

using the anhydrate notation. If the photochemical changes occur in the solid state, it should be much easier for hydrate crystal rather than for the anhydrate. In the former crystal only the sliding of molecules will be required for the dimer formation, and therefore the geometrical conditions favour the monohydrate crystal.

The authors are grateful to Takeda Chemical Industries, Ltd. for making a computer available, and indebted to Dr M. Nishikawa and Mr K. Kamiya for the calculations. We are also indebted to Professor T. Ashida of Osaka University and Dr A. Furusaki of Kwansai Gakuin University for their kind help in the calculations.

Acta Cryst. (1969). B25, 1045

The Structure of 3,5-Dichloroanthranilic Acid*

BY S. K. ARORA AND L. M. PANT

National Chemical Laboratory, Poona, India

(Received 18 March 1968 and in revised form 11 June 1968)

The crystals of 3,5-dichloroanthranilic acid, $\text{NH}_2\text{Cl}_2\text{C}_6\text{H}_2\text{COOH}$, are monoclinic, space group $P2_1/a$, with $a=12.49$, $b=17.02$, $c=3.80$ Å; $\beta=92.7^\circ$; ρ_o , 1.700 g.cm $^{-3}$; ρ_c for $Z=4$, 1.705 g.cm $^{-3}$; μ for Cu $K\alpha$, 70.4 cm $^{-1}$.

The effect of intramolecular overcrowding between the carboxylic group and the amino group is to cause the exocyclic carbon atom and the nitrogen atom to be displaced from the aromatic plane in opposite directions by 0.063 Å and 0.045 Å respectively. One of the chlorine atoms is displaced from the aromatic plane by 0.078 Å owing to intermolecular interactions.

Introduction

The structure of 3,5-dichloroanthranilic acid is interesting in the sense that the molecule shows distortions from planarity which can be accounted for as being a result of the presence of both intermolecular and intramolecular overcrowding. The present study is a continuation of similar structural studies of simple aromatic compounds made in this laboratory.

The crystals grown from acetic acid are needles elongated along the c axis; they are monoclinic, space group $P2_1/a$, with

$$a=12.49, b=17.02, c=3.80 \text{ \AA}; \beta=92.7^\circ; \\ \rho_o, 1.700 \text{ g.cm}^{-3}; \rho_c \text{ for } Z=4, 1.705 \text{ g.cm}^{-3}; \\ \mu \text{ for Cu } K\alpha, 70.4 \text{ cm}^{-1}.$$

Experimental

The axial lengths were determined from equatorial Weissenberg photographs.

Reflexions of the type $hk0$ to $hk3$ were obtained from equi-inclination Weissenberg photographs by the use of Cu radiation and a crystal of roughly 0.3×0.6 mm 2 cross-section. The visually estimated intensities from

* Communication No. 2001 from the National Chemical Laboratory, Poona, India.

References

- COULSON, C. A. (1961). *Valence*, p. 352. Oxford Univ. Press.
 COULSON, C. A. & DANIELSSON, U. (1954). *Ark. Fys.* **8**, 239 and 245.
 FURBERG, S. & HORDVIK, A. (1956). *Acta Chem. Scand.* **10**, 135.
 GERDIL, R. (1961). *Acta Cryst.* **14**, 333.
 HOOGSTEEN, K. (1963). *Acta Cryst.* **16**, 28.
 REEKE, G. & MARSH, R. (1966). *Acta Cryst.* **20**, 703.
 TANAKA, J. & TANAKA, M. (1967). *Nature, Lond.* **213**, 68.
 WILSON, A. J. C. (1942). *Nature, Lond.* **150**, 151.
 WULFF, D. L. & FRANKEL, G. (1961). *Biochim. Biophys. Acta*, **51**, 332.

extended spots were corrected for the Lorentz-polarization-Tunell factor as well as for the effect of spot extension; absorption was neglected. In all, 506 reflexions (including 5 unobserved reflexions) out of nearly 1374 possible for these layers were used for refinement; $0,6,0$ and $0,12,0$ appeared to be Renninger reflexions and were left out. The scaling of different layers was done with the help of common reflexions in zero-layer Weissenberg photographs along the other axes.

Determination and refinement of the structure

The structure was solved with the help of Patterson projections and refined to an R value of 12.2% using individual isotropic temperature factors; the scale factors used at this stage were 1.00, 1.03, 1.07 and 0.89 for the zero to third layers respectively and the individual isotropic temperature factors were all within the range 1.8 Å 2 to 2.2 Å 2 . Temperature factors of the form

$$\exp[-(a_{11}h^2 + a_{22}k^2 + a_{33}l^2 + 2a_{12}hk + 2a_{13}hl + 2a_{23}kl)]$$

were then introduced and the a_{ij} were refined (Rollett & Davis, 1955) along with the atomic parameters, to an R value of 10.5%. The final atomic parameters are given in Table 1 and F_o and F_c in Table 2. Owing probably to absorption effects and imperfect scaling, the thermal parameters did not seem reliable and have not been given.

1965) and 1,3-diamino-2,4,6-trinitrobenzene (Holden, 1967). The C-N bond length, 1.307 Å is close to the values observed in the last two compounds cited above, but is shorter than those observed in the two crystallographically independent molecules of anthranilic acid (Brown, 1968).

The effect of intramolecular overcrowding between the carboxylic group and the amino group, and between the amino group and the chlorine atom Cl(1) on the benzene ring, is to displace the carbon atoms C(1), C(2) and C(3), to which these groups are attached, by -0.028 Å, 0.031 Å and -0.023 Å respectively from the aromatic plane; the other three atoms C(4), C(5) and C(6) of the ring lie in the aromatic plane within the limits of experimental error (Table 4). The exocyclic carbon atom C(7), the nitrogen atom N and the chlorine atom Cl(1) are displaced respectively 0.063 Å, -0.045 Å and -0.027 Å from the aromatic plane. The overcrowding between the amino and the carboxylic groups also causes the carboxylic group to depart from the aromatic plane by 6° in spite of strong conjugation across the exocyclic bond C(1)-C(7), as indicated by the relatively short length 1.421 Å of this bond (Table 3).

The chlorine atom Cl(2) is displaced 0.078 Å from the aromatic plane; this large deviation appears to be due to intermolecular overcrowding and is clear from Figs. 2 and 3 which show the (001) and the (010) projections of the structure respectively. The atom Cl(1) (*xyz*) has one rather short intermolecular bond Cl(1)-Cl(2) ($\frac{1}{2}+x, \frac{1}{2}-y, 1+z$), 3.53 Å, whereas the atom Cl(2) (*xyz*) has, in addition to the Cl(1)-Cl(2) bond two shorter bonds Cl(2)-N($\frac{1}{2}-x, \frac{1}{2}+y, 1-z$),

3.41 Å, and Cl(2)-O(1) ($\frac{1}{2}-x, \frac{1}{2}+y, \bar{z}$), 3.27 Å. The large deviation of the Cl(2) atom from the aromatic plane is presumably due to one of these contacts. It is seen from Table 4 that atoms Cl(2) (*xyz*) and N($\frac{1}{2}-x, \frac{1}{2}+y, 1-z$) lie on opposite sides of the aromatic plane while Cl(2) and O(1) ($\frac{1}{2}-x, \frac{1}{2}+y, \bar{z}$) lie on the same side of it. It is thus clear that the neighbouring amino group is mainly responsible for the deviation of Cl(2) from the aromatic plane.

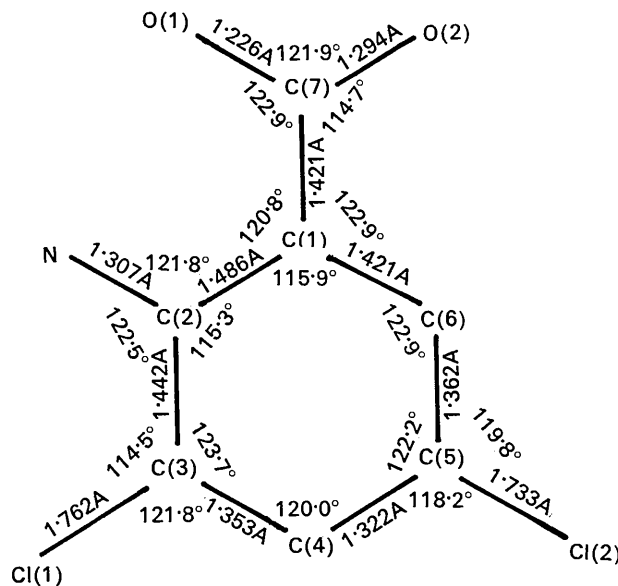


Fig. 1. Bond lengths and angles in 3,5-dichloroanthranilic acid.

Table 4. Equations of planes

(1) Benzene ring	$0.3537x' - 0.1605y' - 0.9215z' + 0.1674 = 0$
(2) Carboxylic group	$0.3469x' - 0.2714y' - 0.8984z' + 0.2454 = 0$
(3) Plane through O(1), O(2) and dimer centre	$-0.4893x' + 0.1592y' + 0.8577z' = 0$

Angles between different planes

	(2)	(3)
(1)	6.0°	10.4°
(2)	-	8.5

Deviations of atoms from different planes (Å)

	Planes		
	(1)	(2)	(3)
C(1)	-0.028	-0.193	-0.184
C(2)	0.031	—	—
C(3)	-0.023	—	—
C(4)	0.003	—	—
C(5)	0.001	—	—
C(6)	0.007	—	—
C(7)	0.063	—	-0.109
O(1)	-0.076	—	—
O(2)	0.126	—	—
N	-0.045	—	—
Cl(1)	-0.027	—	—
Cl(2)	0.078	—	—
N ($\frac{1}{2}-x, \frac{1}{2}+y, 1-z$)	-2.170	—	—
O(1) ($\frac{1}{2}-x, \frac{1}{2}+y, \bar{z}$)	1.490	—	—

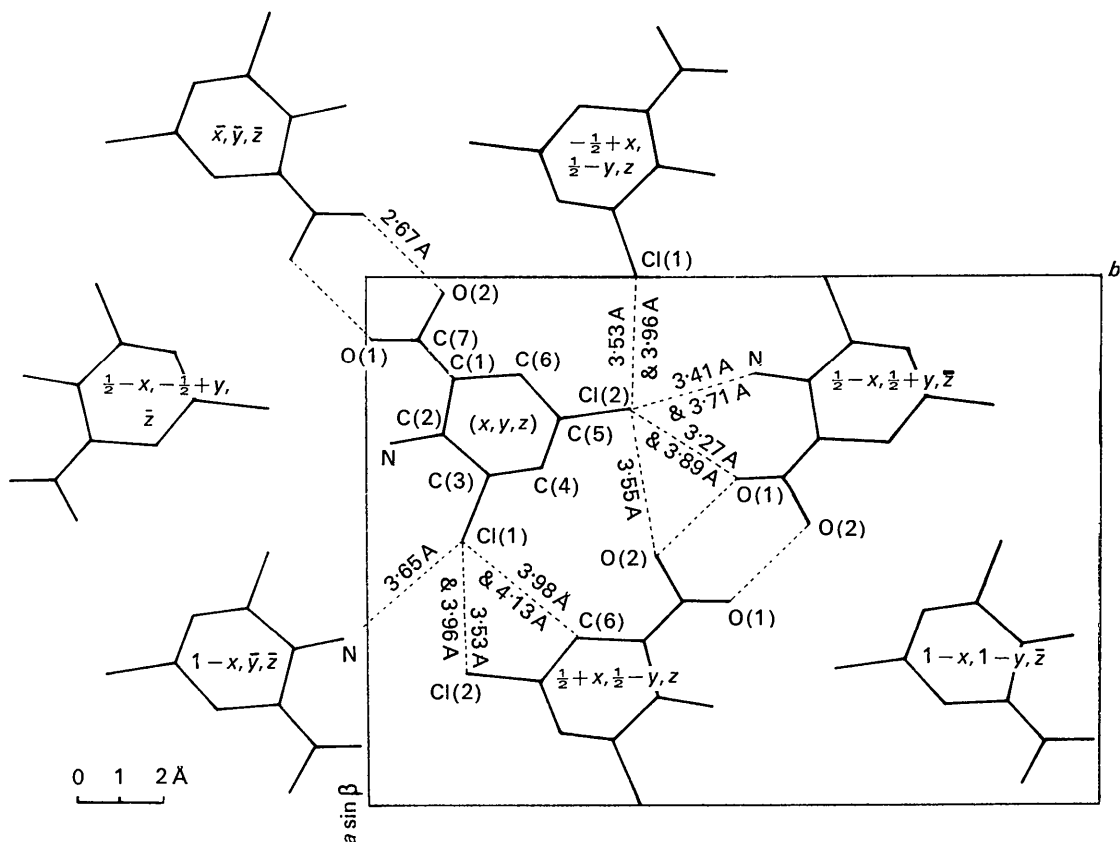


Fig. 2. The (001) projection of the structure.

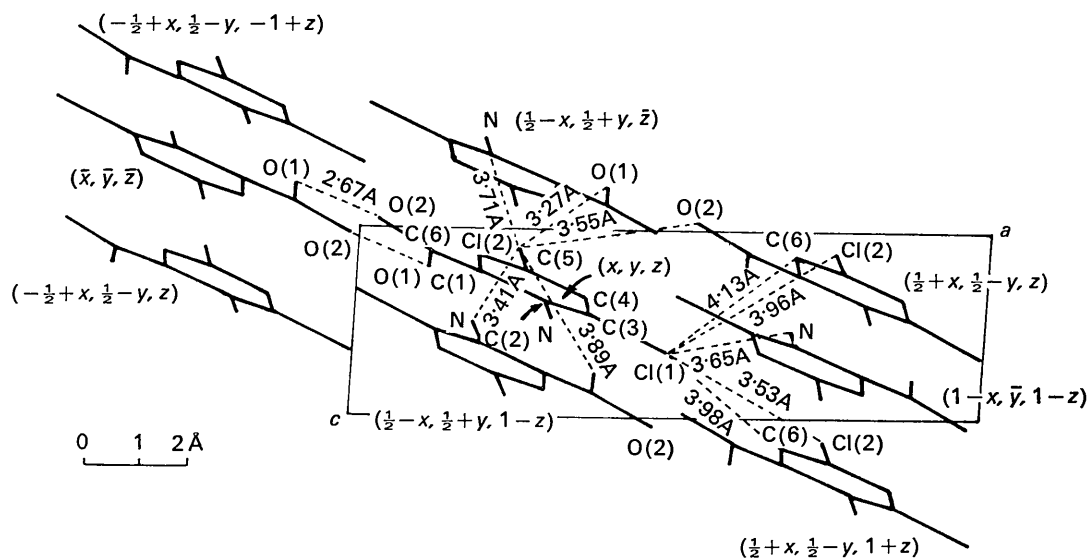


Fig. 3. The (010) projection of the structure.

References

- BROWN, C. J. (1968). *Proc. Roy. Soc. A* **302**, 185.
 CADY, H. & LARSON, A. C. (1965). *Acta Cryst.* **18**, 485.
 HOLDEN, J. (1967). *Acta Cryst.* **22**, 545.
 ROLLETT, J. S. & DAVIES, D. R. (1955). *Acta Cryst.* **8**, 125.
 SAKORE, T. D. & PANT, L. M. (1966). *Acta Cryst.* **21**, 715.