

Molecular Packing Modes of Acyl Halides.

III. The Crystal and Molecular Structure of Muconyl Chloride

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The structure of muconyl chloride ($C_6H_4Cl_2O_2$) has been determined from diffractometer data and refined to $R = 0.05$ and $R_w = 0.06$. The crystals are orthorhombic, space group *Cmca*, with $a = 6.476$ (1), $b = 9.839$ (1), $c = 12.070$ (2) Å, $Z = 4$. The planar centrosymmetric molecules, lying on mirror planes, are linked together in the plane by short, nearly linear C—Cl···Cl—C contacts of 3.63 Å, and C—H···O contacts of 2.63, 2.77 Å; interactions between the planes are of the antiparallel C⁺=O⁻ dipole–dipole type. The conformation of the C:C:C:O group is antiplanar, in contrast to the synplanar arrangement in most carboxylic acids, amides and esters. No short Cl···O contacts are observed.

Introduction

In part II the analysis of a small aromatic acyl chloride (TCl) was presented. The evidence for Cl···O interactions in TCl encouraged us to investigate the packing modes of small non-aromatic acyl chlorides. This paper describes the analysis of muconyl chloride (MCl).

Experimental

Colourless orthorhombic crystals of MCl, grown by sublimation, show the {001}, {110} and {111} forms. To avoid contact with moisture the crystals were sealed in lithium borate capillaries.

Cell constants were determined by least squares from 13 medium- and high-order ($\theta > 20^\circ$) reflections measured on a Siemens diffractometer with Mo $K\alpha$ radiation.

Crystal data

Muconyl chloride, $C_6H_4Cl_2O_2$, $M_r = 179.0$, m.p. $65^\circ C$, $a = 6.476$ (1), $b = 9.839$ (1), $c = 12.070$ (2) Å, $U = 769.1$ Å³, $Z = 4$, $D_c = 1.545$ g cm⁻³, $F(000) = 360$, $\mu(\text{Mo } K\alpha) = 7.74$ cm⁻¹. Space group *Cmca* or *C2cb* from systematic absences: hkl for $h + k$ odd, $h0l$ for l odd, $hk0$ for h and k odd; the former proved to be correct by the present analysis.

A crystal, $0.27 \times 0.57 \times 0.42$ mm measured normal to the faces (001), (110) and (111), was mounted along $a^* - 2b^*$ on a Siemens automatic diffractometer controlled by an IBM on-line computer. 1767 reflections were recorded and processed in the same manner

as for TCl. The reflections were averaged to yield 466 independent reflections, of which 38 had $F_o^2 < \sigma(F_o^2)$ and were treated as unobserved.

Structure determination

Intensity statistics, based on the second and third moment tests (Foster & Hargreaves, 1963), as well as the $N(z)$ test (Howells, Phillips & Rogers, 1950) indicated a centrosymmetric space group. *Cmca*, with $Z = 4$, requires a molecule with $2/m$ symmetry lying on the mirror plane (100). Preliminary X-ray photographs, showing very strong $I(h00)$, indicated that the molecule lies on the (100) plane and thus supported the assumption that the space group is *Cmca*.

Attempts to solve the structure from packing considerations and the *SEARCH* procedure (Rabinovich & Schmidt, 1966) failed because the synplanar conformation of the C=O bond with respect to the C=C double bond used as a model (Leiserowitz & Schmidt, 1965; Dunitz & Strickler, 1968; Leiserowitz, 1976) proved to be incorrect. The structure was eventually solved by *SEARCH* with an antiplanar model.

The program yielded four trial structures which were tested at low resolution ($\sin \theta/\lambda < 0.26$ Å⁻¹) by rigid-body least squares in which only the scale factor and the Eulerian angle ψ were adjusted; R for one of these structures converged to 0.16. Full-matrix least-squares anisotropic refinement resulted in $R = 0.05$, $R_w = 0.06$.*

* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33412 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

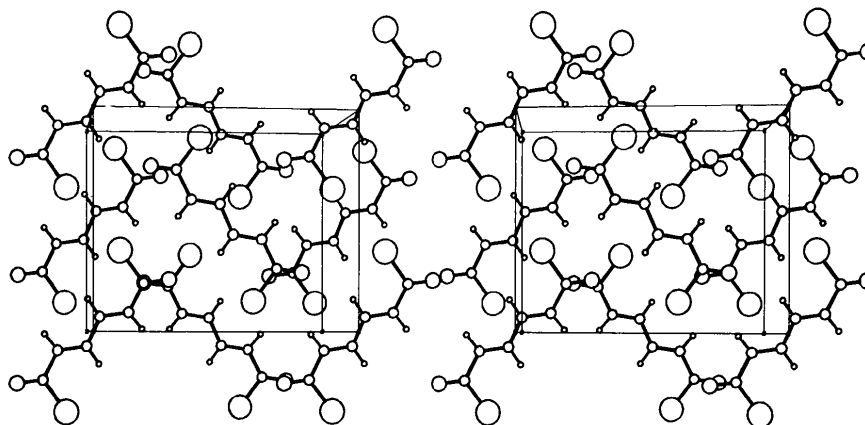


Fig. 3. Stereoscopic view of the packing along [100]. The origin of the unit cell is at the bottom left-hand corner with *b* vertical and *c* horizontal.

Table 3. *Short intermolecular contacts* (Å)

O...C(1) ^I	3.50	C(3)...C(3) ^{IV}	3.57
O...H(1) ^I	2.63	O...C(2) ^V	3.62
C(1)...Cl ^{II}	3.62	O...H(2) ^V	2.77
Cl...H(1) ^{II}	3.38	Cl...H(2) ^V	3.02
C(1)...Cl ^{III}	3.92	C(2)...Cl ^{VI}	3.91
C(2)...Cl ^{III}	3.94	Cl...Cl ^{VII}	3.63
C(3)...O ^{IV}	3.26		

Roman numeral superscripts refer to the molecules in the following equivalent positions relative to the reference molecule at *x,y,z*.

(I)	$-x,$	$\frac{1}{2}-y,$	$-\frac{1}{2}+z$	(V)	$x,$	$\frac{1}{2}+y,$	$\frac{1}{2}-z$
(II)	$\frac{1}{2}-x,$	$\frac{1}{2}-y,$	$-z$	(VI)	$x,$	$-\frac{1}{2}+y,$	$\frac{1}{2}-z$
(III)	$\frac{1}{2}+x,$	$-\frac{1}{2}+y,$	z	(VII)	$-x,$	$1-y,$	$-z$
(IV)	$\frac{1}{2}+x,$	$y,$	$\frac{1}{2}-z$				

TCl, this widening is due to the in-plane 1,4 C...Cl repulsion; the latter and the 1,5 H...Cl distance are 3.05 and 2.59 Å and 3.04 and 2.64 Å in MCl and TCl respectively.

Packing arrangement

Fig. 2 shows the packing in the *bc* plane. The planar molecules lie on mirror planes at $x = 0$ (white) and $x = \frac{1}{2}$ (black), forming a sheet-like structure. Fig. 3 is a stereoscopic view of the packing along [100].

In contrast to TCl, no short Cl...O interactions are present. On the other hand, the Cl...Cl contacts of 3.63 Å form C-Cl...Cl angles of 174° which are similar to those found in many chloroaromatic compounds (Sakurai, Sundaralingam & Jeffrey, 1963; Miller, Paul & Curtin, 1974).

The carbonyl bonds overlap antiparallel, the C...O distances being 3.26 Å. A similar arrangement was found in anhydrous diacetylhydrazide (Shintani, 1960)

and perdeuterated violuric acid (Craven & Mascarenhas, 1964), where the molecules also lie on mirror planes with C...O distances of 3.25 and 3.11, 3.15 Å respectively, indicating an antiparallel C⁺=O⁻ dipole-dipole interaction.

The shortest O...H distances are 2.63 and 2.77 Å. Other short intermolecular interactions are listed in Table 3.

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