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Thermally Induced Acyl Migration in Salicylamides. 2. Structures of the Products, *N*-Acetylsalicylamide and *N*-Benzoylsalicylamide*

By K. Vyas, V. Mohan Rao† and H. Manohar‡

Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore 560 012, *India*

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Abstract. *N*-Acetylsalicylamide (II*a*), $C_9H_9NO_3$, $M_r = 179{\cdot}18$, triclinic, $P\bar{1}$, $a = 4{\cdot}566\ (9)$, $b = 10{\cdot}043\ (8)$, $c = 9{\cdot}340\ (9)$ Å, $\alpha = 94{\cdot}45\ (7)$, $\beta = 94{\cdot}23\ (7)$, $\gamma = 97{\cdot}22\ (6)°$, $V = 422\ (1)$ Å^3, $Z = 2$, $D_m = 1{\cdot}39$, $D_x = 1{\cdot}411$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu = 1{\cdot}16$ cm^{-1}, $F(000) = 188$, $T = 295$ K, $R = 0{\cdot}062$ for 1148 reflections. *N*-Benzoylsalicylamide (II*b*), $C_{14}H_{11}NO_3$, $M_r = 241{\cdot}2$, monoclinic, $P2_1/n$, $a = 4{\cdot}903\ (2)$, $b = 18{\cdot}487\ (6)$, $c = 13{\cdot}087\ (5)$ Å, $\beta = 98{\cdot}14\ (3)°$, $V = 1174{\cdot}3\ (8)$ Å^3, $Z = 4$, $D_m = 1{\cdot}36$, $D_x = 1{\cdot}360$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu = 1{\cdot}04$ cm^{-1}, $F(000) = 504$, $T = 295$ K, $R = 0{\cdot}038$ for 1156 reflections. Both molecules are virtually planar. In the lattice the molecules are held together by hydrogen bonds. There is a symmetrical bifurcated hydrogen bond of the O—H···O type in (II*b*).

Introduction. Studies on thermally induced acyl migration from the O to the N position in salicylamides are in progress in this laboratory. The structures of the reactants, namely, *O*-acetylsalicylamide (I*a*) and *O*-benzoylsalicylamide (I*b*), are reported in the preceeding paper (Vyas, Mohan Rao & Manohar, 1987). The X-ray structure analyses of the products (II*a*) and (II*b*), reported herein, were undertaken to allow a comparison to be made with the structures of the reactants (I*a*) and (I*b*), in order to understand the changes in the migration origin, the migration terminus and the migrating group after the rearrangement.

Experimental. Compound (II*a*) prepared by refluxing the *O*-acetyl derivative in MeOH for 8 h (Gordon, 1967). Compound (II*b*) prepared by acidifying an ammoniacal solution of *O*-benzoylsalicylamide (McConnan & Thitherley, 1906); twinned crystals were frequent in the crop as indicated by X-ray photographs. A good crystal free from twinning was selected for data collection. Experimental conditions and refinement details are listed in Table 1. Lp corrections, no absorption correction. Structures solved by direct methods using *SHELX*76 (Sheldrick, 1976) for (II*a*) and *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980) for (II*b*). H-atom positions from ΔF synthesis. (II*a*): full-matrix least-squares refinement on F using *UCLALS*1 (Gantzel, Sparks & Trueblood, 1961), with $w = (a + |F_o| + c|F_o|^2)^{-1}$ (Cruickshank, Bujosa, Lovell & Truter, 1961) where $a = 8{\cdot}0$ and $c = 0{\cdot}01$. H-atom positions (with $B = 5{\cdot}0$ Å^2) included in structure-factor calculations. (II*b*): full-matrix refinement on F using *SHELX*76 (Sheldrick, 1976), $w = 2{\cdot}095/[\sigma^2(F_o) + 0{\cdot}00036|F_o|^2]$. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974). *ORTEP*II (Johnson, 1976) and *PLUTO* (Motherwell & Clegg, 1978) were used for diagrams.

Table 1. *Experimental conditions and refinement details*

	(II*a*)	(II*b*)
Method of measuring D_m	Flotation (in aqueous KI)	Flotation (in aqueous KI)
Solvent used for crystallization	Chloroform	*N,N*-Dimethylformamide
Crystal shape	Thin plates	Thin plates
Crystal size (mm)	0·63 × 0·25 × 0·03	0·50 × 0·30 × 0·06
Diffractometer	CAD-4	Syntex $P2_1$
Radiation	Graphite-monochromatized Mo $K\alpha$	Graphite-monochromatized Mo $K\alpha$
Scan mode	$\omega/2\theta$	$\theta/2\theta$
No. of reflections for measuring lattice parameters, θ range (°)	17, 5–25	15, 10–20
$(\sin\theta/\lambda)_{\max}$ (Å^{-1})	0·70	0·54
Range of h	$-6 \le h \le 6$	$0 \le h \le 5$
k	$-14 \le k \le 14$	$0 \le k \le 19$
l	$0 \le l \le 13$	$-14 \le l \le 14$
Standard reflections	021, 004	$11\bar{1}$, $02\bar{2}$, 131
Fluctuations (%)	< 2	< 2
No. of reflections measured	2649	1682
No. of unique observed reflections $[I > 3\sigma(I)]$	1148	1156
R_{int}	0·045	0·020
No. of parameters	118	207
R, wR, S	0·062, 0·075, 2·54	0·038, 0·052, 2·28
$(\Delta\rho)_{\min}$, $(\Delta\rho)_{\max}$ (e Å^{-3})	−0·28, 0·20	−0·09, 0·11
$(\Delta/\sigma)_{\max}$	0·04	0·06

Discussion. The perspective views of the molecules with numbering schemes are shown in Fig. 1. The bond lengths and angles involving non-H atoms are given in Fig. 2. Positional coordinates for non-H atoms are

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† Present address: Indian Explosives (Gomia), Giridih, Bihar-829112, India.

‡ Author to whom correspondence should be addressed.

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provided in Table 2. Figs. 3 and 4 give the packing diagrams for compounds (II*a*) and (II*b*).*

There is a significant difference between the two C—N bonds, C(7)—N(1) [1·395 (4) Å] and N(1)—C(8) [1·357 (4) Å] in (II*a*), which is not observed in (II*b*). This can be explained in terms of the effect of the substituent at C(8), which is an electron-donating methyl group in (II*a*), but an electron-withdrawing phenyl group in (II*b*). This difference is also reflected in the elongation of the carbonyl bond C(8)—O(3) [1·237 (4) Å] in (II*a*) compared to the corresponding value [1·214 (3) Å] in (II*b*), and C(7)—O(1) bond lengths [1·216 (4) and 1·217 (2) Å] in the two compounds respectively. The effect of substituents on the benzene ring is normally shown up in unsymmetrical external angles. Such a distortion is observed at C(1) in both the compounds and at C(9) in (II*b*).

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* Lists of structure factors, anisotropic thermal parameters, intermolecular separations, H-atom positions and their isotropic temperature factors, bond lengths and angles, and least-squares planes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43699 (26 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

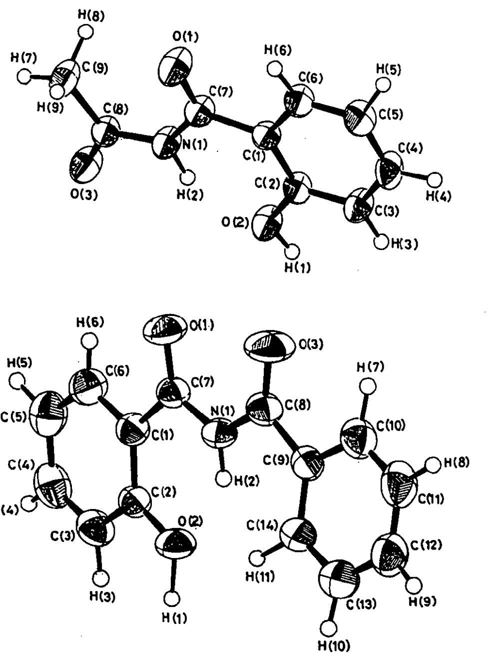

Fig. 1. Perspective views of molecules (II*a*) (top) and (II*b*) (bottom).

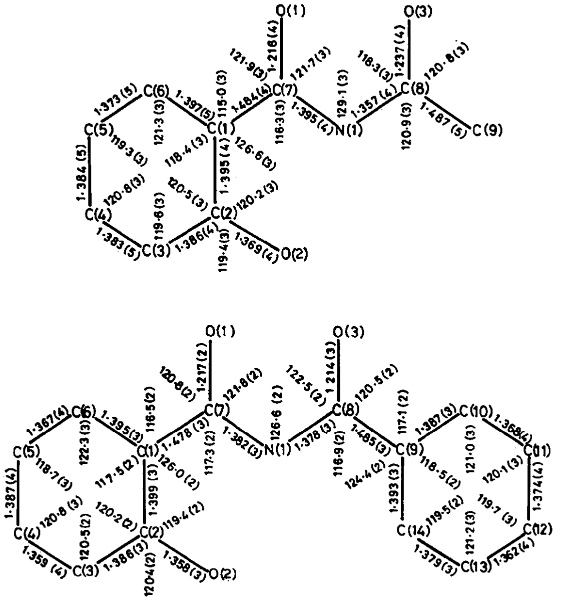

Fig. 2. Bond lengths (Å) and angles (°) of non-H atoms with the numbering scheme for (II*a*) (top) and (II*b*) (bottom).

Table 2. *Fractional atomic coordinates* (× 10⁴) *and equivalent isotropic temperature factors for non-*H *atoms in N-acetylsalicylamide* (II*a*) *and N-benzoylsalicylamide* (II*b*), *with e.s.d.'s in parentheses*

$$B_{\rm iso}=\tfrac{4}{3}\textstyle\sum_i\sum_j B_{ij}\mathbf{a}_i.\mathbf{a}_j;\ U_{\rm iso}=\tfrac{1}{3}\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	(II*a*)				(II*b*)			
	x	*y*	*z*	$B_{\rm iso}$(Å² × 10)	*x*	*y*	*z*	$U_{\rm iso}$(Å² × 10⁴)
O(1)	6847 (6)	3974 (3)	6278 (3)	50 (1)	4783 (4)	2253 (1)	5404 (1)	685 (7)
O(2)	2512 (5)	495 (2)	3901 (2)	38 (1)	3119 (4)	2360 (1)	2211 (1)	592 (6)
O(3)	10 (6)	1613 (2)	7857 (3)	44 (1)	8399 (4)	3352 (1)	5355 (1)	792 (8)
N(1)	3151 (6)	2212 (3)	6234 (3)	34 (1)	5805 (4)	2829 (1)	3972 (1)	446 (7)
C(1)	6085 (7)	2479 (3)	4162 (3)	28 (1)	2204 (4)	1906 (1)	3831 (2)	423 (7)
C(2)	4696 (7)	1315 (3)	3351 (3)	30 (1)	1605 (5)	1928 (1)	2754 (2)	426 (8)
C(3)	5532 (7)	973 (3)	1987 (3)	36 (1)	−531 (5)	1515 (1)	2247 (2)	539 (8)
C(4)	7733 (8)	1799 (4)	1425 (3)	40 (1)	−2021 (6)	1073 (1)	2787 (2)	620 (10)
C(5)	9121 (8)	2962 (4)	2208 (4)	40 (1)	−1443 (6)	1027 (1)	3854 (2)	631 (11)
C(6)	8280 (8)	3299 (3)	3556 (3)	35 (1)	635 (5)	1443 (1)	4355 (2)	546 (9)
C(7)	5437 (7)	2973 (3)	5629 (3)	32 (1)	4338 (5)	2337 (1)	4473 (2)	445 (8)
C(8)	2104 (7)	2413 (3)	7545 (3)	32 (1)	7804 (5)	3298 (1)	4426 (2)	479 (8)
C(9)	3396 (9)	3582 (4)	8570 (4)	45 (1)	9245 (5)	3742 (1)	3722 (2)	441 (8)
C(10)					11030 (5)	4272 (1)	4170 (2)	575 (9)
C(11)					12489 (6)	4695 (2)	3582 (2)	693 (11)
C(12)					12212 (7)	4596 (2)	2532 (2)	674 (11)
C(13)					10493 (6)	4073 (1)	2080 (2)	666 (11)
C(14)					8975 (5)	3647 (1)	2656 (2)	525 (9)

The increase in the two C—N bond lengths in both structures [1·395 (4) and 1·357 (4) Å in (II*a*) and 1·382 (3) and 1·378 (3) Å in (II*b*)] as compared to the values, 1·339 (5) and 1·321 (2) Å, in the reactants (I*a*) and (I*b*) respectively, is noteworthy. The migrating origin, O(2), also undergoes a noticeable change as a result of the reaction. The bond length C(2)—O(2) is shortened in both the structures, 1·369 (4) Å in (II*a*) and 1·358 (3) Å in (II*b*), as in salicylamide (Sasada, Takano & Kakudo, 1964), when compared to 1·401 (4) and 1·399 (2) Å in (I*a*) and (I*b*) respectively.

The phenolic ring makes dihedral angles of 3·0 (2)° (II*a*) and 3·7 (1)° (II*b*) with the amide group plane [C(1), C(7), O(1), N(1)] and 3·2 (1)° (II*a*) and 4·7 (1)° (II*b*) with the acyl group plane [N(1), C(8), C(9), O(3)]. The angles between the amide group and acyl group planes are 0·2 (2)° (II*a*) and 6·1 (1)° (II*b*), indicating that the molecules of (II*a*) and (II*b*) are virtually planar, in contrast to those of (I*a*) and (I*b*).

In both structures the molecules are stacked along the shortest axis *a* and are held together by hydrogen bonds (Figs. 3 and 4). The hydrogen-bond parameters are given in Table 3. In both (II*a*) and (II*b*) there is an intramolecular N—H···O hydrogen bond between the imide N(1) and phenolic O(2) atoms. The formation of these hydrogen bonds apparently stabilizes the planar configuration of the substituents in the products and results in more efficient packing of the molecules as compared to the reactants. This is indicated by the reduction in the molecular volumes by 6·5 and 5·0% in going from (I*a*) to (II*a*) and (I*b*) to (II*b*) respectively. An interesting point to be noted is the configuration of the two carbonyl groups, C(7)=O(1) and C(8)=O(3); it is *E* for the acetyl derivative (II*a*) and *Z* for the benzoyl derivative (II*b*).* This difference is probably a result of different types of intermolecular hydrogen bonds found in the two structures. In (II*a*) there is an intermolecular hydrogen bond between the phenolic O(2) and acyl carbonyl O(3) atoms of a molecule related by a centre of symmetry. On the other hand, in (II*b*) a symmetrical bifurcated hydrogen bond is observed, where the phenolic O(2) atom is the donor and the two carbonyl O(1) and O(3) atoms of a glide-related molecule are the acceptors. Note that the atom H(1), involved in the bifurcated hydrogen bond, has a comparatively high thermal parameter [$U = 0{\cdot}16$ (2) Å^2].

Table 3. *Hydrogen-bond lengths* (Å) *and angles* (°) *in* (II*a*) *and* (II*b*)

	D—H···*A*	*D*—H	*D*···*A*	H···*A*	*DHA*
*(II*a*)	N(1)—H(2)···O(2^{i})	0·93	2·646 (3)	1·88	139
	O(2)—H(1)···O(3^{ii})	0·90	2·659 (3)	1·77	171
(II*b*)	N(1)—H(2)···O(2^{i})	0·89 (3)	2·634 (2)	1·92 (2)	137 (2)
	O(2)—H(1)···O(1^{iii})	1·11 (5)	2·772 (2)	1·84 (5)	139 (4)
	O(2)—H(1)···O(3^{iii})	1·11 (5)	2·783 (2)	1·94 (5)	129 (3)

Symmetry code: (i) x, y, z; (ii) $-x, -y, 1-z$; (iii) $-\frac{1}{2}+x, \frac{1}{2}-y, -\frac{1}{2}+z$.

* E.s.d.'s for the parameters involving H atoms are not provided as the H atoms were not refined.

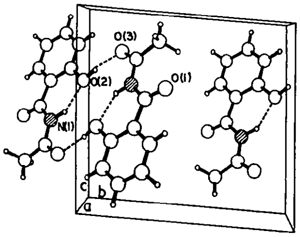

Fig. 3. Molecular packing of (II*a*). Broken lines indicate hydrogen bonds.

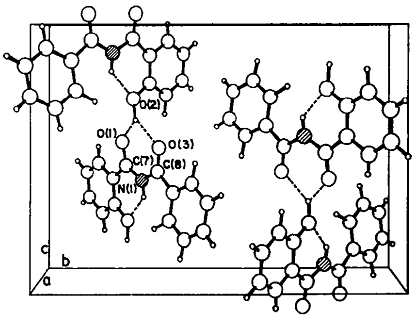

Fig. 4. Molecular packing of (II*b*). Broken lines indicate hydrogen bonds.

A careful examination of (II*b*) indicates that the molecule possesses pseudo-symmetry. This is supported by the atomic coordinates which reveal the presence of a pseudo-diad axis through N(1) and closely parallel to the *c* axis. Therefore, there is a possibility of slight disorder for the molecule, with O(2) fractionally occupying a position close to H(11), all other atoms related by this axis being of the same type. This may explain (*a*) the appearance of H(11) in the difference map, with relatively high electron density (~0·8 e Å^{-3}) compared to other H atoms (~0·5 to 0·2 e Å^{-3}); (*b*) the lower isotropic thermal parameter for H(11) [$U = 0{\cdot}013$ (4) Å^2]; and (*c*) the relatively longer bond length C(14)—H(11) [1·16 (2) Å]. The close agreement in other bond parameters of atoms related by pseudo-symmetry may also be noted (Fig. 2).

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Structure of Dodecyldimethylpropylammonium Bromide Hemihydrate

BY TOORU TAGA AND KATSUNOSUKE MACHIDA

Faculty of Pharmaceutical Sciences, Kyoto University, Sakyo-ku, Kyoto 606, *Japan*

AND NORIYUKI KIMURA, SOICHI HAYASHI, JUNZO UMEMURA AND TOHRU TAKENAKA

Institute for Chemical Research, Kyoto University, Uji, Kyoto-fu 611, *Japan*

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Abstract. $C_{17}H_{38}N^+.Br^-.\frac{1}{2}H_2O$, $M_r = 345\cdot4$, triclinic, $P\bar{1}$, $a = 8\cdot362\ (2)$, $b = 9\cdot161\ (2)$, $c = 27\cdot457\ (2)$ Å, $\alpha = 76\cdot68\ (2)$, $\beta = 82\cdot90\ (2)$, $\gamma = 85\cdot90\ (2)^\circ$, $V = 2029\ (1)$ Å^3, $Z = 4$, $D_x = 1\cdot13$ Mg m^{-3}, $\lambda(\text{Mo}\ K\alpha) = 0\cdot71069$ Å, $\mu = 2\cdot14$ mm^{-1}, $F(000) = 748$, $T = 295$ K, $R = 0\cdot067$ for 4506 observed reflections. The molecules are packed in a bilayer parallel to the (001) plane. The zigzag dodecyl chain is not strictly extended, and the curved chains are arranged in a deformed orthorhombic packing at the central region of the bilayer. The ammonium group is surrounded by four or five Br ions in a distorted trigonal bipyramidal arrangement. Each Br ion accepts one hydrogen bond from the water molecule.

Introduction. This work is part of our continuous studies on the crystal properties and molecular packing of alkylammonium halides with various alkyl chain lengths. Both the hemihydrate and the monohydrate of dodecyldimethylpropylammonium bromide crystallize from the solution containing ethyl acetate and water at room temperature, but the hemihydrate form was obtained from the solution containing a small amount of water. The crystal structure of the monohydrate was determined previously (Taga, Machida, Kimura, Hayashi, Umemura & Takenaka, 1986), and the present paper deals with the structure determination of the hemihydrate so that it may be compared with that of the monohydrate structure.

Experimental. Colourless transparent plate-like crystal, $0\cdot15 \times 0\cdot2 \times 0\cdot2$ mm; Rigaku AFC-5RU diffractometer, graphite-monochromated Mo $K\alpha$ radiation; lattice parameters from 18 reflections with $22\cdot0 < 2\theta < 34\cdot8^\circ$; three standard reflections measured every 56 reflections, no significant change in intensities; 6045 observed reflections within the range $2\theta < 55^\circ$ $(0 \le h \le 10,\ -11 \le k \le 11,\ -32 \le l \le 32)$; 4506 unique reflections with $F_o > 3\sigma(F)$ used for structure determination; 3601 unobserved, $R_{\text{int}} = 0\cdot017$. Structure solved by direct methods using *MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978); refined by full-matrix least squares; $\sum w(|F_o| - |F_c|)^2$ minimized, $w = [\sigma^2(F) + (0\cdot023F)^2]^{-1}$; non-H atoms anisotropic; H atoms from difference map, isotropic; $R = 0\cdot067$, $wR = 0\cdot076$, $S = 1\cdot98$; $(\Delta/\sigma)_{\text{max}} = 0\cdot50$; max. residual electron density $0\cdot59$ e Å^{-3}. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974). All computations performed on a FACOM

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