Solid-state Transformations and Crystal Structure Analysis of α- and β-*o*-Acetamidobenzamide

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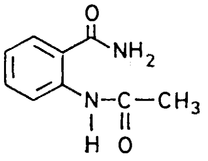
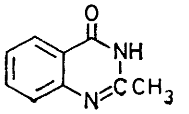
o-Acetamidobenzamide (I) has been found to crystallize in at least two distinct forms, both of which undergo complex thermal solid-state transformations which result in the formation of anhydrous 2-methylquinazol-4-one (II). We discuss the first transformation in this series which is a solid-state polymorphic transformation of (Iα) to (Iβ), occurring at 150 °C with the heat of transformation of 0.7 kcal mol^{-1}. Single crystal *X*-ray structure determinations of (Iα and β) revealed that the transformation involves loss of an intramolecular N–H • • • O hydrogen bond from (Iα) and formation of a new intermolecular N–H • • • O hydrogen bond in the structure of (Iβ). Two other intermolecular hydrogen bonds are present in both (Iα and β). The significance of these hydrogen-bond interactions to the mechanisms of disordering in solid-state transformations is discussed. Crystal data for the two polymorphic forms of (I) are: (Iα), $P2_1/n$, a = 4.952(2) Å, b = 14.496(2), c = 12.471(3), β = 93.99(3)°; (Iβ), $P2_1/c$, a = 7.807(2) Å, b = 9.039(3), c = 12.706(3), β = 101.12(2)°.

HAGLER and LEISEROWITZ have demonstrated how hydrogen-bonding interactions influence the crystal packing modes of primary and secondary amides, and that the frequent occurrence of polymorphic modifications among amide compounds results from the possibility of forming different hydrogen-bonding schemes of nearly the same energies.[1] We have investigated the structural and solid-state chemical properties of *o*-acetamidobenzamide (I), a compound which contains both a primary amido-group and a secondary acetamido-group, and have found that two polymorphs do exist and that one can be converted *via* a solid-state reaction to the other polymorph. This transformation occurs simultaneously with a solid-state cyclodehydration reaction. The crystal structures of the α- and β-forms of (I) were solved and are discussed in terms of both their unusual solid-state thermal properties, and the hydrogen-bonding patterns proposed by Leiserowitz.



(I)



(II)

EXPERIMENTAL

Crystal Preparation.—*o*-Acetamidobenzamide was prepared by a known procedures from acetylanthranil and ammonia, and *via* acetylation of *o*-aminobenzamide.[2] Two different crystalline forms (Iα and β) can be isolated depending on recrystallization conditions. Compound (Iα) may be obtained as tiny crystallites by supercooling acetone or methanol solutions. Large needle-shaped α-crystals suitable for *X*-ray analysis were obtained by recrystallization from tetrahydrofuran solution. Block-like crystals of (Iβ) were grown from water, methanol, or acetone solutions. Prolonged heating of any of these solutions, and subsequent cooling to room temperature, gives a mixture of (I) and (II).

Crystals of (Iα) can be converted into (Iβ) by dissolving in excess methanol and allowing slow crystal growth to take place. Rapid crystallization from concentrated solutions, starting with either α- or β-crystals, gives the α-form. α-Crystals are also formed by rapid recooling of a melt of either α- or β-crystals. Preliminary chemical and spectroscopic characterization of these two crystal forms has been discussed previously.[3]

The preparation and characterization of the quinazolone (II) from rearrangement of (I) in basic solution has been reported.[2] Compound (II) can be recrystallized from water or alcohol solutions. Sublimation at 100 °C at ambient pressure gives large clear rhombohedral shaped crystals.

The structure of an intermediate (III) has not yet been elucidated. The following chemical and physical data

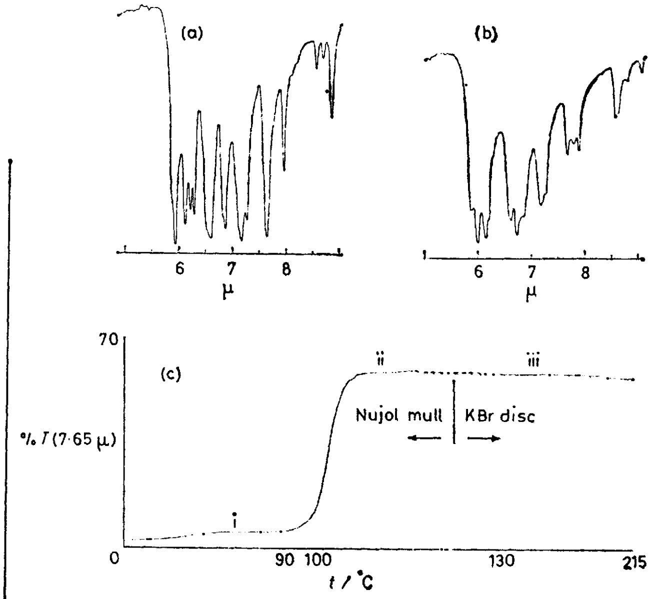


FIGURE 1 (*a*) I.r. spectrum of (Iα) showing the 7.65 μ band; (*b*) the corresponding spectrum of (Iβ); (*c*) the change in percentage transmission at 7.65 μ of (Iα) as it is heated on an i.r. hot stage. The sample changes from (Iα) at i, to (Iβ) at ii, to quinazolone (II) at iii, as verified by full scan i.r. curves run at these points suggest that it may be a hydrated form of (II). Compound (III) is prepared by recrystallizing (I) from aqueous $NaHCO_3$ solution to give tan needles. Elemental analysis agrees with the composition of $C_9H_{10}N_2O_2$. The i.r. and n.m.r. spectra match that of (Iβ), but the m.p. behaviour of (III) is distinctly different from that of (Iβ). Compound (III) melts at 174—177 °C, resolidifies at 180°, then remelts at >200 °C. This melting behaviour is reproducible and does not depend on the heating rate or method of measurement.

TABLE 1

Crystal data

Polymorph	(Iα)	(Iβ)
Formula	$C_9H_{10}N_2O_2$	$C_9H_{10}N_2O_2$
Molecular weight	178.2	178.2
Space group	$P2_1/n$	$P2_1/c$
a (Å)	4.952 (2)	7.807(2)
b (Å)	14.496 (2)	9.039 (3)
c (Å)	12.471 (3)	12.706 (3)
β (°)	93.99 (3)°	101.12 (2)°
V (Å^3)	893.04	879.74
Z	4	4
D/g cm^{-3}	1.325 (obs. 1.312)	1.345

TABLE 2

Data collection

	(Iα)	(Iβ)
Diffractometer	Nonius Cad-4	Nonius Cad-4
Radiation	Cu-K_α	Mo-K_α
Monochromatization	Ni filter	Graphite-crystal monochromator
2θ limits	75°	25°
Number of unique reflections measured	2 035	1 772
Number of ' observed ' reflections for which $F_o^2 > 3\sigma(F_o^2)$	603	820
Weighting scheme	$w = 1/\sigma(F_o)^2$	$w = 1/\sigma(F_o)^2$
R_w*	0.07	0.05
R	0.06	0.04

* Reliability factor, weighted, $R_w = \left[\frac{\Sigma w(|F_o| - |F_c|)^2}{\Sigma w F_o^2}\right]^{\frac{1}{2}}$

TABLE 3

Positional and thermal parameters and their estimated standard deviations

Atom	x	y	z	$B(1,1)$	$B(2,2)$	$B(3,3)$	$B(1,2)$	$B(1,3)$	$B(2,3)$
				(Iα)					
O(1)	−0.330(1)	0.110 8(3)	0.005 0(3)	0.084(3)	0.003 8(2)	0.005 8(3)	−0.005(2)	−0.016(2)	0.000 9(5)
O(2)	−0.293(1)	0.418 5(3)	0.165 2(4)	0.088(3)	0.004 6(3)	0.008 7(4)	0.004(2)	−0.010(2)	−0.004 4(6)
N(1)	−0.247(1)	−0.009 2(4)	0.115 6(4)	0.063(3)	0.004 5(3)	0.006 7(4)	−0.003(2)	−0.012(2)	0.000 6(7)
N(2)	−0.273(1)	0.272 3(4)	0.102 2(4)	0.051(3)	0.004 2(3)	0.005 6(4)	0.001(2)	−0.009(2)	−0.000 9(7)
C(1)	−0.067(1)	0.231 1(5)	0.169 4(5)	0.031(3)	0.005 7(4)	0.004 5(5)	−0.005(2)	0.005(2)	0.000 5(8)
C(2)	−0.031(1)	0.134 5(5)	0.162 0(5)	0.041(3)	0.004 3(4)	0.005 6(5)	−0.001(2)	0.003(2)	0.000 7(8)
C(3)	0.181(1)	0.093 5(5)	0.225 2(5)	0.039(4)	0.005 4(5)	0.007 2(6)	0.001(2)	0.003(3)	0.000 9(9)
C(4)	0.347(1)	0.144 0(6)	0.295 3(6)	0.037(4)	0.008 0(5)	0.007 7(6)	−0.004(3)	−0.007(3)	0.003 4(10)
C(5)	0.303(2)	0.236 1(6)	0.303 8(6)	0.048(4)	0.008 3(6)	0.006 1(6)	−0.009(3)	−0.002(3)	−0.001 7(10)
C(6)	0.097(1)	0.281 3(5)	0.243 4(6)	0.051(4)	0.004 8(4)	0.006 9(6)	−0.003(3)	−0.004(3)	−0.002 2(9)
C(7)	−0.216(2)	0.078 1(5)	0.087 8(5)	0.055(4)	0.003 6(4)	0.006 5(5)	−0.003(2)	0.003(3)	−0.001 6(8)
C(8)	−0.374(2)	0.358 6(5)	0.103 3(5)	0.056(4)	0.004 0(4)	0.006 1(5)	0.000(2)	0.005(3)	0.001 5(8)
C(9)	−0.603(2)	0.373 7(5)	0.019 0(6)	0.061(5)	0.004 2(4)	0.009 3(6)	0.006(3)	−0.004(3)	0.001 0(9)
H(3)	0.19(1)	0.030(4)	0.217(4)	4.0					
H(4)	0.50(1)	0.117(4)	0.335(4)	4.0					
H(5)	0.41(1)	0.275(4)	0.341(4)	4.0					
H(6)	0.06(1)	0.354(4)	0.284(4)	4.0					
H(7)	−0.20(1)	−0.023(4)	0.173(4)	4.0					
H(8)	−0.38(1)	−0.043(4)	0.074(4)	4.0					
H(9)	−0.34(1)	0.234(4)	0.060(4)	4.0					
H(10)	−0.68(1)	0.315(4)	−0.004(4)	4.0					
H(11)	−0.57(1)	0.417(4)	−0.030(4)	4.0					
H(12)	−0.72(1)	0.401(4)	0.045(4)	4.0					
				(Iβ)					
O(1)	0.306 4(3)	0.454 4(3)	0.065 5(2)	0.015 0(4)	0.007 4(3)	0.005 2(2)	−0.004 8(7)	0.006 2(4)	−0.004 8(4)
O(2)	0.454 2(3)	0.445 2(3)	0.328 7(2)	0.018 8(5)	0.006 3(3)	0.008 4(2)	−0.001 4(8)	0.000 1(6)	0.001 8(5)
N(1)	0.492 2(3)	0.646 3(3)	0.097 1(2)	0.012 6(5)	0.007 7(4)	0.006 1(2)	−0.003 6(8)	0.007 3(5)	−0.005 0(5)
N(2)	0.469 0(4)	0.693 3(3)	0.327 9(2)	0.014 0(5)	0.005 6(3)	0.004 5(2)	−0.000 8(8)	0.001 3(5)	−0.001 4(5)
C(1)	0.291 9(4)	0.714 3(4)	0.273 1(3)	0.011 3(6)	0.005 2(4)	0.003 8(2)	0.000 3(9)	0.003 0(6)	0.000 0(6)
C(2)	0.233 3(4)	0.655 1(4)	0.172 1(3)	0.009 4(6)	0.005 7(4)	0.004 1(2)	−0.000 6(9)	0.003 2(6)	0.000 0(6)
C(3)	0.060 2(4)	0.673 7(4)	0.124 8(3)	0.012 8(6)	0.008 7(5)	0.005 4(3)	−0.002 3(10)	0.003 1(7)	0.000 1(7)
C(4)	−0.051 5(5)	0.753 1(5)	0.174 4(3)	0.009 6(6)	0.012 2(6)	0.008 6(3)	0.003 2(11)	0.004 3(7)	−0.000 6(8)
C(5)	0.009 7(5)	0.814 0(4)	0.273 0(3)	0.017 4(7)	0.011 2(6)	0.008 5(3)	0.006 2(11)	0.011 7(7)	−0.004 0(8)
C(6)	0.180 6(5)	0.794 5(4)	0.323 5(3)	0.016 1(7)	0.010 5(5)	0.005 0(2)	0.001 3(11)	0.006 5(7)	−0.003 4(7)
C(7)	0.347 9(4)	0.575 8(4)	0.108 4(2)	0.010 6(6)	0.007 2(4)	0.003 0(2)	0.000 4(9)	0.002 2(6)	0.000 3(6)
C(8)	0.539 0(4)	0.558 9(4)	0.353 6(3)	0.014 8(6)	0.007 9(5)	0.003 7(2)	0.001 9(10)	0.002 9(6)	−0.000 3(6)
C(9)	0.723 2(5)	0.557 0(4)	0.413 3(3)	0.016 3(8)	0.010 5(6)	0.008 2(3)	0.001 4(12)	−0.002 9(9)	−0.001 8(9)
H(1)	0.572(4)	0.605(4)	0.052(3)	4.7(9)					
H(2)	0.518(4)	0.734(4)	0.120(2)	3.5(8)					
H(3)	0.024(3)	0.639(3)	0.058(2)	1.9(6)					
H(4)	−0.172(4)	0.766(3)	0.142(2)	2.6(7)					
H(5)	−0.058(4)	0.859(4)	0.305(3)	5.3(9)					
H(6)	0.226(4)	0.834(3)	0.392(2)	3.7(8)					
H(7)	0.522(4)	0.771(4)	0.350(2)	3.6(8)					
H(8)	0.776(4)	0.647(3)	0.426(2)	3.1(7)					
H(9)	0.790(5)	0.509(5)	0.365(3)	7.8(12)					
H(10)	0.741(5)	0.482(5)	0.465(3)	7.3(11)					

The form of the anisotropic thermal parameter is: $\exp[-(B(1,1)HH + B(2,2)KK + B(3,3)LL + B(1,2)HK + B(1,3)HL + B(2,3)KL)]$.

When the sample is heated to 175° and then resolidified, the i.r. spectrum and m.p. match that of (Iα). When heated to the second melt at *ca.* 210°, and recooled, the i.r. spectrum matches that of (II). Weissenberg and oscillation *X*-ray diffraction film patterns of single crystals of (III) are very similar but not identical to those of (Iβ).

Thermal Characterization.—Preliminary m.p. and thermal conversion studies were done on a Fisher-Johns Mel-Temp apparatus. The m.p.s reported here are from runs made on a DuPont 900 differential thermal analyser or a Perkin-Elmer DSC-2 differential scanning calorimeter (d.s.c.) (heating rates were 20 °C min^{-1}). Thermal gravimetric analyses (t.g.a.) were run on a Perkin-Elmer TGS-1 instrument.

High temperature i.r. studies were done using a horizontal heated stage attachment on a Perkin-Elmer 21 i.r. spectrometer. Both KBr pellets and Nujol mulls were used. Nujol mulls were employed to study the transitions from room temperature to 125 °C, and a KBr pellet was used in the 125—215 °C range. The spectrometer was fixed at 7.65 μ on a strong absorption in the α-form but not in the β-form (see Figure 1). The Nujol sample was heated on the hot stage to 125 °C over 25 min, and then the KBr pellet was heated to 215 °C. (The temperatures on the heated stage were not calibrated, so may not correspond precisely with the d.s.c. measurements.)

Attempts to study thermal transitions in single crystals of (Iα or β) have so far been unsuccessful. Both samples sublime before any detectable solid-state change has taken place. This is true at low (*e.g.*, 130 °C for 24 h) or high temperature (160 °C for 5 min). *X*-Ray powder patterns before and after transformation were obtained on powdered samples in thin-walled glass capillaries which were heated in an oil-bath and then cooled to room temperature before analysis.

Structure Determination.—Crystal data are listed in Table 1, and data collection details in Table 2. Both structures were solved using direct methods procedures taken from ref. 4. *E* Maps computed from models with the highest figures of merit revealed all the non-hydrogen atoms. These atomic parameters were refined isotropically and then anisotropically, and difference density maps revealed all the hydrogen atoms. All parameters were then refined until convergence (the hydrogens were fixed at *B* 4.0 for the α-form; an extinction coefficient correction was used for the β-form). The final unweighted *R* values were 0.06 for the α-form and 0.04 for the β-form.

The final atomic co-ordinates are listed in Table 3. Least squares planes results, observed bond lengths and angles, and structure factor tables are contained in Supplementary Publications No. SUP 22828 (14 pp.).*

RESULTS

Characterization of Phase Transformations.—The d.s.c. curves obtained for (Iα and β) and (III) are shown in Figure 2. Each compound clearly undergoes multiple transitions. These d.s.c. curves are highly reproducible from sample to sample and agree roughly with observations and measurements made on a Fisher-Johns m.p. apparatus. Each sample eventually melts at *ca.* 230 °C, at which stage the samples are indistinguishable by i.r. and elemental analysis and have been converted completely into (II). A t.g.a. analysis of (Iβ) showed a loss of weight equivalent to 1 mole of water per mole of (Iβ) between 50 and 100 °C, consistent with its dehydration to give (II).

Since (Iα and β) appear to have identical m.p.s, and since the transition energy of 0.7 kcal mol^{-1} is consistent with the difference in lattice energies of several other hydrogen-bonded systems,[1] we considered that (Iα) was undergoing a transition to (Iβ) at point A in Figure 2, and the observed m.p. was actually that of (Iβ). To test this idea we set up a heated-state apparatus on an i.r. spectrophotometer to allow us to run i.r. spectra both before and after transition A. Figure 1 shows the results of fixed wavelength–variable temperature absorption at 7.65 μ. By observing the 7.65 μ band, which is present in (Iα) but not in (Iβ), we were also able to monitor the polymorphic transition itself. Full scan i.r. curves taken at points i—iii in Figure 1 match those of standard spectra of (Iα and β) and (II), respectively. The temperature of the abrupt transition from (Iα) to (Iβ) is lower than that of the d.s.c. transformations, but the

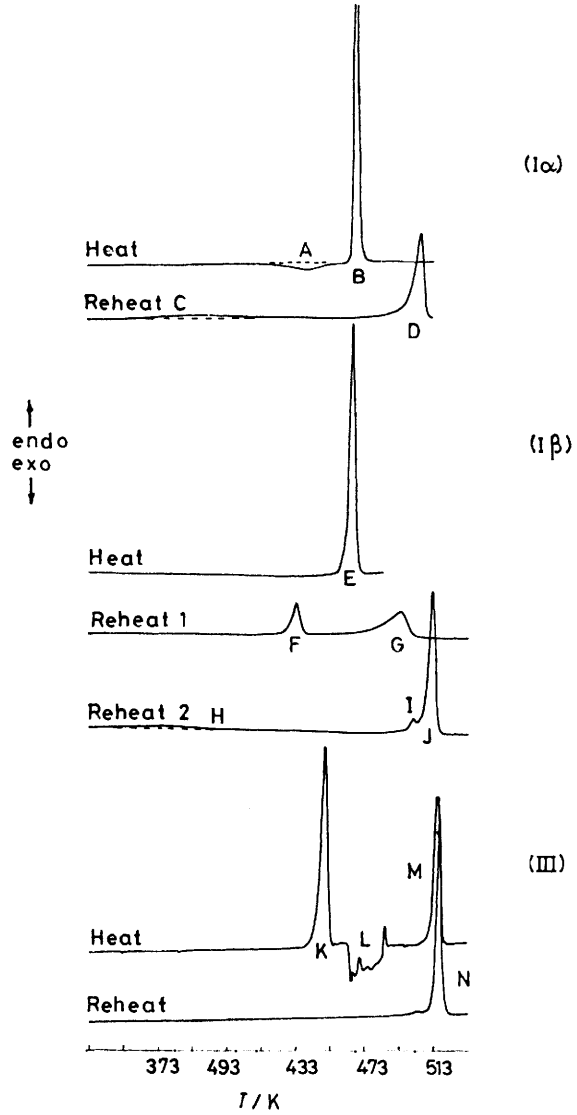


FIGURE 2 Differential scanning calorimetry curves of (*a*) (Iα), (*b*) (Iβ), and (*c*) (III). The heats of transformation (in kcal mol^{-1}) associated with each phase change are: A, 0.7; B, 8.6; C, 2.1; D, 5.3; E, 9.2; F, *ca.* 6; G, 12.0; H, 1.9; I and J, 12.3; K, 7.7; L. 4.1; M, 6.3; N, 6.3

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* For details of Supplementary Publications see Notice to Authors No. 7 in *J.C.S. Perkin II*, 1979, Index issue.

samples are in significantly different forms (KBr pellet or Nujol mull *versus* a plain, finely ground powder), and the heated-stage temperatures are not as accurate as those of the d.s.c. measurements. We also found that the *X*-ray powder pattern of (Iα) changed to that of (Iβ) when a glass capillary containing (Iα) was heated at 110 °C for 15 min.

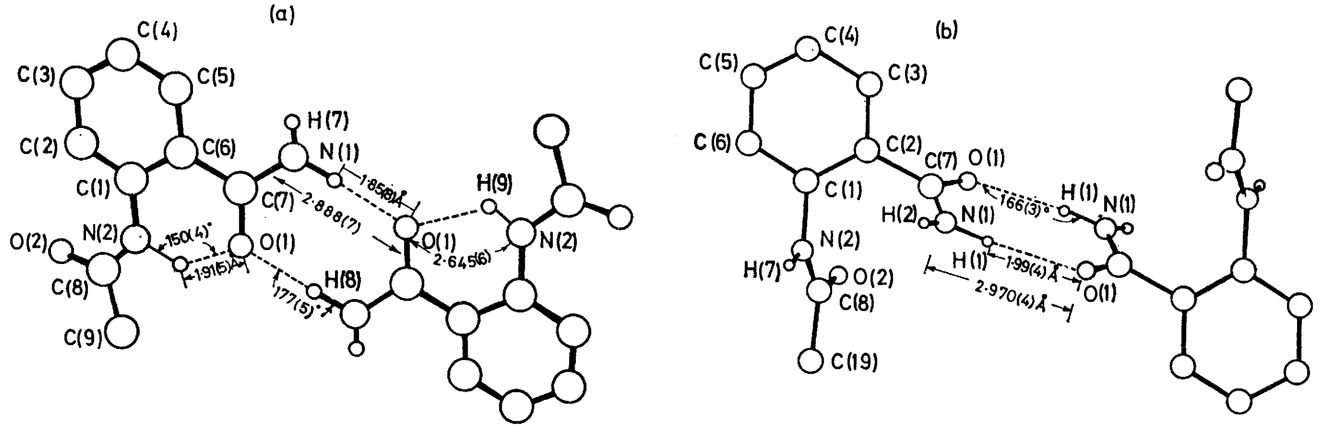


FIGURE 3 The geometry of the *i*-related dimer contacts between the primary amide groups of (*a*) (Iα) and (*b*) (Iβ)

The transitions C, F, H, K, and L in Figure 2 have not been fully characterized yet, but it seems likely that they are due to various solid solutions or possibly eutectic mixtures resulting from the condensation and subsequent dehydration of (I) during the heating cycles. Further work is in progress to understand these transitions.

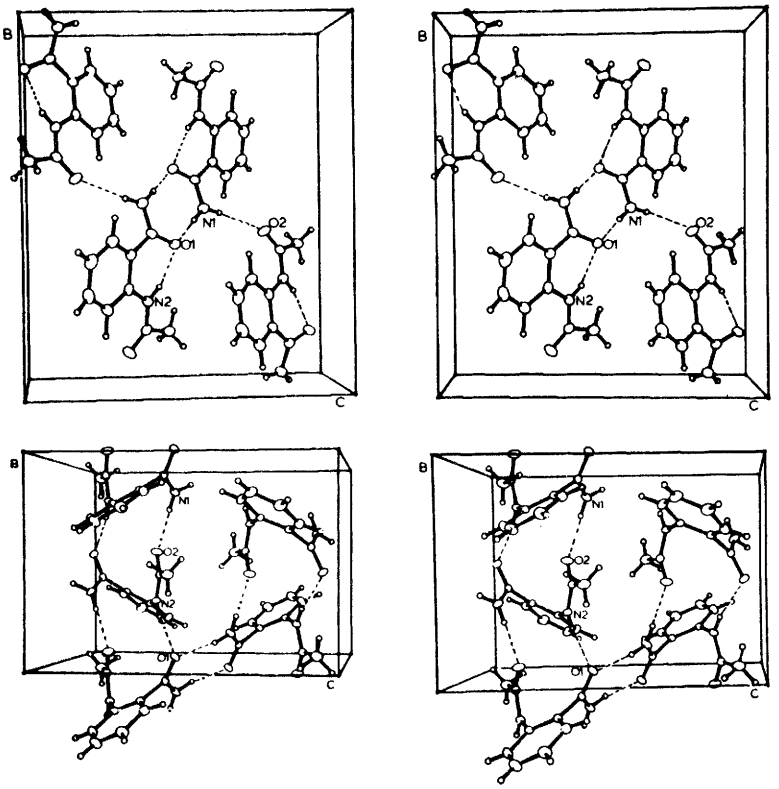


FIGURE 4 Stereopair views along [100] of the unit cells of (*a*) (Iα) and (*b*) (Iβ)

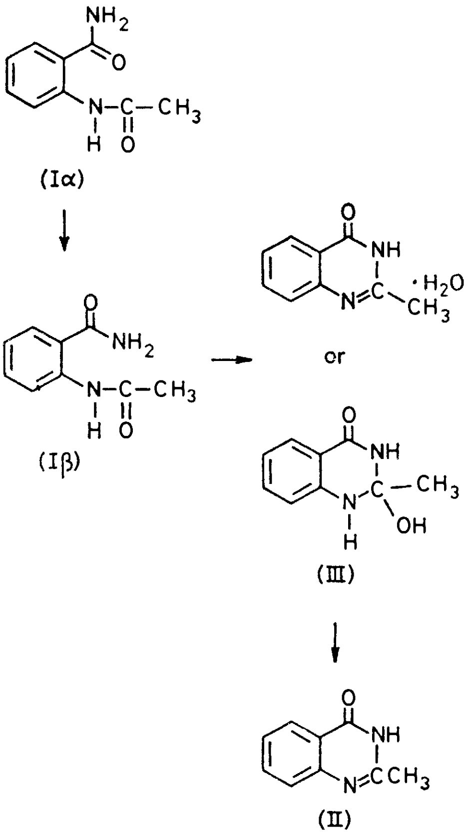
Crystal Structure Analysis.—Based on the extensive studies of crystal packing modes of primary amides, and of *N*-methylamides reported by Leiserowitz,[5a,b] the structures of (Iα and β) (which contain both a primary amide and a secondary amide) are interesting in the way their conformations are distorted to allow the maximum number of hydrogen bonds to be established. As seen in Figure 3, both (Iα and β) have cyclic *i*-related dimers formed by hydrogen bonding between their primary amide groups. The geometry of the hydrogen bonds in these dimer interactions does not differ significantly from that reported by Leiserowitz, but the primary amide group of (Iβ) is twisted 52° from the plane of its phenyl ring. This twist is even larger than the 49° angle observed for *o*-chlorobenzamide where the amide and chlorine groups are sterically overcrowded.[6] In (Iα), this severe twisting does not take place. In fact the primary amide group is twisted only 8° from the phenyl ring, while a minimum energy conformation is postulated to be at *ca.* 25°.[5a] We believe the unusual primary amide dihedral angles result from the structure having to accommodate additional hydrogen bonds involving the secondary amide substituents.

In (Iα), the secondary amide hydrogen forms an intramolecular hydrogen bond to the primary amide oxygen [N(2)-H(9) · · · O(1)]. In (Iβ) the same atoms are involved in a hydrogen bond, but now the bond is an intermolecular bond between screw-related molecules. A third intermolecular contact between the primary amide hydrogen and O(2) of the secondary amide occurs in (Iα and β) (in both cases between screw-related molecules). Stereoviews of (Iα and β) (Figure 4) illustrate these hydrogen-bonding modes.

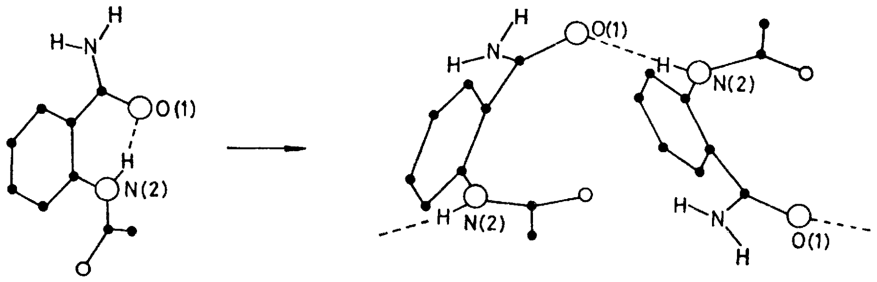
DISCUSSION

The thermal and spectroscopic studies of (Iα and β) indicate that a complex series of polymorphic transformations and chemical reactions are taking place during the conversion of (Iα or β) into (II), which accounts for the previously reported observations of irreproducible m.p. behaviour and i.r. spectra of *o*-acetamidobenzamide.[7-9] The d.s.c. curves in Figure 2 show the conversion of (Iα) into (Iβ) at A, the loss of (Iβ), and formation of a new phase at C (also at F and H), and then formation of impure (II) (D, G) consistent with the series of steps in Scheme 1. These transformations do not occur independently, so phase C in Figure 2 is probably a mixture of (Iβ), (III), and (II). Repeated cooling and reheating of (Iα), (Iβ), or (III) will eventually give pure (II), as shown by a d.s.c. curve in which the only transition is the melting of (II).

We have investigated the details of the structural changes involved in the first of these transformations, (Iα) to (Iβ). From the stereoviews of their respective unit cells (Figure 4), one can see that *i*-related dimers form between molecules on adjacent screw axes in both unit cells. In addition, an intermolecular hydrogen bond between O(2) and a primary amide hydrogen occurs along the screw axes in both structures. These interactions could remain intact during the solid-state transformation, while the molecules in (Iα) rotate about the *c*-axis to generate (Iβ). The *c*-axes are about the same length in the two structures as would be expected from this mechanism; the *a*-axis increases significantly as the molecular plane rotates out of the (100) plane, and the *b*-axis decreases significantly as the molecular planes approach (010), also consistent with the proposed mechanism. The most significant chemical difference between the two structures is the mode of formation of the hydrogen bond between the primary amide carbonyl and the secondary amide hydrogen [N(2)-H(9) · · · O(1)]. In (Iα) this hydrogen bond is intramolecular, whereas in (Iβ) it is intermolecular and forms a continuous hydrogen-bonded chain between screw-related molecules. Scheme 2 shows the conformational changes needed to effect this change in hydrogen bonding.



SCHEME 1



SCHEME 2

A mechanism in which only one hydrogen bond is broken and reformed is consistent with the d.s.c. data, which shows a facile solid-state transformation involving only 0.7 kcal mol^{-1} with no previous melt or resolidification of (Iα). We have as yet been unable to effect this transformation in a single crystal so we do not have direct confirmation of this mechanism.

Regardless of the actual mechanism taking place here, it is evident that hydrogen-bonding modes are important in the mechanism of disordering, or ' unpacking ', of the structure of (Iα) just as Leiserowitz and his co-workers have shown them to be important in the growth, or packing, of amide structures. For the same reasons that cyclic *i*-related hydrogen-bonded dimers may form preferentially when amides crystallize, this dimer interaction may be the last of the several hydrogen bonds present in a structure such as (Iα) to dissociate when a transformation occurs. We believe from preliminary structural analyses of (II), and of the proposed intermediate (III), that the cyclic dimer feature plays a significant role in the disordering mechanisms of the entire solid-state sequence from (Iα) to (II). We are continuing our investigation of the solid-state transformations and reactions in this sequence and have also begun studying the solid-state behaviour of other multifunctional amides which are derivatives of anthranilic acid.

We gratefully acknowledge the assistance of the Molecular Structure Corporation in solving the crystal structure of (Iβ), and of D. Markhoe and W. Conway, 3M Analytical Labs, for running the d.s.c., d.t.a., and t.g.a. measurements. We thank Dr. T. Lewis, 3M Central Research Laboratory, and Dr. W. Gleason, St. Catherine's College, for helpful discussions and encouragement.

[0/027 *Received*, *7th January*, 1980]

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