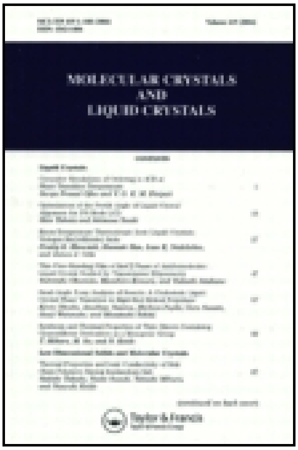

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Solid State Acyl Migration in Salicylamides. An X-Ray Study of the O- and N-Propionyl Derivatives

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SOLID STATE ACYL MIGRATION IN SALICYLAMIDES. AN X-RAY STUDY OF THE O- AND N-PROPIONYL DERIVATIVES.

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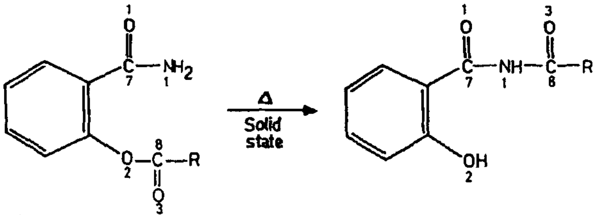
Introduction :

In recent years there has been an upsurge of interest in the study of organic reactions in the solid state.[1-3] It is now realised that the crystalline matrix provides an extraordinary spatial control on the initiation and progress of these reactions. Electronic and dipolar effects which are important in solution are replaced by structural and geometric effects in solids. These 'spatial' or 'topochemical' aspects are important in understanding the mechanistic details of the reaction. In our laboratory, the thermally induced acyl migration in salicylamides from O- to N- position in the solid state has been under study (Scheme 1). The structures of the acetyl and benzoyl derivatives (**Ia**,**IIa**, **Ib** and **IIb**) have been reported.[4,5] As an extension of this work, the propionyl salicylamides (**Ic** and **IIc**) are taken up for investigation and the results are reported herein.



(Ia), R = CH_3 (IIa), R = CH_3

(Ib), R = C_6H_5 (IIb), R = C_6H_5

(Ic), R = C_2H_5 (IIc), R = C_2H_5

Scheme 1

Experimental :

Ic is prepared by the acylation of salicylamide using propionyl chloride by a method similar to that reported for **Ib**.[6] The reaction **Ic** ⟶ **IIc** is found to take place at ~85°C in polycrystalline samples. **IIc** is independently prepared by acidifying an ammoniacal solution of **Ic**. Crystals of **Ic** and **IIc** suitable for diffraction studies are grown from ethyl acetate and chloroform solutions respectively. The crystal data are :-

Ic : $C_{14}H_{11}NO_3$, MP=193.19, monoclinic, $P2_1/n$, Z=4, $\underline{a}$ = 5.241(1), $\underline{b}$ = 7.648(1), $\underline{c}$ = 24.457(1) Å, β = 94.50(1)°, V = 977 $Å^3$, D_m = 1.32, D_c = 1.31 gcm^{-3}. **IIc** : $C_{14}H_{11}NO_3$, MP=193.19, monoclinic, $P2_1/c$, Z=4, $\underline{a}$ = 5.615(2), $\underline{b}$ = 18.778(3), $\underline{c}$ = 9.367(2) Å, β = 101.99(2)°, V = 966 $Å^3$, D_m = 1.32, D_c = 1.33 gcm^{-3}.

Intensity data are collected on a CAD4

diffractometer using monochromated Cu-Kα radiation. The structures are solved by direct methods (MULTAN 80)[7] and refined using full matrix least squares procedures (SHELX 76).[8] The final R values for **Ic** and **IIc** are 0.048 for 1649 reflections and 0.080 for 1368 reflections respectively.

Discussion :

In the structure of **Ic** two intermolecular N-H...O hydrogen bonds, involving O(1) and N(1) atoms are observed, one (N...O = 2.94 Å) between centrosymmetrically related molecules and the other (3.03 Å) between the original molecule and the unit-translated molecule along $\underset{\sim}{a}$. The dihedral angle between the amide group and the benzene ring is 32.2°, while that between the acyl group and the benzene ring is 93.3°. The molecular structure of **Ic** is shown in Fig.1.

In the structure of **IIc**, there is an intramolecular O-H...O hydrogen bond (O...O = 2.58 Å) between O(1) and O(2) and an intermolecular hydrogen bond (N...O = 2.96 Å) involving N(1) and O(3) of centrosymmetrically related molecules. The phenolic ring makes dihedral angles of 7.2° and 6.6° with the planes of the amide and acyl groups respectively. The molecular structure of **IIc** is shown in Fig.2.

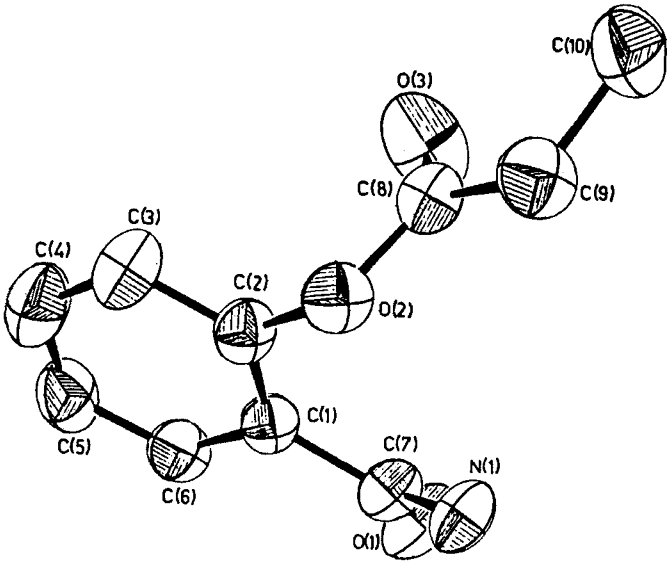


Fig.1. Molecular Structure of **Ic**

An attempt has been made to understand the mechanism of the reaction on the basis of the crystal structures of the reactants. The reaction may be viewed as a nucleophilic addition at the carbonyl carbon atom C(8), the nucleophile being the amide nitrogen atom N(1), with a lone pair of electrons. The important step in the reaction is the bond formation between C(8) and N(1). The following parameters are, therefore, of relevance. The contact, C(8)...N(1), should satisfy the distance criterion for the reaction to occur.[9] The angle(α),

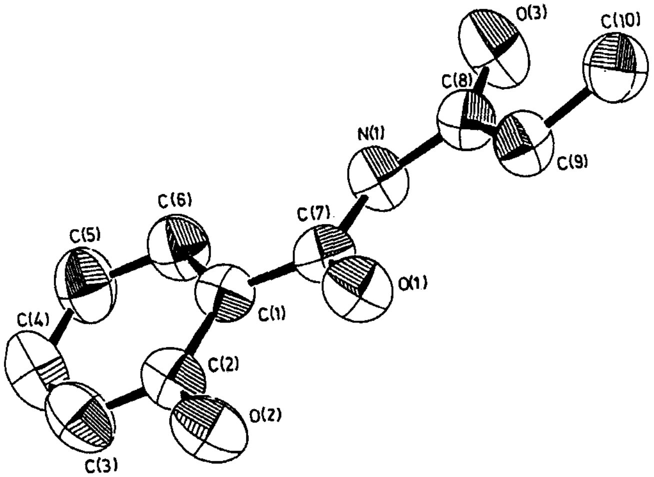


Fig.2. Molecular structure of **IIc**

N(1)-C(8)-O(3), which represents the direction of approach of the nucleophile is expected to be ~109°.[10] If the lone pair on N(1) points towards C(8), then the angle(α'), C(7)-N(1)-C(8), should be ~90°, as the amide nitrogen is sp^2 hybridised. These parameters for **Ia, Ib** and **Ic** are given in Table 1. In the case of **Ia**, both the inter- and intra-molecular contacts are less than 4.2 Å, within which range solid state reactions are known to occur. However, considering the intra-molecular distance of 3.27 Å, which is the shortest and the corresponding angles α and α', an intra-molecular mechanism appears more likely. In the other

Table 1 : Structural parameters for O-acyl Salicylamides

	Ia	Ib	Ic
Intra-molecular			
C(8)...N(1)(Å)	3.27	3.52	3.34
α' (°)	81.1	79.4	86.5
α (°)	101.7	116.1	110.6
Inter-molecular			
C(8)...N(1)(Å)	3.88, 3.91	-	-
α' (°)	111.0, 106.0	-	-
α (°)	132.5, 68.4	-	-

structures, however, there is strong support for the intra-molecular mechanism, as the inter-molecular contacts are all greater than 5.0 Å. Kinetic and microscopic studies are under way to support these results.

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