

C(2) is induced in oxyallobetul-2-ene and, following the removal of the lactone bridge across ring *E*, the final hydrogenated product is triterpane *F*. The mechanism is paralleled by the loss of an equatorial β -OH from gammaceran-3 β -ol which after hydrogenation gives gammacerane which has been identified in a Green River shale oil (Hills, Whitehead, Anders, Cummins & Robinson, 1966).

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Molecular Packing Modes of Acyl Halides.

I. Introduction

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This is one of seven papers dealing with the effects of the carbonyl halide functional group on the molecular structures and packing modes of five diacyl halides: terephthaloyl chloride, muconyl chloride, biphenyl-2,2'-dicarbonyl chloride, adamantane-1,3-dicarbonyl chloride and terephthaloyl bromide. Interest in the packing modes and molecular geometry originated from work on solid-state chemistry and the need to understand and control the factors determining the structures of molecular crystals. In the absence of a general method for *ab initio* prediction of packing arrangements and conformations in molecular crystals, interest centres on systems containing functional groups, e.g. carboxylic acids and amides, whose interactions are relatively stronger than the usual van der Waals forces and often dominate the molecular packing in a predictable way. A survey of available structural data indicated that $X \cdots O$ ($X = \text{Cl}, \text{Br}$) interactions exist in some acyl halides and molecular complexes and presumably play, to some extent, a similar role to that of the hydrogen bond in determining the packing arrangements. The aim of the present work was to establish whether the packing modes of diacyl halides are dominated chiefly by the $X \cdots O$ interactions, or whether other factors such as $\text{C}^+=\text{O}^-$ dipole-dipole, $X \cdots X$ or $\text{C}-\text{H} \cdots \text{O}$ interactions play a contributive, or even decisive, role in the crystallization of these compounds. A complementary purpose was to augment the available geometrical data on the $-\text{C} \begin{array}{l} \text{O} \\ \parallel \\ \text{X} \end{array}$ group.

This series is concerned with the crystallographic studies of the carbonyl halide functional group and its effects on the molecular structures and packing modes of diacyl halides.

In parts II–VI the crystal and molecular structures of five compounds are analysed: terephthaloyl chloride, muconyl chloride, biphenyl-2,2'-dicarbonyl chloride, adamantane-1,3-dicarbonyl chloride and terephthaloyl

bromide. In part VII a discussion and a summary of the study are presented.

Interest in the packing modes of functional groups originated from work on solid-state organic reactions which possess a distinct advantage over fluid processes in that the geometry of the initial state of the system can be determined by X-ray methods. The correlation between the known initial structure of the reactant species and the geometry of the products formed in these reactions bears a great deal of information and can provide a basis for a discussion of the reactivity and the mechanism of these reactions.

Numerous solid-state reactions have been studied and rationalized in terms of the correlations between the initial and final geometries of the species involved. The first extensive contribution to the understanding of lattice-controlled reactions was made by Schmidt and his co-workers (Schmidt, 1967, 1971) who exploited the correlation between the packing modes of olefinic compounds and the geometry of the products formed by photochemical reactions to understand, analyse and set forth rules for the mechanisms of these reactions. Similarly, thermally-induced lattice-controlled reactions were investigated by Paul & Curtin (1973).

Recently, heterogeneous gas/solid reactions have been studied, e.g. the bromination of 4,4'-dimethylchalcone (Rabinovich & Shakked, 1974; Green, Rabinovich, Shakked, Hope & Swansen, 1978) and the dehydrohalogenation by ammonia or amines of solid dihalobutane derivatives (Friedman, Gati, Lahav, Rabinovich & Shakked, 1975; Rabinovich & Shakked, 1977, 1978*a,b*). It was found that the controlling factor of the mechanism in these reactions is the molecular conformations in the solid rather than the packing arrangements of the ensemble of the molecules. Of interest in this context is the extensive current activity in the area of asymmetric synthesis in chiral crystals, where both the molecular conformations and packing modes play a decisive role in the interpretation of the reaction mechanism (Green, Lahav & Rabinovich, 1978; Rabinovich & Shakked, 1974, 1975).

Despite the activity in the field of solid organic chemistry, the choice of systems and compounds for study was heuristic as no general rules or predictions could be set forth relating the structural formula of any given chemical species to its conformation and packing mode in the crystalline state. Thus a thorough and systematic study of this field calls for a need to understand and control the factors determining the geometrical aspects of molecules in molecular crystals.

The lack, as yet, of a general *ab initio* solution to the problem of tailoring predictable structure types is mitigated, to some extent, by semi-empirical rules and experience gained from attempts based on minimum-energy considerations which yielded successful predictions of molecular packing arrangements and conformations (e.g. Kitaigorodsky, 1973; Rabinovich

& Schmidt, 1966; Coiro, Giacomello & Giglio, 1971; Coiro, Giglio, Lucano & Puliti, 1973; Williams, 1969; Warshel, Huler, Rabinovich & Shakked, 1974).

However, there exist systems in which the crystal engineering problem appears to be more favourable to *a priori* prediction. These systems incorporate chemical functional groups known to involve an inter- or intramolecular non-bonded interaction relatively stronger than the usual van der Waals forces. The role played by such functional groups in determining the packing arrangements of organic molecules has long been established. It is well known that carboxylic acids, alcohols, phenols, hydroxides, amides, etc., pack in a fashion that makes possible the formation of hydrogen bonds between adjacent molecules (Pimentel & McClellan, 1960). An important point in this context is the interplay between the functional group and its attached residue. Analyses of the molecular packing modes of primary amides and carboxylic acids (Leiserowitz & Schmidt, 1969; Leiserowitz, 1976) have shown that the symmetry and packing of these molecules are governed by the interplay between the ability of the functional groups to form hydrogen bonds on the one hand, and the spatial requirement of the attached residue on the other.

Additional, though less conclusive, evidence for the specificity of packing modes due to functional groups not involving hydrogen bonds is provided in some other cases where a short C—H...O=C non-bonded interaction and close C⁺=O⁻ dipole-dipole contacts are observed (Sutor, 1963; Bolton, 1964; Rabinovich, Schmidt & Shakked, 1970; Leiserowitz, 1976).

Extending this line of investigation we have chosen to study the molecular packing modes of a number of dicarbonyl halides in relation to the $R-C \begin{matrix} \diagup O \\ \diagdown X \end{matrix}$ functional group ($X = Cl, Br$) and its attached residue (R). In choosing these compounds we have entered almost a *terra incognita*, since the available published crystal structure data on acyl halides were scanty. On the other hand this group is very reactive even in the solid state and therefore can, in principle, participate in solid-state reactions.

Any interaction envisaged for the carbonyl halide group must be considerably weaker than that of the corresponding acid or amide, as shown by the melting points: those of the dicarbonyl halides are much lower than those of the corresponding dicarboxylic acids, although their molecular weights are higher; the melting points of the monocarbonyl halides are even lower.

Available data concerning carbonyl halide...carbonyl halide interactions were limited. Only in two of the known structures, phosgene (Zaslow, Atoji & Lipscomb, 1952) and oxalyl bromide (Groth & Hassel, 1962), was definite evidence for specific X...O interactions observed. In oxalyl bromide every molecule is linked to four others in a layer by means of short

Br...O contacts of 3.27 Å with the C—Br vector pointing linearly towards the O atom lone-pair lobe axis, the C—Br...O and Br...O=C angles being 168 and 120° respectively. In phosgene the molecules are linked in spirals with Cl...O contacts of 3.12 Å accompanied by C—Cl...O and Cl...O=C angles of 162 and 134°. In oxalyl chloride, however, there is no evidence for Cl...O interaction, the shortest contacts being 3.5 and 3.6 Å. An additional, though hypothetical, indication for Cl...O=C interaction was postulated by a plausible packing arrangement of terephthaloyl chloride based on molecular geometry and preliminary crystal data (part II). The C=O...Cl angle in the postulated structure was *ca* 120° and the shortest Cl...O intermolecular contact was 2.8 Å. Other intermolecular contacts in this model were acceptable.

Nevertheless, this meagre and inconclusive evidence for X...O interactions was supplemented by data on halogenated quinones (Gaultier, Hauw & Schvoerer, 1971) and on hetero-complexes (Hassel & Rømming, 1962; Bent, 1968) involving oxygen (>O or =O) and halogen (X—X, X—R). In all these interactions the X...O contact is appreciably shorter than the sum of the van der Waals radii and the vector R—X is pointing directly towards the lone-pair lobe of the O atom. Hassel and his co-workers discussed the X...O interactions in such complexes (*e.g.* acetone/bromine, 1,4-dioxane/oxalyl chloride) in terms of charge transfer between the electron-pair donor (oxygen) and an electron-pair acceptor (halogen). The geometry of the interaction $D \cdots A - S'$, where *A* is the acceptor, *D* the



donor, *S* and *S'* the respective substituents, is analogous to that of a hydrogen bond: the angles $S' - A \cdots D$ and $S - D \cdots A$ are approximately 180 and 120° respectively.

The foregoing survey has displayed the existence of and the role played by X...O interactions in determining the packing modes of some acyl halides and molecular complexes incorporating these interactions. To pursue this study further, we have undertaken the structure analyses of a series of diacyl halides to establish whether the packing modes are dominated chiefly by X...O interactions, or whether other factors, such as C⁺=O⁻ dipole-dipole, C—H...O and X...X interactions, also play an important role in the crystallization of acyl halides.

A complementary purpose of this work was to determine the geometry of the carbonyl halide moiety in acyl halides, since the data available on the bond lengths and angles of the $\text{C} \begin{array}{l} \nearrow \text{O} \\ \searrow \text{X} \end{array}$ group were scanty and were determined by methods other than X-ray diffraction for some small molecules (Simonetta & Beltrame, 1972).

Acyl halides have low melting points, are very reactive and their crystallization and crystal growing

are difficult, so that the selection of compounds was determined by the availability of single crystals suitable for X-ray analysis. Nevertheless, only compounds comprising two carbonyl halide groups were chosen in order to enhance the expected effects on the one hand, and to raise the melting points of the materials on the other.

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