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Dimorphic Forms of 2-Amino-4-(*N*-methylanilino)-6-isopropenyl-*s*-triazine

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2-Amino-4-(*N*-methylanilino)-6-isopropenyl-*s*-triazine (AMIT) was prepared by the reaction of N^1-methyl-N^1-phenylbiguanide with methyl methacrylate, as has previously reported.[1] In this paper, it has been found that AMIT has dimorphic forms. In the case of the recrystallization of AMIT from methanol, two different crystals were obtained. The sample immediately crystallized was named AMIT-β, while that slowly crystallized was named AMIT-α. AMIT-β melted at 104°C and immediately solidified into a crystal that melted at 118°C. AMIT-α melted at 118°C. When the acetone solution of AMIT-α was poured into water, AMIT-β was precipitated. AMIT-α was also obtained by the crystallization of AMIT-β or an AMIT-α and β mixture from benzene. AMIT-α and β were easily changeable by crystallization by different procedures.

TABLE 1. ELEMENTARY ANALYSES AND NMR DATA OF AMIT

Sample	Elementary analyses C%	H%	N%	NMR data (DMSO-d_6, 35°C) (ppm)
AMIT-α	64.60	6.06	29.84	H_a, 5.40(q)
AMIT-β	64.81	6.19	29.67	H_b, 6.22(d)
				CH_3, 2.00(s)
Calcd for $C_{13}H_{15}N_5$	64.71	6.27	29.02	N–CH_3, 3.45(s)
				NH_2, 6.79(s)
				C_6H_5, 7.32(s)

The results of the elementary analyses and the NMR data of AMIT-α and β are shown in Table 1. The elementary analytical results were identical with the calculated value of AMIT. The NMR data in DMSO-d_6 were also identical with each other. The ultraviolet spectra of AMIT-α and β in ethanol, water, or cyclohexane were identical. From the above results, it was found that AMIT-α and β were the same compound.

The existence of two crystal forms has been confirmed by the entirely different X-ray powder diagrams for AMIT-α and β. Some absorptions of the infrared spectra of AMIT-α and β were different when the infrared spectra was measured in the crystal state in potassium bromide disks. The differences were shown in the absorptions of amino groups and isopropenyl groups. The N–H stretching absorptions were at 3325 (small), 3290, and 3190 cm^{-1} for AMIT-α, but they were at 3450, 3280, 3180 cm^{-1} for AMIT-β. The NH_2 bending absorptions of AMIT-α were at 1642 and 640 cm^{-1}, while that of AMIT-β were at 1620 and 655 cm^{-1}. The bending absorption of the isopropenyl group was at 940 cm^{-1} for AMIT-α and at 918 cm^{-1} for AMIT-β. The absorptions of the phenyl (760 and 695 cm^{-1}) and *s*-triazinyl (825 cm^{-1}) groups were identical with each other. From the above results, it was assumed that there was a different interaction between the proton of the amino group and the π electrons of the isopropenyl group of AMIT in crystals.

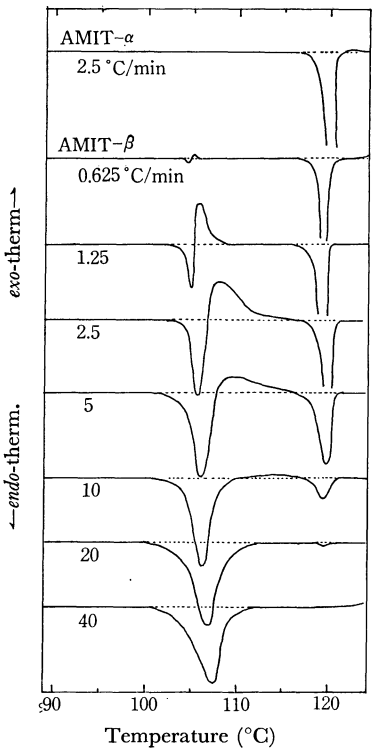

Fig. 1. DSC curves of AMIT-α and AMIT-β.

TABLE 2. ΔH OF AMIT-α AND β

Sample	Heating rate (°C/min)	ΔH_β	ΔH_{cr}	ΔH_α (kcal/mol)	$\Delta H_\beta'$
AMIT-α	2.6	—	—	6.6	—
AMIT-β	0.625	0.1	0.1	6.8	6.8
	1.25	2.8	2.5	6.9	7.2
	2.5	4.3	4.2	5.7	5.8
	5	6.0	2.6	3.4	6.8
	10	6.5	0.3	0.7	6.9
	20	6.4	—	0.1	6.5
	40	6.7	—	—	6.7

The thermal behavior of samples was examined by the technique of a differential scanning calorimeter (DSC). The results are shown in Fig. 1. AMIT-α showed only an endothermic peak at 118°C by fusion, and the heat of fusion of AMIT-α was 6.6 kcal/mol. On the other hand, AMIT-β showed two endothermic peaks, at 104 and 118°C, by fusion, and one exothermic peak between the two endothermic peaks. This exotherm was caused by crystallization. The heat of

1) Y. Yuki, T. Kakurai, and T. Noguchi, This Bulletin, **43**, 2123 (1970).

fusion at 104°C (ΔH_β), the heat of fusion at 118°C (ΔH_α) and the heat of crystallization (ΔH_{cr}) of AMIT-β are summed up in Table 2. These heats depended on the heating rate. ΔH_β was increased as the heating rate became faster. On the other hand, ΔH_α decreased as the heating rate became faster. ΔH_α was 6.8 kcal/mol at a heating rate of 0.625°C/min. This value was almost equal to the ΔH of AMIT-α. This is thought to be because the heat of fusion of AMIT-β is compensated for by the heat of crystallization. The theoretical heat of fusion of AMIT-β ($\Delta H_\beta'$) was obtained from Eq. (1):

$$\Delta H_\beta' = \Delta H_\beta + \Delta H_\alpha - \Delta H_{cr} \quad (1)$$

The values of $\Delta H_\beta'$ are also described in Table 2, and the mean value of $\Delta H_\beta'$ was 6.8 kcal/mol.

The infrared spectra of the sample that was heated at 115°C was identical with that of AMIT-α. From the above results, AMIT-β can be said to be the thermodynamically unstable crystal form compared with AMIT-α, and it can be seen that AMIT-β crystallizes after melting at 104°C into the stable form, AMIT-α.