2-Chlorothioxanthone

By Shirley S. C. Chu and H. T. Yang

Institute of Technology, Southern Methodist University, Dallas, Texas 75275, U.S.A.

Abstract. $C_{13}H_7OSCl$, triclinic, $P\bar{1}$, $Z=2$, M.W. 246·72, $a=3·873$ (1), $b=7·210$ (2), $c=19·567$ (4) Å, $\alpha=86·93$ (2), $\beta=102·64$ (2), $\gamma=98·00$ (2)°, $D_x=1·552$, $D_m=1·53$ g cm^{-3} (by flotation), $\lambda(\text{Cu } K\alpha)=1·5418$ Å, $\mu(\text{Cu } K\alpha)=46·53$ cm^{-1}, final residual $R=0·051$.

Introduction. Samples of 2-chlorothioxanthone (I) were obtained through the courtesy of Dr Andrew L. Ternay Jr of the Chemistry Department of the University of Texas at Arlington. Single crystals in the form of clear prisms were grown from a mixture of solutions of acetone and tetrachloroethylene. The unit-cell parameters were obtained by measuring '+' and '−' 2θ values of 15 reflections. The space group was determined to be $P\bar{1}$. The intensity data were collected on a Syntex $P\bar{1}$ automatic diffractometer at 3° C with a crystal approximately $0·35\times0·35\times0·50$ mm in size. A $\theta/2\theta$ scanning mode with graphite-monochromated Cu $K\alpha$ radiation was used to measure 1280 independent reflections with 2θ values below 115°, of which 1145 reflections were considered as observed by the criterion $I>2·0\sigma(I)$, where $\sigma(I)$ was determined from counting statistics. The intensity data were reduced to structure factors by the application of Lorentz and polarization factors, and no absorption corrections were applied.

(I)
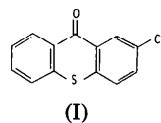
The structure was determined by the heavy-atom method, and the correct space group was proved to be $P\bar{1}$, as also shown by the centrosymmetric distribution of normalized structure factors. The ratios between $\langle E \rangle$, $\langle E^2 \rangle$, and $\langle E^2-1 \rangle$ are 0·807, 1·093 and 1·085, respectively. The refinement was carried out by the full-matrix least-squares method with isotropic temperature factors and the block-diagonal least-squares
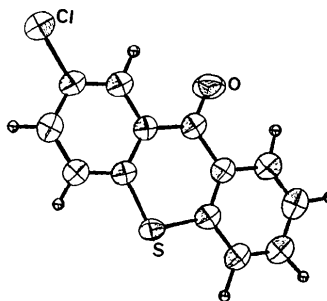

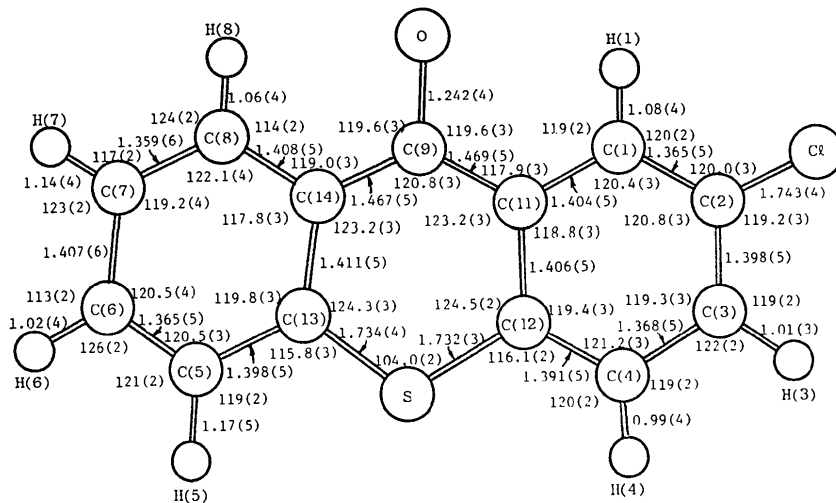Fig. 1. The configuration of one molecule of 2-chlorothioxanthone.

Fig. 2. Bond lengths (Å) and angles (°) of 2-chlorothioxanthone.

Table 1. *Fractional atomic coordinates* ($\times 10^4$, *except* $\times 10^3$ *for* H) *and thermal parameters*

The estimated standard deviations are given in parentheses and refer to the last positions of respective values. The expression for the temperature factor exponent consistent with B values in Å^2 is

$$\frac{1}{4}(h^2a^{*2}B_{11} + k^2b^{*2}B_{22} + l^2c^{*2}B_{33} + 2hka^*b^*B_{12} + 2hla^*c^*B_{13} + 2klb^*c^*B_{23}) .$$

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cl	9393 (3)	8131 (1)	647 (0)	4·68 (5)	4·57 (4)	4·61 (4)	−0·04 (3)	1·13 (4)	1·05 (3)
S	4425 (2)	993 (1)	2311 (0)	3·62 (5)	3·11 (3)	3·62 (4)	−0·04 (3)	0·59 (3)	−0·18 (2)
O	6304 (8)	6779 (4)	3106 (1)	7·74 (19)	3·73 (11)	5·52 (14)	−0·39 (11)	2·51 (12)	−1·24 (10)
C(1)	7422 (9)	6401 (5)	1786 (2)	2·90 (18)	3·85 (15)	3·85 (16)	0·34 (12)	0·23 (12)	0·21 (11)
C(2)	8028 (9)	6181 (5)	1135 (2)	2·77 (18)	3·97 (15)	3·80 (16)	0·38 (12)	0·46 (12)	0·81 (11)
C(3)	7533 (10)	4404 (5)	849 (2)	2·90 (18)	4·81 (17)	3·63 (16)	0·61 (13)	0·37 (12)	0·00 (13)
C(4)	6433 (9)	2872 (5)	1228 (2)	2·79 (18)	4·07 (15)	3·47 (14)	0·45 (13)	−0·08 (11)	−0·22 (11)
C(5)	2704 (9)	302 (5)	3552 (2)	2·76 (19)	4·58 (17)	4·21 (17)	−0·03 (13)	0·43 (13)	0·62 (14)
C(6)	2137 (11)	726 (6)	4187 (2)	4·02 (21)	5·23 (19)	4·05 (17)	−0·06 (15)	0·60 (14)	0·75 (14)
C(7)	2741 (11)	2592 (6)	4406 (2)	3·63 (21)	6·35 (22)	3·84 (17)	0·33 (16)	0·75 (13)	−0·04 (15)
C(8)	3810 (10)	3978 (5)	3969 (2)	4·09 (21)	4·83 (18)	3·56 (16)	0·22 (14)	0·25 (13)	−0·54 (13)
C(9)	5689 (9)	5166 (5)	2877 (2)	2·83 (18)	3·90 (15)	3·65 (14)	0·31 (12)	0·26 (12)	−0·06 (11)
C(11)	6316 (8)	4839 (4)	2182 (2)	1·93 (16)	3·41 (13)	3·62 (14)	0·40 (11)	−0·01 (11)	−0·09 (11)
C(12)	5783 (9)	3053 (4)	1891 (2)	2·14 (16)	3·43 (14)	3·37 (14)	0·34 (11)	−0·31 (11)	−0·06 (11)
C(13)	3835 (9)	1719 (5)	3104 (2)	2·53 (18)	3·96 (15)	3·53 (14)	0·43 (12)	−0·15 (11)	0·03 (11)
C(14)	4472 (9)	3600 (5)	3314 (2)	2·16 (17)	4·01 (15)	3·44 (14)	0·33 (12)	−0·09 (11)	−0·28 (11)

Table 1 (*cont.*)

	x	y	z	B_{Iso}
H(1)	812 (10)	776 (5)	202 (2)	3·4 (9)
H(3)	805 (8)	428 (4)	37 (1)	0·5 (6)
H(4)	630 (11)	161 (5)	104 (2)	2·8 (9)
H(5)	212 (12)	−124 (6)	336 (2)	4·8 (11)
H(6)	132 (9)	−20 (5)	455 (2)	2·5 (8)
H(7)	236 (9)	301 (5)	494 (2)	2·3 (8)
H(8)	447 (10)	541 (5)	410 (2)	3·2 (9)

method with anisotropic temperature factors. All the H atoms were located on a difference Fourier synthesis. The isotropic temperature factors were used for H atoms in the final refinements. The weight of the reflexion was assigned as $1/[\sigma(F)]^2$, where $\sigma(F)$ was calculated from counting statistics. The quantity $\sum w(||F_o| - |F_c||)^2$ was minimized. The final R index $(\sum ||F_o| - |F_c||/\sum |F_o|)$ was 0·051. The magnitude of $[\sum w(F_o - F_c)^2/(m-n)]^{1/2}$, where m is the number of reflexions and n is the number of parameters refined, was 0·92. The atomic scattering factors used for Cl, S, O, and C atoms were those from *International Tables for X-ray Crystallography* (1962). For H the values given by Stewart, Davidson & Simpson (1965) were used. The final positional and thermal parameters are given in Table 1.*

---

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31744 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.
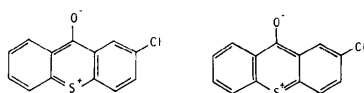

Fig. 3. The resonance structure of 2-chlorothioxanthone.

The ·computer programs used in this analysis were the *ORFLS* program (Busing, Martin & Levy, 1962), block-diagonal least-squares program (Shiono, 1971), Zalkin Fourier synthesis program modified by Dr R. Shiono of the University of Pittsburgh, and a number of structure interpretation programs (Shiono, 1971; Chu, 1973). All calculations were carried out on a CDC CYBER 72 computer in the Bradfield Computing Laboratory at Southern Methodist University.

Discussion. The determination of this crystal structure is a continuation of studies on thioxanthone 10-oxide (Chu, 1976). The derivative of 2-chlorothioxanthone instead of thioxanthone was studied because of the difficulty involved in obtaining single crystals of thioxanthone (twinned crystals were always obtained by recrystallization).

An *ORTEP* drawing of the configuration of a 2-chlorothioxanthone molecule is shown in Fig. 1 (Johnson, 1965). The identification of the atoms and the bond lengths and bond angles with their standard deviations are shown in Fig. 2. The mean value of the two C–S bond lengths is $1·733 \pm 0·003$ Å, and the C–S–C bond angle is $104·0 \pm 0·2°$. The C–S bond length is significantly shorter than that in other thioxanthine derivatives, as compared to $1·749$ Å in α-chlorprothixene (II) (Post, Kennard & Horn, 1974), and $1·75$ Å in α-flupenthixol (III) (Post, Kennard, Sheldrick & Horn, 1975). This indicates that there is considerable delocalization in the central ring of the thioxanthone ring system. It is further demonstrated by the essential planar configuration of the thioxanthine ring. The folding angle between the least-squares planes of the two benzene rings is $179·0°$ as compared to $141·6°$ in α-chlorprothixene, $152°$ in α-flupenthixol, and $155·7°$· in thioxanthone 10-oxide. The planarity of the thioxanthine ring is shown in Table 2. The delocalization
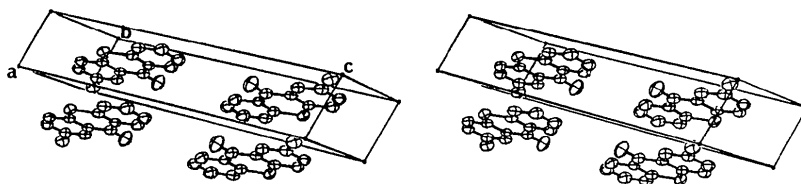
Fig. 4. The stereoscopic drawing of molecular packing of 2-chlorothioxanthone, excluding hydrogen atoms, in the unit cell.

is further evidenced by the lengthening of the C(9)–O, C(11)–C(12), and C(13)–C(14) bonds and the shortening of the C(9)–C(11), C(9)–C(14), S–C(12), and S–C(13) bonds as compared with those in thioxanthone 10-oxide (Chu, 1976). Furthermore, the short intermolecular distance of 3·43 Å between S and O $(x, -1+y,z)$ indicates that the resonance structures shown in Fig. 3 are significant.

Table 2. *Least-squares planes and displacements (Å) of atoms from the planes*

Equation of planes: $Ax + By + Cz = D$, where x,y,z are in Å.

Plane	A	B	C	D
(a)	0·9096	−0·2217	0·1930	2·2693
(b)	0·9035	−0·2155	0·2089	2·3492
(c)	0·9062	−0·2192	0·2016	2·2962

	(a)	(b)	(c)
Cl	−0·016*		−0·029*
S	0·004*	−0·010*	0·012
O	−0·041*	0·073*	0·070*
C(1)	−0·003		0·001
C(2)	0·000		−0·008
C(3)	0·001		−0·013
C(4)	0·002		−0·008
C(5)		0·002	0·006
C(6)		−0·003	−0·009
C(7)		0·008	−0·006
C(8)		−0·012	−0·022
C(9)	−0·004*	0·015*	0·019
C(11)	0·006		0·017
C(12)	−0·006		−0·003
C(13)		−0·006	0·002
C(14)		0·011	0·012

Dihedral angles between the least-squares planes (a) and (b) 179·0, (a) and (c) 0·5, (b) and (c) 0·5°.

* Atoms excluded from the calculation of the least-squares planes.
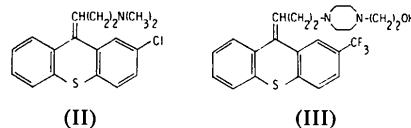
The packing of the molecules in the crystal is shown in the stereoscopic drawing in Fig. 4. With the exception of the 3·43 Å intermolecular separation between S and O, there are no other intermolecular contacts less than van der Waals distances. The molecules are stacked along the direction of the *a* axis, and the interplanar separation between the molecules is 3·53 Å.

References

Busing, W. R., Martin, K. O. & Levy, H. A. (1962). *ORFLS*. Oak Ridge National Laboratory Report ORNL-TM-305.
Chu, S. S. C. (1973). Structural Interpretation Programs. Institute of Technology, Southern Methodist Univ.
Chu, S. S. C. (1976). *Acta Cryst.* B32, 1583–1585.
International Tables for X-ray Crystallography (1962). Vol. III, pp. 201–207. Birmingham: Kynoch Press.
Johnson, C. K. (1965). *ORTEP*. Oak Ridge National Laboratory Report ORNL-3794.
Post, M. L., Kennard, O. & Horn, A. S. (1974). *Acta Cryst.* B30, 1644–1646.
Post, M. L., Kennard, O., Sheldrick, G. M. & Horn, A. S. (1975). *Acta Cryst.* B31, 2366–2368.
Shiono, R. (1971). Tech. Rep. 49, Crystallography Department, Univ. of Pittsburgh.
Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* 42, 3175–3187.