Molecular Packing Modes of Acyl Halides.
VII. Discussion and Summary

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From the analyses of the acyl halide crystal structures in the previous parts, we observe that no single primary interaction dominates the packing modes of these compounds. The postulated hal $\cdots$ O interaction observed in oxalyl bromide was found only in terephthaloyl chloride. Instead, hal $\cdots$ hal interactions and/or antiparallel $C^+=O^-$ dipole–dipole interactions were observed; $C-H\cdots O$ contacts were observed in all the crystal structures analysed. The aromatic acyl halides, except biphenyl-2,2′-dicarbonyl chloride, pack with a 4 Å short axis.

1. Introduction

In parts II–VI the results of the analyses of terephthaloyl chloride (TCl), muconyl chloride (MCl), biphenyl-2,2′-dicarbonyl chloride (BCl), adamantane-1,3-dicarbonyl chloride (ACl) and terephthaloyl bromide (TBr) were given. It was found that several types of interactions govern the packing modes of these compounds.

In this paper we discuss in detail each of these interactions, and their influence on the packing.

In § 7 a discussion of the geometry of the carbonyl halide moiety in relation to its attached residue is given.

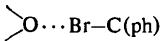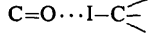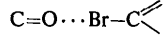## 2. The halogen $\cdots$ oxygen interaction

As mentioned in part I, the existence of attractive interactions between bonded halogen and O atoms in molecular complexes has been established by Hassel and co-workers (Hassel & Rømming, 1962). They consider the interaction as a charge transfer between an electron-pair donor (O,N,S) and an electron-pair acceptor (halogen). the geometry of the interaction is shown in part I, and is similar to that of a hydrogen bond.

In addition to the complexes analysed by Hassel, short linear (or nearly linear) $C-hal\cdots O$ intermolecular interactions were also found in a series of crystalline compounds where the halogen and the O atoms are in the same molecule (homo-complexes). Some examples, together with oxalyl bromide and terephthaloyl chloride, are given in Table 1. Other examples are given by Gaultier, Hauw & Schvoerer (1971) who observed $C-hal\cdots$ carbonyl interactions in a series of halogenated quinones. In all the examples in Table 1, and in most of the halogenated quinones, the $C-hal$ vector is pointing towards the O atom lone-pair lobe. Generally, the scale of donor and acceptor strength observed for the hetero-complexes studied by Hassel is obeyed. On this scale the $C-hal\cdots O=C$ interaction in the acyl halides and in the halogenated

Table 1. Hal $\cdots$ O *interactions in homo-complexes*

ph = phenyl. Sum of van der Waals radii: O $\cdots$ Cl 3·27, O $\cdots$ Br 3·37, O $\cdots$ I 3·57 Å.

Compound	Interaction	Contact	$\angle$O$\cdots$hal–S′
3-Methoxy-5β,19-cyclo-5,10-secoandrostatrien-17-yl bromobenzoate (*a*)	$>$O$\cdots$Br–C(ph)	2·93 Å	177°
Beyerol monoethylidene iodoacetate (*b*)	C=O$\cdots$I–C$\stackrel{\nwarrow}{\swarrow}$	3·12	170
2,3,7,8-Tetrachlorodibenzo[1,4]dioxin (*c*)	O$\cdots$Cl–C(ph)	3·09	173
		3·13	170
N-(*p*-Bromophenyl)sydnone (*d*)	C=O$\cdots$Br–C(ph)	3·16	170
Oxalyl bromide (*e*)	C=O$\cdots$Br–C$\stackrel{\nearrow}{\searrow}$	3·27	169
Terephthaloyl chloride (*f*)	C=O$\cdots$Cl–C(ph)	3·32	168

References: (*a*) Hope & Christensen (1968). (*b*) O'Connell & Maslen (1968). (*c*) Boer, van Remoortere, North & Neuman (1972). (*d*) Bärnighausen, Jellinek, Munnik & Vos (1963). (*e*) Groth & Hassel (1962). (*f*) Part II of this series.

quinones is almost the weakest, as both the O and the C substituent of the halogen are sp^2 hybridized. On this scale Br interactions are stronger than those of Cl (Bent, 1968).

A recent theoretical study of the intermolecular C=O···Cl–Cl interaction in the system formaldehyde–chlorine has proved the existence of this bond and has shown that the heat of formation of this complex is 0·5 kcal mol^{-1} at an equilibrium distance of 3·1 Å, which is slightly shorter than the sum of the van der Waals radii for O and Cl. The Cl–Cl···O and C=O···Cl angles are 180 and 140° respectively (Leroy, Louterman-Leloup, Gaultier & Schvoerer, 1975).

Because of its weakness, the hal···O interaction is not always present in compounds containing halogen and O atoms. For example, in halogenated quinone derivatives the occurrence of the interaction depends on the type of quinone involved and the other substituents. The interaction occurs in almost all halogenated naphthoquinones, but is weak or absent in the presence of NH_2 or OH substituents, where hydrogen bonds are dominant. In benzoquinones, C$^+$···O$^-$ and/or hal···hal interactions may be competitive with the hal···O interaction. In anthraquinones it is not observed at all, hal···hal interactions being present. Isosubstituted I, Br and Cl derivatives which show hal···O interactions are isomorphous, or, at least, if the hal···O interaction is present in one, it is also present in the other halogen derivatives.

The acyl bromides and chlorides analysed thus far are not isomorphous. In oxalyl bromide the packing is dominated by the hal···O interaction; in oxalyl chloride the shortest linear C–Cl···O contact is 3·60 Å (van der Waals distance = 3·27 Å) and the packing is dominated by C$^+$···O$^-$ interactions with C···O distances of 3·0 and 3·2 Å (§ 6). The difference in intermolecular interactions is also reflected in the melting points: the melting point of oxalyl bromide (−19 °C) is lower than that of oxalyl chloride (−12 °C). For isomorphous structures the Br···O interaction should be stronger than the Cl···O and the melting point of the bromide higher than that of the chloride.

TCl packs with hal···O interactions, while in TBr the competitive hal···hal interaction takes over. Here also the difference in the interactions is reflected by the melting points: 83–84 °C for the chloride and 85 °C for the bromide.

The fact that TCl and TBr are not isomorphous is rather surprising. One would expect the stronger Br···O interaction to result in a structure similar to that of TCl. It seems possible, therefore, that the competitive hal···hal interactions are stronger in the bromide, thus explaining its observed structure.

It was observed that in oxalyl bromide and TCl the hal···O contacts are between molecules related by a twofold screw axis and generate nearly planar infinite

layers. The same type of packing was also observed for the halogenated quinones (Bernstein, Cohen & Leiserowitz, 1974) where this interaction occurs. In the latter, as well as in the acyl halides, hal···O=C contacts have not been observed to give rings across centres of inversion.

3. Halogen···halogen contacts

Because of their exposed positions in many molecules, halogen atoms often participate in short interactions. Sakurai, Sundaralingam & Jeffrey (1963) recognized, from the examination of a series of Cl-containing compounds where short C–Cl···Cl–C contacts occur, that there is an orientation factor associated with these short contacts: either the two bonds are nearly collinear (C–Cl···Cl–C angles of 160 ± 10°) or the two bonds are nearly perpendicular to one another (C–Cl···Cl–C angles of 175 and 80°). Short hal···hal contacts of the latter type were also found in crystals of molecular halogen (Wells, 1962) and polyhalogen compounds (Boswijk, van der Heide, Vos & Wiebenga, 1956; Carpenter & Richards, 1962). Nuclear quadrupole resonance studies of I_2 (Robinson, Dehmelt & Gordy, 1954) and minimum-energy calculations of Cl_2 (Hillier & Rice, 1967; Nyburg, 1968; Mason, 1970) indicate electron delocalization or transfer in these short intermolecular contacts, as in the Hassel-type interactions. These results suggest that the perpendicular C–Cl···Cl–C interactions are of the same nature. The same arguments cannot be applied to the linear geometry; Bent (1968) suggests an explanation for this geometry using a method developed by Linnett (1964) where it is considered that electrons of different spins occupy different orbitals.

Green, Leser & Schmidt (1978) observed that dichloro-substituted aromatic and related molecules tend to crystallize in modifications having a short cell axis of ca 4 Å. They recognized also the existence of a hal···hal affinity, i.e. a general tendency of halogen-substituted molecules to crystallize with at least one hal···hal contact shorter than 4 Å.

The Cl···Cl affinity is observed in all the acyl chlorides studied. In BCl there is a Cl···Cl contact of 3·88 Å between molecules related by translation in **b**; in TCl there exists a Cl···Cl contact of 3·72 Å between molecules related by a twofold screw axis, and of 3·90 Å up a stack axis; in ACl there is a Cl···Cl contact of 3·58 Å with one of the C–Cl vectors pointing linearly to the other Cl atom (C–Cl···Cl–C angles are 122 and 172°); in MCl there is a Cl···Cl contact of 3·62 Å between molecules related by translation along **b** [the C–Cl···Cl–C angles are 174°, in agreement with the classification of Sakurai et al. (1963)]; this type of interaction was also found in TBr, which shows Br···Br contacts of 3·57 Å (van der

Waals distance = 3·70 Å) and C—Br···Br—C angles of 159° (there is also a contact of 3·90 Å, and another of 4·06 Å up a stack axis).

The Cl···Cl interaction may be responsible for the antiplanar conformation of the C=C—C=O group in MCl, instead of the usually observed synplanar disposition (Leiserowitz & Schmidt, 1965; Dunitz & Strickler, 1968). Models of the crystal structure of MCl with synplanar and antiplanar conformations, obtained by SEARCH (Rabinovich & Schmidt, 1966), show the C atom skeleton approximately in the same position. In both conformations C—H···O interactions are present, so that they cannot be held responsible for the antiplanar conformation. Antiplanar models show C=O bonds overlapping antiparallel and short Cl···Cl, but not Cl···O contacts. On the other hand, while Cl···O interactions are present in the synplanar models, C=O bonds are either antiparallel (but offset, and do not overlap, and thus the dipole–dipole interactions are weak), or parallel; the shortest Cl···Cl contacts are greater than 4 Å. The stronger antiparallel C$^+$=O$^-$ dipole–dipole interactions and the short Cl···Cl contacts favour in this case the antiplanar conformation.

4. C—H···O=C contacts

The shortest H···O contacts observed in the crystal structures analysed are: 2·68 in TCl, 2·77 and 2·63 in MCl, 2·61 and 2·69 in BCl, 2·67 in ACl and 2·54 Å in TBr.

A study (Sutor, 1963) of short (<3·1 Å) C···O contacts* indicates that many involve hydrogen bonds of the C—H···O=C type where the first C atom is bonded to a hetero-atom (C=X) or to electronegative groups, or else forms part of a conjugated system; the C—H···O and H—C···O angles are reported to lie in the ranges 154–173° and 5–18° respectively. In our work, the H atoms involved in hydrogen bonding are of the required methylidyne type. Table 2 lists the short C···O and H···O distances and the C—H···O, H—C···O and H···O—C angles. Agreement of the first two angles with those given by Sutor (1963) is not satisfactory in most cases. On the other hand, we find rather small deviations of the third angle from 120° [except for the H—C···O system in MCl and the H(3)—C(3)···O system in TBr] and thus the vector H···O either aligns itself along the lone-pair axis of the O atom or lies in a plane half-way between the two lone pairs. These alternatives are reflected in the deviations of the H atoms from the >C=O plane (listed in the last column of the table) which cluster around 0 and 1·4 Å. Similar results are found, for example, in cis-1,2-dichlorodibenzoyl- and cis-1,2-dibenzoylethylene (Rabinovich, Schmidt & Shakked, 1970) and in a series of carboxylic acids which crystallize in sheet-like structures (Leiserowitz, 1976); in the latter the C—H···O interactions between molecules in the layers are indicated as responsible for the layer-like crystal structure.

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* The van der Waals radii of C, O and H are 1·70, 1·52 and 1·2 Å respectively (Bondi, 1964).

Table 2. *Distances (Å) and angles (°) in the system* $\overset{\displaystyle H}{\underset{\displaystyle /}{}}$ C···O=C

System	C···O	H···O	∠C—H···O	∠H—C···O	∠H···O=C	Deviation (Å)*
TCl						
H(1)—C(1)···O	3·39	2·68	125	41	126	1·41
MCl						
H(1)—C(1)···O	3·50	2·63	152	20	160	0
H(2)—C(2)···O	3·62	2·77	150	41	106	0
BCl						
H(6)—C(6)···O	3·45	2·61	145	38	117	1·24
H(4)—C(4)···O	3·30	2·69	118	22	124	1·34
ACl						
H(62)—C(6)···O(2)	3·43	2·67	133	34	127	1·34
H(91)—C(9)···O(1)	3·77	2·87	179	1	137	0
TBr						
H(3)···C(3)···O	3·37	2·54	139	30	146	26

* Deviation from the plane O=C<.

In the above examples each lone-pair lobe of the carbonyl O atom is involved in only one donor–acceptor interaction. In the carboxylic acids one lone pair is involved in O—H$\cdots$O and the other in C—H$\cdots$O interactions. In these compounds the hydroxyl O atom has a free long-pair lobe but it generally does not participate in C—H$\cdots$O interactions. This is indicated as the reason for the antiplanar conformation of the C=C—O=C groups, observed in the triclinic and monoclinic forms of fumaric acid (Brown, 1966; Bednowitz & Post, 1966) and in monomethyl *trans,trans*-muconate (Rabinovich & Schmidt, 1967) and also for a disordered conformation of the carboxyl group in *trans,trans*-muconic acid (Bernstein & Leiserowitz, 1972). In the *cis*-dibenzoylethylenes every O atom is involved in two C—H$\cdots$O interactions – one for every lone-pair lobe. Where more than two H$\cdots$O short contacts involve the same O atom, one shows a C=O$\cdots$H angle of 160° and the other two make angles of 120 ± 20°. This suggests that one of these is not a C—H$\cdots$O interaction.

In TCl one lone-pair lobe of an O atom is involved in a Cl$\cdots$O interaction and the other in a C—H$\cdots$O. In BCl the O atom is involved in two C—H$\cdots$O interactions – one for each lone-pair lobe.

In MCl two H atoms make short contacts with the O atom; the C—H vectors of both point nearly to the same lone-pair lobe with C=O$\cdots$H angles of 106 and 160°.

In ACl, also, only one lone-pair lobe participates in a C—H$\cdots$O interaction, the second remaining free. In both structures the O atom is involved in a C$^+$=O$^-$ dipole–dipole interaction (§ 6).

5. The 4 Å axis

All the aromatic acyl halides analysed, except BCl, crystallize with a short (4 Å) crystallographic axis.

TCl crystallizes with $a = 3\cdot902$ Å. The molecules are planar and their interplanar distance is $3\cdot52$ Å. The plane of the molecules is inclined only 14° to the *bc* plane and the molecules form a sheet-like structure on the (100) plane.

TBr crystallizes with $a = 4\cdot063$ Å. The molecules are nearly planar (the carbonyl chloride group is
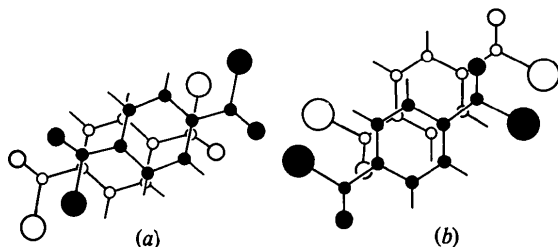
rotated only 7·7° from the phenyl ring) and the interplanar distance between their best planes is 3·48 Å. The molecules, which are tilted from the (100) plane by 37·3°, lie approximately in the (20$\bar{1}$) plane.

Fig. 1(a) and (b) shows the projections of TCl and TBr along the normal to the benzene ring, with two overlapping molecules.

6. Antiparallel C$^+$=O$^-$ dipole–dipole interaction

While muconic acid (Bernstein & Leiserowitz, 1972) crystallizes with a 4 Å axis, muconyl chloride crystallizes in space group *Cmca* with the shortest axis $a = 6\cdot48$ Å, the planar molecules forming layers on mirror planes separated by 3·24 Å ($= a/2$) from one another. Overlapping of the C atoms cannot be expected, since the interplanar distance is shorter than 3·4 Å. The C=O bonds, however, overlap antiparallel forming dipole–dipole interactions that are probably responsible for this packing.

Similar packing and C$\cdots$O distances of 3·26 and 3·14, 3·15 Å are found, respectively, in anhydrous diacetohydrazide (Shintani, 1960) and perdeuterated violuric acid monohydrate (Craven & Mascarenhas, 1964), indicating the existence of electrostatic attraction between the C$^+$=O$^-$ antiparallel dipoles. In these compounds the molecules are also planar and lie on crystallographic mirror planes. The C$\cdots$O distances are nearly the same as the spacings between the molecular layers (Table 3), and are shorter than the sum of the van der Waals radii of 3·30 Å for C and O (Rudman, 1971).

In ACl the C=O groups also lie on crystallographic mirror planes and in antiparallel direction but are offset and do not overlap; the C$\cdots$O distances are 3·49 and 3·55 Å (longer than the 3·41 Å interlayer separation). A similar arrangement was observed in barbituric acid dihydrate (Jeffrey, Ghose & Warwicker, 1961) where the C$\cdots$O distance is 3·50 Å and the interlayer separation is 3·12 Å. Both structures crystallize in space group *Pnma* with $Z = 4$, the molecules lying on crystallographic mirror planes.

Structures consisting of molecules lying on crystallographic mirror planes are uncommon for organic crystals. Some examples are listed in Table 3. Structures with this arrangement are also found for highly polar molecules, such as metanilic acid, $NH_3^+C_6H_4SO_3^-$ (Hall & Maslen, 1965), and 1,2,3,4-tetrachloro-5,6-di-*n*-propylcalicene (Shimanouchi, Sasada, Ashida, Kakudo, Murata & Kitahara, 1969) where this unusual symmetry is attributed to the balancing of dipolar interactions not only within but also between molecular layers. This suggests that for the molecules listed in Table 3(ii) this arrangement is due to the antiparallel C$^+$=O$^-$ dipole–dipole interaction.

Fig. 1. Projections of (a) TCl and (b) TBr along the normal to the benzene ring.

Table 3. *Organic molecules lying on crystallographic mirror planes*

Compound	Space group	Z	Axis perpendicular to m plane	$C \cdots O$ distance	Distance between layers	Interactions in layers
(i) Interlayer interaction: antiparallel $C^+{=}O^-$						
Anhydrous diacetohydrazide (a)	Cmca	4	$a = 6.51$ Å	3.26 Å	3.25 Å	N–H$\cdots$O
Perdeuterated violuric acid monohydrate (b)	Cmc2$_1$	4	$a = 6.217$	3.14 3.15	3.11	O–H$\cdots$O, N–H$\cdots$O
Barbituric acid dihydrate (c)	Pnma	4	$b = 6.24$	3.50	3.12	O–H$\cdots$O, N–H$\cdots$O
Muconyl chloride (d)	Cmca	4	$a = 6.476$	3.26	3.24	C–H$\cdots$O, Cl$\cdots$Cl
Adamantane-1,3-dicarbonyl chloride (e)*	Pnma	4	$b = 6.817$	3.49	3.41	C–H$\cdots$O, Cl$\cdots$Cl
(ii) Interlayer interaction: molecular dipoles						
Metanilic acid ($NH_3{}^+C_6H_4SO_3{}^-$) (f)	Pnma	4	$b = 6.756$		3.38	Molecular dipole
1,2,3,4-Tetrachloro-5,6-di-n-propylcalicene (g)	Pnma	4	$b = 7.017$		3.51	Molecular dipole
Clopidol (h)	P2$_1$/m	2	$b = 6.932$		3.47	Molecular dipole

References: (a) Shintani (1960). (b) Craven & Mascarenhas (1964). (c) Jeffrey, Ghose & Warwicker (1961). (d) Part III of this series. (e) Part V of this series. (f) Hall & Maslen (1965). (g) Shimanouchi *et al.* (1969). (h) Boer (1972).

* Only the two COCl groups and their carbon bridging atoms lie on the mirror plane.

On the other hand, C=O bonds of adjacent molecules overlapping antiparallel with C$\cdots$O distances of 3.21, 3.09 and 3.09 Å are found, respectively, in dilituric acid trihydrate (Craven, Martínez-Carrera & Jeffrey, 1964), tetrahydroxy-1,4-benzoquinone dihydrate (Klug, 1965) and 2,6-dichloro-1,4-benzoquinone (Rees, 1970) where, contrary to the structures listed in Table 3(i), the molecules do not lie on mirror planes. This may be attributed to the presence of other $C^+\cdots O^-$ interactions (for example, of the type discussed by Bolton, 1964), which prevent the formation of molecular layers in mirror planes.

In anhydrous diacetohydrazide as in the above acid hydrates the molecules are held together in layers by NH$\cdots$O, O(w)H$\cdots$O (w = water), or OH$\cdots$O hydrogen bonds. Carbonyl groups that participate in dipole–dipole interactions are involed in only one hydrogen bond, so that one of the O atom lone pairs remains free.

Both the MCl and ACl molecules are held together in layers by short Cl$\cdots$Cl and C–H$\cdots$O interactions. Again, in these two compounds, one O atom lone-pair lobe remains free. In 2,6-dichloro-1,4-benzoquinone the carbonyl group involved in antiparallel C$\cdots$O interaction has one lone-pair lobe involved in a C–H$\cdots$O interaction. The other carbonyl group is involved in a C$\cdots$O interaction of the type discussed by Bolton (1964) with a C$\cdots$O distance of 2.8 Å and a C=O$\cdots$C angle of 160°; the two O atom lone-pair lobes do not participate in any other interaction. In this

benzoquinone there are Cl$\cdots$Cl but no O$\cdots$Cl interactions. Similarly, Cl$\cdots$O interactions were not observed in halogenated benzoquinones where C$\cdots$O interactions are present.

A $C^+{=}O^-$ antiparallel disposition is also found in BCl (intramolecular C$\cdots$O distance = 3.38 Å). In this compound there is also an intermolecular C$\cdots$O contact of 3.30 Å with the C=O bond pointing linearly towards a benzene-ring C atom. In TBr the C=O bond overlaps the C–C bond of the benzene ring, the C$\cdots$O distance being 3.44 Å. Hence, all acyl halides so far studied exhibit short C$\cdots$O contacts, except TCl and oxalyl bromide where the packing is dominated by the hal$\cdots$O interaction. These observations suggest that the hal$\cdots$O interactions dominate the packing only when C$\cdots$O interactions do not exist.

7. Geometry of the carbonyl halide group

The second purpose of this work was to determine the conformation and the dimensions of the COX group with relation to its attached residue.

Bond lengths and angles in the CCOX group of the acyl halides analysed by us with their respective e.s.d.'s are listed in Table 4.

The length of the C=O bond seems to be independent, within experimental error, of the halogen and of the residue attached. The mean C=O length is 1.175 (7) Å. This value agrees well with those obtained

Table 4. *Bond lengths* (Å) *and angles* (°) *of the* C—C$\stackrel{O}{\underset{X}{\diagdown}}$ *group in the five acyl halides analysed*

Compound	C=O	C–X	C–C	O=C–X	C–C=O	C–C–X
TCl (part II)	1·185 (3)	1·769 (3)	1·486 (3)	118·7 (2)	125·9 (2)	115·4 (2)
MCl (part III)	1·169 (3)	1·772 (2)	1·454 (3)	119·0 (2)	125·1 (2)	115·9 (2)
BCl (part IV)	1·162 (4)	1·771 (4)	1·476 (5)	116·6 (3)	127·4 (3)	116·0 (2)
ACl (part V)	1·177 (5)	1·809 (4)	1·517 (5)	117·4 (3)	128·5 (3)	114·1 (2)
	1·173 (5)	1·791 (4)	1·515 (5)	118·0 (3)	126·9 (3)	115·1 (3)
TBr (part VI)	1·181 (6)	1·931 (6)	1·502 (7)	119·4 (5)	124·3 (5)	116·3 (3)

for other acyl halides (Simonetta & Beltrame, 1972) by electron diffraction and microwave spectroscopy, varying from 1·162 in carbonyl chloride fluoride to 1·21 (4) Å in chloroacetyl chloride. On average, this bond is shorter in acyl halides than in carboxylic acids, esters, ketones and aldehydes, indicating more double-bond character (Bertier & Serre, 1966). These results are confirmed by the higher C=O stretching frequency obtained by infrared spectroscopy for TCl, TBr and ACl [1778, 1776 and 1780 cm^{-1} respectively (in CCl$_4$ solution)], compared with 1710 and 1715 cm^{-1}, respectively, for benzoic acid (Thompson & Jameson, 1958) and adamantane-1,3-dicarboxylic acid.

In contrast to the C=O bond, the C—Cl length is not independent of the attached residue. The C—Cl lengths in ACl (1·791 and 1·809 Å) are longer than those in the other three acyl chlorides (1·769, 1·772 and 1·771 Å). This lengthening may be explained by the change in hybridization of the C atom. The difference between the two C—Cl bonds in ACl itself was attributed to an intermolecular Cl···Cl interaction (part V).

The C—Cl length in the acyl halides and the C—Br (1·931 Å) in TBr are longer than the accepted values of 1·736 and 1·89 Å for an sp^2 C atom bonded to Cl and Br respectively (Dewar & Schmeising, 1960). Long C—X bonds were also observed in the acyl halides examined by electron diffraction and microwave spectroscopy (Simonetta & Beltrame, 1972). This lengthening may be attributed to the lone pair of the carbonyl O atom (Bent, 1960): 'Attached to atom A or B of an abnormally long bond $A—B$ is at least one atom with an unshared pair'.

The presence of the unshared pair also implies a shortening of the C=O bond, and the effect may be represented (Bent, 1968; Weiler-Feilchenfeld, 1972) by

$$A—B—\ddot{C} \leftrightarrow A\vdots B=C^+.$$
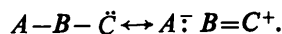
The halogen A attracts electrons from the O atom, thereby decreasing the negative charge on the latter. This process reduces the polarity of the C=O bond giving it more of a covalent double-bond character.

Table 5 lists bond lengths and angles of the CCOX group for some molecular addition compounds containing acyl halides. The average values of the C—Cl (1·71 Å) and C=O (1·23 Å) bonds in the complexes with AlCl$_3$ and SbCl$_5$ are shorter and longer respectively

than in the uncomplexed acyl chlorides (Table 4), since the unshared pair participates in a metal–oxygen bond. In the complexes 1,4-dioxane–oxalyl chloride and 1,4-dioxane–oxalyl bromide the C—X and C=O distances are of the order of those expected for the free molecule since the hal···O interaction is very weak, not affecting the unshared pair.

The value of the C(1)—C—X bond angle is nearly the same for all the acyl halides studied, except ACl, the average being 115·9° (for ACl it is 114·6°). These values are, as expected, somewhat smaller than the corresponding ones in the acyl halide complexes with AlCl$_3$ and SbCl$_5$ [118° for C(1)(sp^2) and 115° for C(1)(sp^3)].

The average values of the C(1)—C=O bond angles are 125·9° for C(1)(sp^2) and 127·2° for C(1)(sp^3). As expected, these values are larger than the 123° found for carboxylic acids (Kanters, Kroon, Peerdeman & Schoone, 1967), due to the higher double-bond character of the C=O bond in the uncomplexed acyl halides. They are also larger than the corresponding ones in the acyl halides complexed with AlCl$_3$ and SbCl$_5$ [123° for C(1)(sp^2) and 124° for C(1)(sp^3)].

It was observed that the bond lengths and angles of the residue attached to the carbonyl halide group in acyl halides are similar to those found in the corresponding carboxylic acid (for TCl, TBr and MCl) or the unsubstituted molecules (in BCl and ACl). The quinonoid character of the phenyl ring in TCl and TBr, *i.e.* the shorter central C—C bond, is in agreement with the result of the analyses of 15 published derivatives of terephthalic acid (part II).

The C(3)—C(2)—C(4) angle (123·5°) in TCl and the C(1)—C(2)—C(3) angle in MCl (126·0°) are significantly larger than the corresponding ones in the respective carboxylic acids (120·0 and 122·5°), probably due to the in-plane 1,4 C···Cl repulsion, which is balanced by the widening of these angles (Kitaigorodskii, 1961). The 1,4 C···Cl distances of 3·04 and 3·05 Å, respectively, in TCl and MCl are significantly shorter than the sum of the van der Waals radii of C and Cl, 3·45 Å. As mentioned above, the C—C—Cl angle is nearly the same for both compounds.

Values of the C—C—Cl angles, the C—C—C—Cl torsion angles and the 1,4 C···Cl distances are listed in Table 6. The 1,4 C···Cl distance is nearly the same for all the compounds listed, varying from 2·98 Å in

Table 5. *Geometry of the* C(1)—C$\underset{X}{\overset{O}{\lessgtr}}$ *group in acyl halides participating in molecular complexes*

	Bond lengths (Å)			Bond angles (°)			
	C=O	C—X	C(1)—C	O—C—X	C(1)—C=O	C(1)—C—X	References
Complexes with 1,4-dioxane							
Oxalyl chloride	1·15 (3)	1·73 (3)	1·58 (3)	123	123	109	1
Oxalyl bromide	1·12 (4)	1·96 (3)	1·50 (3)	118	133	108	1
Complexes with aluminium trichloride							
Benzoyl chloride	1·23 (1)	1·72 (1)	1·42 (1)	119 (1)	124 (1)	117 (1)	2
Propionyl chloride	1·22 (1)	1·70 (1)	1·48 (1)	119·1 (3)	124·5 (5)	116·4 (4)	3
o-Toluyl chloride	1·235 (6)	1·721 (4)	1·442 (6)	117·0 (2)	124·3 (3)	118·7 (2)	5
m-Toluoyl chloride	1·232 (5)	1·710 (5)	1·445 (5)	118·2 (1)	123·2 (2)	118·6 (1)	5
p-Toluoyl chloride	1·235 (3)	1·712 (1)	1·432 (3)	118·5 (1)	122·4 (4)	119·1 (1)	5
Complexes with antimony pentachloride							
Benzoyl chloride	1·236 (7)	1·712 (5)	1·45 (1)	121·1 (2)	121·0 (2)	117·9 (2)	6
Succinyl chloride	1·21 (1)	1·71 (1)	1·51 (1)	123·1 (4)	124·0 (1)	113·0 (4)	4
m-Toluoyl chloride	1·211 (6)	1·710 (4)	1·45 (1)	119·0 (1)	122·7 (2)	118·3 (1)	6
p-Toluoyl chloride	1·22 (1)	1·73 (1)	1·43 (1)	119·4 (2)	122·3 (3)	118·3 (2)	7
Averages for complexes with AlCl₃ and SbCl₅							
C(1)(sp^2)	1·23	1·71	1·44	119·1	123	118	
C(1)(sp^3)	1·22	1·71	1·50	121·1	124	115	

References: (1) Damm, Hassel & Rømming (1965). (2) Rasmussen & Broch (1966). (3) Le Carpentier & Weiss (1972a). (4) Le Carpentier & Weiss (1972b). (5) Chevrier, Le Carpentier & Weiss (1972a). (6) Chevrier, Le Carpentier & Weiss (1972b). (7) Chevrier, Le Carpentier & Weiss (1972c).

Table 6. *Geometry of the* C_α—C_β—C—X *system in acyl halides*

τ is the C_α—C_β—C—X torsion angle.

	Angles (°)			Distance (Å)
Compound	C—C—C	C_β—C—X	τ	$C_\alpha \cdots X$
Terephthaloyl chloride	123·5	115·4	1·25	3·04
Muconyl chloride	126·0	116·0	0	3·05
Biphenyl-2,2'-dicarbonyl chloride	120·6	116·0	8·7	2·99
Terephthaloyl bromide	123·0	116·2	7·7	3·17
Complexes with antimony pentachloride				
Benzoyl chloride	123·3	117·9	0	3·06
m-Toluoyl chloride	122·5	118·6	0	3·01
p-Toluoyl chloride	122·8	118·3	0	3·02
Complexes with aluminium trichloride				
o-Toluoyl chloride	119·6	118·7	8·9	2·98
m-Toluoyl chloride	122·5	118·6	0	3·02
p-Toluoyl chloride	122·3	119·1	5·6	3·03

aluminium trichloride–*o*-toluoyl chloride to 3·06 Å in antimony pentachloride–benzoyl chloride.

In the complexes with antimony pentachloride and in aluminium trichloride–*m*-toluoyl chloride $\tau = 0°$, and the in-plane C$\cdots$Cl repulsion is balanced by the widening of the C—C—C angles. In BCl and in aluminium trichloride–*o*-toluoyl chloride the C—C—C angles are not distorted (~120°); the C$\cdots$Cl repulsion

is released by the deviation of the Cl atom from the C—C—C plane, as indicated by the torsion angles τ (8·7 and 8·9° respectively). In TBr the 1,4 C$\cdots$Br repulsion is probably stronger and in addition to the distortion of the C—C—C angles and rotation of the carbonyl bromide group from the phenyl ring the C(2)—C(4) bond (1·502 Å) is longer than the 1·48 Å found for C(phenyl) bonded to a carbonyl C(sp^2).

Table 7. *Intermolecular interactions observed in the present work*

Compound	$X \cdots O$	$X \cdots X$	$C^+ = O^-$	$C-H \cdots O$	$C \cdots O$	m
TCl	+	–	–	+	–	–
MCl	–	+	+	+	+	+
BCl	–	–	+*	+	+	–
ACl	–	+	+	+	+	+
TBr	–	+	–	+	+	–
OCl†	–	–	–	–	+	–
OBr†	+	–	–	–	–	–

* Intramolecular.
† Oxalyl chloride and oxalyl bromide (Groth & Hassel, 1962).

8. Summary

Unlike amides and carboxylic acids, where the packing is determined primarily by the formation of hydrogen bonds, there is no primary interaction that dominates the packing of acyl halides.

The hal $\cdots$ O interaction which was assumed to exist in, and determine the packing modes of, acyl halides, at least in favourable systems, was observed only in TCl. The following interactions (Table 7) were observed to influence the packing of the other acyl halides studied: hal $\cdots$ hal in MCl, ACl and TBr; antiparallel $C^+ = O^-$ dipole–dipole in MCl, BCl (intramolecular) and ACl; C–H $\cdots$ O contacts were observed in all the crystal structures analysed. Short C $\cdots$ O contacts were observed in all acyl halides studied, except for those showing hal $\cdots$ O or intramolecular antiparallel $C^+ = O^-$ interactions. These observations suggest that the hal $\cdots$ O interaction dominates the packing only in those few cases where C $\cdots$ O interactions do not exist. The hal $\cdots$ hal affinity is observed in all acyl halides studied.

The aromatic acyl halides (TCl, TBr, except BCl, where steric hindrance occurs) are planar or nearly planar and pack with a crystallographic 4 Å short axis.

The antiparallel $C^+ = O^-$ dipole–dipole interactions yield crystal structures in which the molecules lie on crystallographic mirror planes, unless other stronger interactions prevent this type of packing.

The acyl chlorides and bromides analysed are not isomorphous. In oxalyl bromide the packing is dominated by the Br $\cdots$ O interaction and in the chloride by the C $\cdots$ O. This difference may be explained by the relative weakness of the Cl $\cdots$ O interaction (compared with the Br $\cdots$ O) which is superseded here by the apparently stronger C $\cdots$ O interaction. TCl packs with a hal $\cdots$ O interaction while in TBr the competitive hal $\cdots$ hal interaction together with a short C $\cdots$ O contact take over. Both pack with a 4 Å short axis but the overlapping of the benzene rings is different.

The way in which a given system actually crystallizes must depend both on the relative energies associated with the different types of interaction and on the degree to which the various possible contacts have compatible spatial requirements.

In view of what has been said above it would appear that, at least in the acyl halides analysed, our hypothesis that the packing modes of these compounds would be determined mainly by the $X \cdots O$ interaction was not substantiated.

The second purpose of this work was to determine the conformation and the dimensions of the COX group in relation to its attached residue. The length of the C=O bond is independent of the halogen attached, the average being 1·175 (7) Å. This value agrees well with the average (1·182 Å) obtained for other acyl halides by electron diffraction and microwave spectroscopy. This bond is shorter than that observed in carboxylic acids, ketones and aldehydes; this result is supported by infrared spectroscopy.

The C–Cl and C–Br bonds are longer than the accepted values for halogens bonded to an sp^2 C atom; they vary with the electronegativity of the atom attached to the carbonyl halide group.

In complexes of acyl chlorides with aluminium trichloride and antimony pentachloride the C–Cl bond is shorter (average for nine compounds = 1·71 Å) and C=O is longer (average for nine compounds = 1·23 Å) than those in the uncomplexed molecule, since the O atom participates in a metal–oxygen bond.

The bond lengths and angles of the residue attached to carbonyl halides are essentially not affected by the COX group.

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