965).

minimized being $\sum w(|F_o| - |F_c|)^2$ with $w = 1.0$. Final atomic coordinates are given in Table 1.

Discussion. The conformation of the oxyclozanide molecule (Fig. 1) is similar to that found in the unsolvated α and β polymorphs (Sindt & Mackay, 1979) but more closely resembles that of the α form. It is virtually planar, the angle between the two rings, *A* and *B*, being only 3.9° (cf. 2.5 and 14.0° for the α and β forms, respectively). The angle between the perpendiculars to the amide group and rings *A* and *B*, 15.4 and 13.2°, respectively, may be compared with 19.1 and 16.8° (α form) and 29.4 and 33.5° (β form). Plane equations and perpendicular distances from the planes are given in Table 2. The bond lengths and angles (Fig. 1) are within 2σ of values found in the α and β forms.

The H-bonding scheme and dimensions (Table 3) are similar to those of the other crystal forms (Sindt &

Mackay, 1979). The molecular packing, Fig. 2, shows the oxyclozanide molecules, which are present as mirror-image conformers, orientated with their long molecular axes approximately parallel to the (011) planes. As in the α polymorph, rings *A* and *B* of one molecule lie over rings *B* and *A* of an adjacent one related by the center of symmetry, allowing considerable overlap of the π -electron systems. The chlorobenzene molecules lie on centers of symmetry, so that the average molecule is generated by centrosymmetric superposition of half-weight atoms. Their orientation is such that the angle between their ring plane and the plane of the oxyclozanide molecule is ca 70°. The ribbons of oxyclozanide molecules resulting from the H-bond interaction, O(1) \cdots O(3), are perpendicular to the rows of chlorobenzene molecules which extend along *a*. Short intermolecular contacts are given in

Table 2. Equations of least-squares planes and deviations from the planes for oxyclozanide

The e.s.d.'s are 0.01 Å.

The plane equations are in the form $pX + qY + rZ + s = 0$, with X , Y and Z expressed in Å, referred to orthogonal axes. Conversion from triclinic to orthogonal coordinates is given by

$$\begin{bmatrix} X \\ Y \\ Z \end{bmatrix} = \begin{bmatrix} a & b \cos \gamma & c \cos \beta \\ 0 & b \sin \gamma & cP \\ 0 & 0 & cQ \end{bmatrix} \begin{bmatrix} x/a \\ y/b \\ z/c \end{bmatrix},$$

where $P = (\cos \alpha - \cos \beta \cos \gamma) / \sin \gamma$, $Q = (1 - \cos^2 \beta - P^2)^{1/2}$.

Plane A: $-0.9833X - 0.1586Y - 0.0892Z + 7.6764 = 0$

Plane B: $-0.9764X - 0.2107Y - 0.0474Z + 8.0455 = 0$

Plane C: $-0.9020X - 0.4107Y - 0.1334Z + 8.8973 = 0$

Plane A	Plane B	Plane C	
C(1)	-0.01 Å	C(1')	+0.03 Å
C(2)	0.00	C(2')	-0.02
C(3)	+0.01	C(3')	0.00
C(4)	-0.01	C(4')	+0.01
C(5)	0.00	C(5')	0.00
C(6)	+0.01	C(6')	-0.02
*C(7)	-0.08	*N	+0.05
*O(1)	+0.05	*O(3)	-0.06
*Cl(1)	-0.03	*Cl(4)	+0.06
*Cl(2)	0.00	*Cl(5)	-0.04
*Cl(3)	+0.07		
		C(1)	0.00 Å
		C(7)	+0.01
		C(1')	0.00
		N	0.00
		O(2)	0.00

* These atoms were not included in the plane calculation.

Table 3. Hydrogen-bond dimensions

E.s.d.'s are in parentheses.

X—H...O	X...O (Å)	H...O (Å)	$\angle X-H...O$ (°)
N—H(N)...O(3)	2.58 (1)	1.93 (1)	123 (1)
O(1)—H(O1)...O(2)	2.44 (1)	1.76 (1)	117 (1)
O(3)—H(O3)...O(1)	2.85 (1)	1.82 (1)	159 (1)

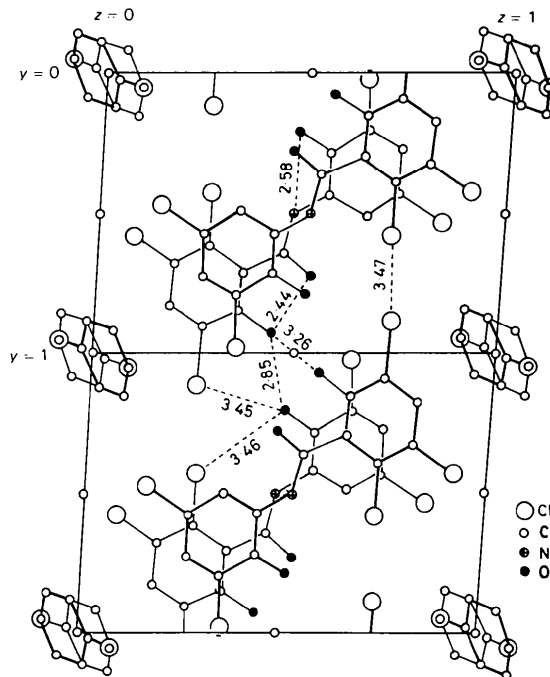
Table 4. Intermolecular approach distances ≤ 3.50 Å

E.s.d.'s range from 0.01 to 0.02 Å.

C(7)...C(1')	3.39	O(1)...O(3 ^{IV})	2.85
C(2)...C(3')	3.50	O(2)...O(3')	3.44
C(6)...C(5')	3.43	Cl(1)...O(3 ^{IV})	3.45
C(1')...N ^{II}	3.42	Cl(1)...Cl(3 ^{IV})	3.47
N...N ^{II}	3.44	O(1)...Cl(4 ^{IV})	3.22
O(1)...O(1 ^{III})	3.26	O(2)...Cl(4 ^{IV})	3.24
C(1')...O(2')	3.46	O(3)...Cl(4 ^V)	3.47
C(2')...O(2')	3.46	Cl(2)...Cl(5 ^{VI})	3.44
N...O(2')	3.41		

Symmetry code

(I)	$1-x$	$1-y$	$1-z$	(IV)	$-1+x$	$1+y$	z
(II)	$2-x$	$1-y$	$1-z$	(V)	$2-x$	$-y$	$1-z$
(III)	$1-x$	$2-y$	$1-z$	(VI)	x	y	$-1+z$

Fig. 2. Projection of the structure down a .Table 4. There are no contacts between the chlorobenzene and oxyclozanide molecules < 3.50 Å.

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References

- CROMER, D. T. & LIBERMAN, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.
- CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* **A24**, 321–324.
- JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.
- SHELDRICK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. Chemistry Laboratory, Cambridge Univ., England.
- SINDT, A. C. & MACKAY, M. F. (1978). *J. Cryst. Mol. Struct.* **8**, 17–25.
- SINDT, A. C. & MACKAY, M. F. (1979). *Acta Cryst.* **B35**, 2103–2108.
- STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.