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Enantiotropy of 2,4-Diamino-6-[2-(2-methyl-1-imidazolyl)ethyl]-1,3,5-triazine

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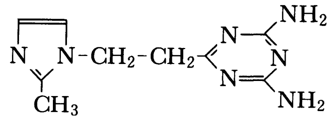
Synopsis. Measurements using elementary analysis, differential thermal analysis, IR spectroscopy, and X-ray diffractometry have revealed that the title triazine assumes two crystalline forms *α* and *β*. The conversion from *α* to *β* proceeds rapidly at 230 °C, whereas the reversal takes place slowly at 60 °C and 95% RH.

2,4-Diamino-6-[2-(2-methyl-1-imidazolyl)ethyl]-1,3,5-triazine (**1**) is widely used as a curing agent for epoxy resin, because it provides good electric and mechanical properties to cured resin.[1] Compound **1** is synthesized from 2-methylimidazole, acrylonitrile, and dicyanodiamide.[2] It consists of a triazine ring, which is π-defficient, and an imidazole ring, which is π-excessive:[3]



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Compound **1** is decomposed into 2,4-diamino-6-vinyl-1,3,5-triazine and 2-methylimidazole at elevated temperature.[4] This paper reports of differential thermal analyses (DTA) on **1** and **1** heat-treated at 230 °C for 25 min which detected different curves, their X-ray powder diffractions which also detected entirely different patterns, and DTA examination of chemical reactivities of **1** and heat-treated **1** to diglycidyl ether of bisphenol A (DGEBA).

Experimental

Materials. Compound **1** was purified before use by repeated recrystallization from methanol solution and dried at 60 °C for 8 h under vacuum. Its high-performance liquid chromatogram registered 99.9% purity. Heat treatment on **1** was carried out at 230 °C for 25 min in an oven (heat-treated **1**). Heat-treated **1** was treated under various conditions (samples *a, b,* and *c*). Pure DGEBA was kindly supplied from Yuka Shell Epoxy Co., Preliminary mixtures of **1** or heat-treated **1** with DGEBA were prepared at a temperature slightly higher than the melting point of DGEBA (46 °C) and mixed well at room temperature.

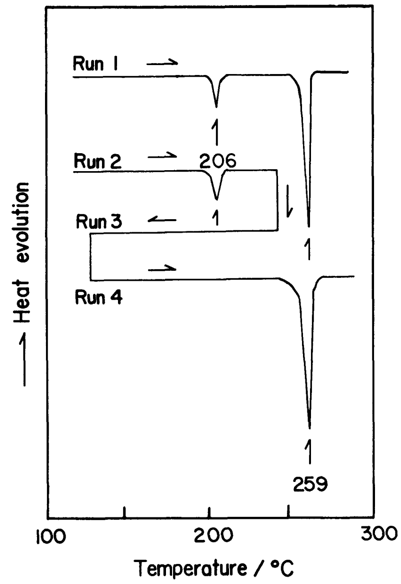


Fig. 1. DTA curves of 2,4-diamino-6-[2-(2-methyl-1-imidazolyl)ethyl]-1,3,5-triazine.

Apparatus and Precedures. IR spectra were taken with KBr pellets on a Hitachi 260-10 Spectrophotometer. A Shimadzu Thermal Analyzer DT-20B was used for DTA. In each run of DTA, 5 mg of sample was loaded and the same amount of Al_2O_3 was used as a reference. The temperature was raised from room temperature to 300 °C at a rate of 5 °C min^{-1}. The apparent activation energy of the reaction of **1** or heat-treated **1** with DGEBA was obtained by the Kissinger method[5] using heating rates ranging from 1 to 20 °C min^{-1}. X-Ray powder diffraction was conducted with a Rigaku X-ray powder diffractometer using graphite monochromatized Cu *Kα* radiation (λ=1.5405 Å).

Results and Discussion

Polymorphic Behavior of 1. The DTA curves of **1** are given in Fig. 1. A small endothermic peak appears at 206 °C and a sharp endothermic peak due to fusion

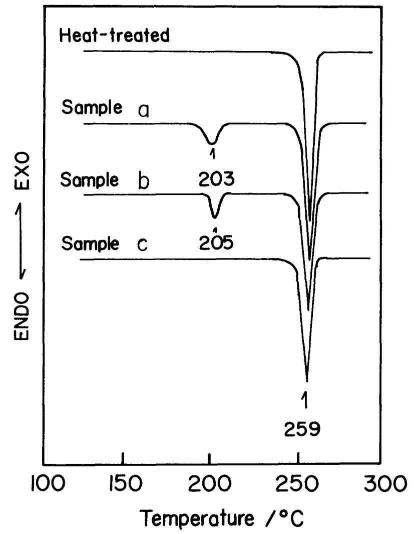


Fig. 2. DTA curves of 2,4-diamino-6-[2-(2-methyl-1-imidazolyl)ethyl]-1,3,5-triazine treated by various conditions after the heat treatment of 230 °C for 25 min. Heat-treated: heat-treated at 230 °C for 25 min.
Sample *a*; Kept at 60 °C, 95% RH for 48 h after the heat treatment. Sample *b*; Recrystallized from a methanol solution after the heat treatment. Sample *c*; Kept at room temperature for 30 d after the heat treatment.

Table 1. Elementary Analysis Data of **1** and Heat-Treated **1**

	C/%	H/%	N/%
Found for **1**	49.21	5.92	44.89
Found for heat-treated **1**	49.25	5.96	45.01
Calcd for $C_9H_{13}N_9$	49.30	5.98	44.72

Table 2. ^{1}H NMR of **1** and Mass Spectral Data of **1** and Heat-Treated **1**

^{1}H NMR (D_2O, 40 °C) (δ/ppm)	MS (75 eV, 140 °C) (m/z)
6.95 (d, H, J=1.5 Hz) 6.82 (d, H, J=1.5 Hz) 4.27 (t, 2H, J=6.8 Hz, $-\overset{\vert}{N}-\mathbf{CH_2}-CH_2-\!\!<$) 2.87 (t, 2H. J=6.8 Hz, $-\overset{\vert}{N}-CH_2-\mathbf{CH_2}-\!\!<$) 2.25 (s, 3H, $-CH_3$)	219(M^+), 204, 191 177, 149, 138, 125, 111, 109, 95, 82, 81

appears at 259 °C (run 1). The same heating process as run 1 was applied above the lower endothermic peak (run 2) and was followed by cooling down to room temperature (run 3). Subsequent heating gave no endothermic peak at 206 °C, but reproduced the sharp endothermic peak at 259 °C (run 4).

In order to interpret the above phenomena, **1** was heated at 230 °C for 25 min. The DTA curve (heat-treated **1** in Fig. 2) shows no endothermic peak at about 206 °C. On the other hand, sample *a* (equal to a heat-treated **1** which was kept at 60 °C and 95% RH for 48 h and dried at 60 °C for 8 h under vacuum) and sample *b* (equal to a heat-treated **1** which was dissolved and recrystallized from methanol solution and dried at 60 °C for 8 h under vacuum) gave a small endothermic peak at 203—205 °C in their DTA curves. The IR spectrum of sample *b* is identical with that of **1**. The small endothermic peak was absent in the DTA curve of sample *c* (equal to a heat-treated **1** which was kept at room temperature for 30 d).

The results of elementary analysis of **1** and heat-treated **1** were idential with the calculated value for $C_9H_{13}N_7$ as indicated in Table 1. In Table 2 are given the ^{1}H NMR data of **1** and the mass spectral data of **1** and heat-treated **1**, which are also identical with each other.

Part of the IR spectra of **1** and heat-treated **1** are given in Fig. 3. In Fig. 3, curve **A** represents the spectrum of **1**, which is essentially the same as those of samples *a* and *b*. Curve **B** represents the spectra of heat-treated **1** and sample *c*. The pronounced difference between curves **A** and **B** consists in the absorptions for the NH_2 stretching and bending. The NH_2 stretching bands appear at 3320 and 3100 cm^{-1} (curve **A**) and at 3475, 3320, and 3100 cm^{-1} (curve **B**). The absorption at 3475 cm^{-1} is possibility due to the stretching of NH_2 in free state.[6] The bending gives rise to the absorption at 1660 cm^{-1} in curve **A** and at 1630 and 1680 cm^{-1} in curve **B**.

Yuki et al. reported[7] an IR spectrum of 2-amino-4-(*N*-methyl-anilino)-6-isopropenyl-1,3,5-triazine (**2**) similar to that of **1** and attributed the difference in NH_2 absorption to different interactions between the proton of amino group and the π electron of isopropenyl group.

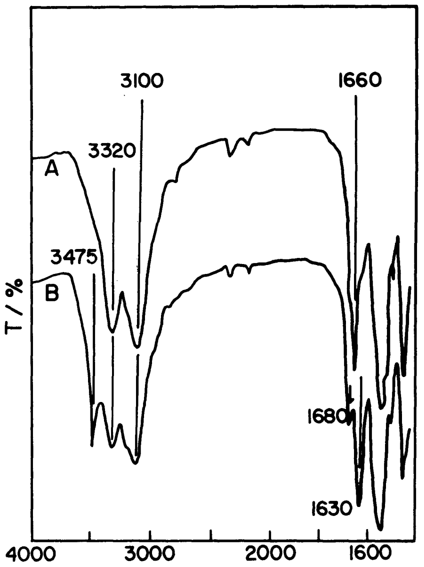


Fig. 3. IR Spectra of 2,4-diamino-6-[2-(2-methyl-1-imidazolyl)ethyl]-1,3,5-triazine (**A**) and heat-treated one at 230 °C for 25 min (**B**).

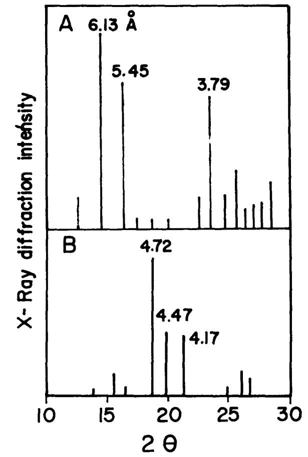


Fig. 4. X-Ray powder diffraction patterns of 2,4-diamino-6-[2-(2-methyl-1-imidazolyl)ethyl]-1,3,5-triazine (**A**) and heat-treated one at 230 °C for 25 min (**B**).

The results so far described are summarized with some inference as follows:

1. Compound **1** and heat-treated **1** give different DTA curves.
2. The measured elementary compositions of **1** and heat-treated **1** are the same as the calculated for $C_9H_{13}N_9$, and the mass spectral data of **1** and heat-treated **1** also are the same with each other.
3. The IR spectra of **1** and heat-treated **1** are different from each other in the absorptions due to NH_2 stretching and bending, suggesting different angles between the imidazole and triazine rings.

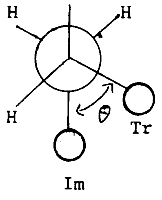
In order to investigate the existence of polymorphic forms of **1**, X-ray powder diffraction patterns of **1** and heat-treated **1** were examined. Both the patterns are entirely different as shown in Fig. 4. A very strong and two strong peaks corresponding to the spacings of 6.13, 5.45, and 3.79 Å, respectively, are observed for **1**, whereas a strong and two medium strong peaks corresponding to the spacings of 4.72, 4.47, and 4.17 Å, respectively, for heat-treated **1**. Samples *a* and *b* gave diffraction patterns similar to **1**, whereas sample *c* gave patterns to similar heat-treated **1**. We refer to the former as the α-form and the latter as the β-form.

Polymorphic phenomenon of triazine compound was previously reported with reference to dimorphic forms of **2** by Yuki et al.[7] Compound **2**, recrystallized from methanol solution, had two different crystalline forms. They referred to the **2** immediately crystallized from methanol solution as the α-form and the **2** slowly crystallized from methanol solution as the β-form. The β-form melts at 104 °C and immediately solidifies into a crystal that melts at 118 °C, while the α-form melts at 118 °C. The X-ray powder diffraction patterns of the α- and β-forms are entirely different. The IR spectrum of **2** that was heated at 115 °C is identical with that of the α-form. From the above results, they concluded that the α-form is a thermodynamically less stable crystal form than the β-form.

The polymorphic phenomena of organic crystals are classified into monotropic and enantiotropic.[8] Compound **2** is polymerized immediately after fusion of its stable form, but **1** is changed gradually from its crystalline form when heated under high humidity as folows:

$$\alpha \underset{60\,^{\circ}\mathrm{C},\ 95\%\ \mathrm{RH},\ 48\ \mathrm{h}}{\overset{230\,^{\circ}\mathrm{C},\ 25\ \mathrm{min}}{\rightleftarrows}} \beta$$

The α-form is transformed into the β-form by beeing heated at 230 °C for 25 min, and the β-form into the α-form by beeing kept at 60 °C under 95% RH for 48 h. Since the α- and β-forms gave exactly the same elementary compositions and mass spectra but different DTA curves, IR spectra, and X-ray diffraction patterns, the α- and β-forms may be considered to be conformationally isomeric with respect to the imidazole and triazine rings connected by the ethylene bridge. On the basis of the wavenumber 3475 $\mathrm{cm^{-1}}$ at which the absorption due to the stretching of freestate $\mathrm{NH_2}$ appears,[6] the α- and β-forms are taken to be antiperiplaner to each other with different angles θ between the imidazole and triazine rings connected by the ethylene bridge. The conformational isomeric situation is illustrated diagramatically below:



Their conformations are supported by chemical reactivities of **1** and heat-treated **1** to DGEBA described in the following section.

Chemical Reactivity of 1 to DGEBA. Compound **1** is widely used as a curing agent for epoxy resin as mentioned before. The reaction of imidazole compound with epoxy resin consists of two steps.[9] The first step is the addition to epoxide of group NH at the 1-position of the imidazole ring. The second step is the ring opening of epoxide by the catalyst produced in the first step. Since in **1** the hydrogen at the 1-position of the imidazole ring is already substituted, the reaction of **1** or heat-treated **1** with DGEBA essentially starts with the second step. The chemical reactivity of **1** and heat-treated **1** to DGEBA was studied by measuring activation energies of the reaction. Apparent activation energies were obtained by the Kissinger equation:[5]

$$\frac{\mathrm{d}(\ln \phi/T_{\mathrm{m}}^{2})}{\mathrm{d}(1/T_{\mathrm{m}})} = -\frac{E}{R} \tag{1}$$

where ϕ is the heating rate in $^{\circ}\mathrm{C\,min^{-1}}$, T_{m} is the absolute temperature of the exothermic peak in DTA curves, and R is the gas constant. The exothermic temperature was measured by changing the heating rate from 1 to 20 $^{\circ}\mathrm{C\,min^{-1}}$. The activation energies calculated according to Eq. 1 are 38.3 $\mathrm{kcal\,mol^{-1}}$ for the mixture of **1** and DGEBA and 25.3 $\mathrm{kcal\,mol^{-1}}$ for that of heat-treated **1** and DGEBA. It is considered that the difference in activation energy results from the difference in the crystalline forms of **1** and heat-treated **1**.

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