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Conformational Analysis of Aminovinylpyrazine by Semiempirical Molecular Orbital Calculations

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ABSTRACT

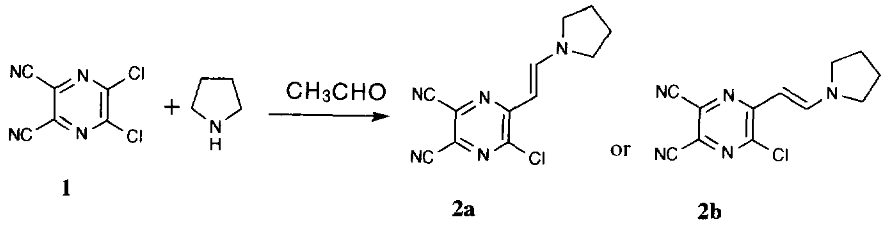
*A conformational analysis of aminovinylpyrazine (**2**) by semiempirical molecular orbital calculations and ^1H-NMR analysis has been performed. The free rotation of the bond between the vinyl group and the pyrrolidine ring was observed at 130°C. Molecular orbital calculations revealed that compound **2** has a planar structure with intramolecular charge-transfer character and the rotational conformer should be included at higher temperature. Copyright © 1997 Elsevier Science Ltd*

Keywords: Conformational analysis, aminovinylpyrazine, MO calculation, MOPAC PM3, Arrhenius plot.

INTRODUCTION

Dicyanopyrazine is of interest as a potential intermediate for industrial uses and can be produced from diaminomaleonitrile (DAMN) as a tetramer of hydrogen cyanide. The chemistry of DAMN has been known for a long time and many patents[1,2] have been published. Herbicidal properties of a series of 2,3-dicyanopyrazines have been studied by Nakamura and co-workers.[3,4]

Recently, Hodagaya patented the usefulness of diaminodicyanopyrazine derivatives as agricultural fungicides.[5] We recently re-evaluated DAMN as a



Scheme 1.

TABLE 1
Heat of Formation of the Optimized Structure for **2a** and **2b**

Conformer	*Heat of formation (kcal/mol)*	
	PM3[a]	*AM1*[b]
2a	114.26	127.76
2b	116.92	132.14

[a]Calculated with PM3.
[b]Calculated with AM1.

raw material for functional dye materials, and some papers related to 2,3-dichloro-5,6-dicyanopyrazine have been published. The reaction of 2,3-dichloro-5,6-dicyanopyrazine (**1**) with amines[6] and enamine[7] afforded the corresponding amino- and vinylamino derivatives, which were evaluated as fluorescent dyes and nonlinear optical materials. New syntheses of pyrazinostyryl fluorescent dyes have been synthesized recently from DAMN.[8] The reaction of **1** with pyrrolidine in the presence of acetaldehyde gave the corresponding aminovinylpyrazine **2** in low yield (Scheme 1).[6] It is proposed that the enamine was initially synthesized in the reaction and reacted with **1** to give **2**.

In this paper, we will report a conformational analysis of aminovinylpyrazine **2** by semiempirical molecular orbital calculations and ^{1}H-NMR analysis.

RESULTS AND DISCUSSION

There are two rotative single bonds in compound **2**. One is the bond between the vinyl group and pyrazine linkage, the other is the bond between the vinyl group and the pyrrolidine ring. Two conformers can be pictured by the rotation of the former (Scheme 1). At first, we evaluate which conformer is more stable. The heats of formation of the optimized structures for **2a** and **2b** are shown in Table 1. Both AM1 and PM3 calculations indicated that **2a** is

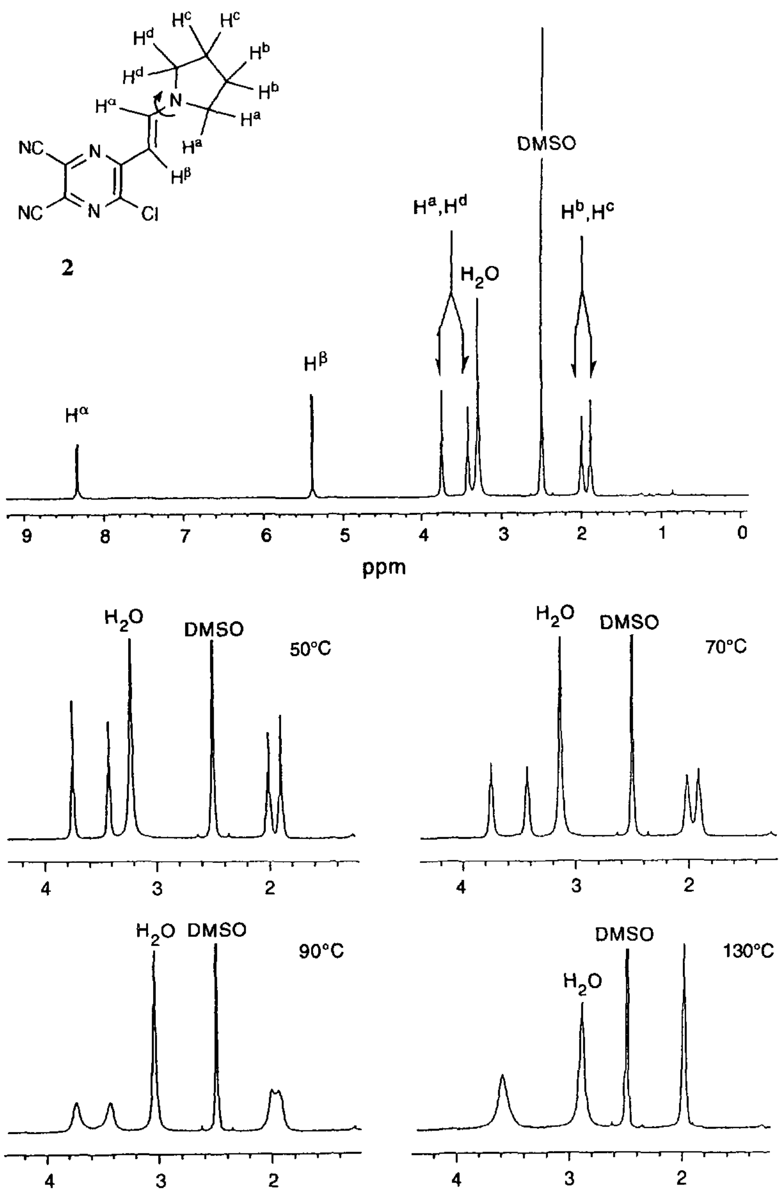


Fig. 1. ^{1}H-NMR (500 MHz) spectrum of **2** at room temperature (a), and the temperature dependence (b).

more stable than **2b**. We will consider **2a** in this report, and discuss the rotation of the bond between the vinyl group and the pyrrolidine ring. The ^{1}H-NMR spectrum (500 MHz) of **2** at room temperature is shown in Fig. 1. The H^α was observed at 8.3 as a doublet of *trans*-coupling ($J = 11.9$ Hz) with

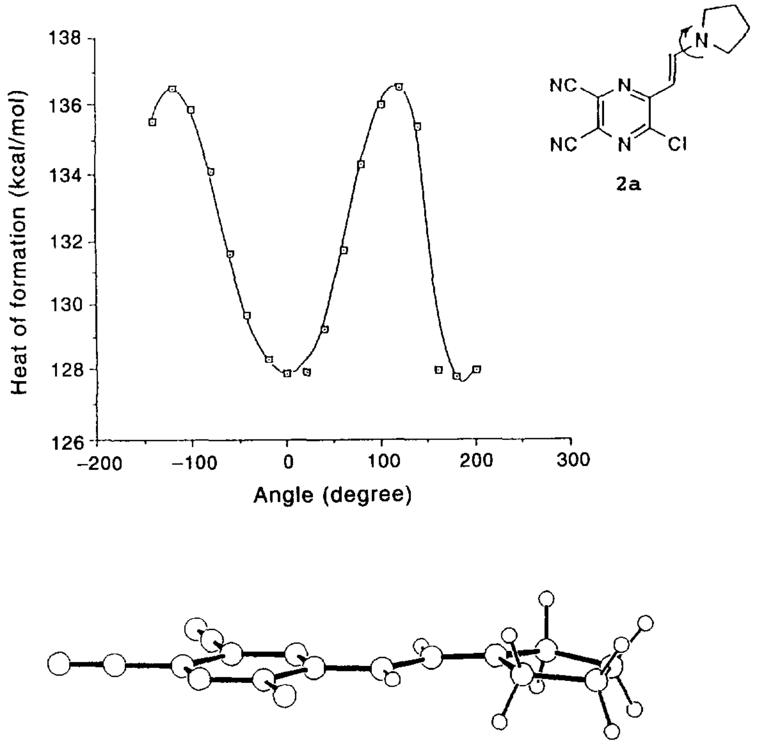


Fig. 2. The calculated energy profile of **2a** by MOPAC version 6 with AM1 (top) and the most stable conformation of **2a** (bottom).

H^{β} which was observed at 5.4 as a doublet. The large difference in the chemical shift of H^{α} and H^{β} is attributed to the ring current effect and to the electron withdrawing effect of the dicyanopyrazine ring. The H^{a} and H^{d} protons were observed at different chemical shifts of 3.4 and 3.7 ppm as a triplet, respectively. The H^{b} and H^{c} were also observed at upper fields of 1.9 and 2.0 as a quintet, respectively.

The temperature dependence of the ^{1}H-NMR of the pyrrolidine ring protons is shown in Fig. 1b. During the increase of temperature from 50 to 90°C, splittings of each signal become ambiguous, and at 130°C, the split signals of H^{a} and H^{d}, and of H^{b} and H^{c}, were completely overlapped, and only one signal for each couple were observed. Free rotation of the bond between the vinyl group and the pyrrolidine ring was observed around 130°C. Conformational analysis was of interest with respect to the structured change of **2**, and was conducted by means of the MOPAC version 6 with AM1 and PM3 parameter sets. The calculated heats of formation were plotted against a dihedral angle between the pyrrolidine ring and the vinyl

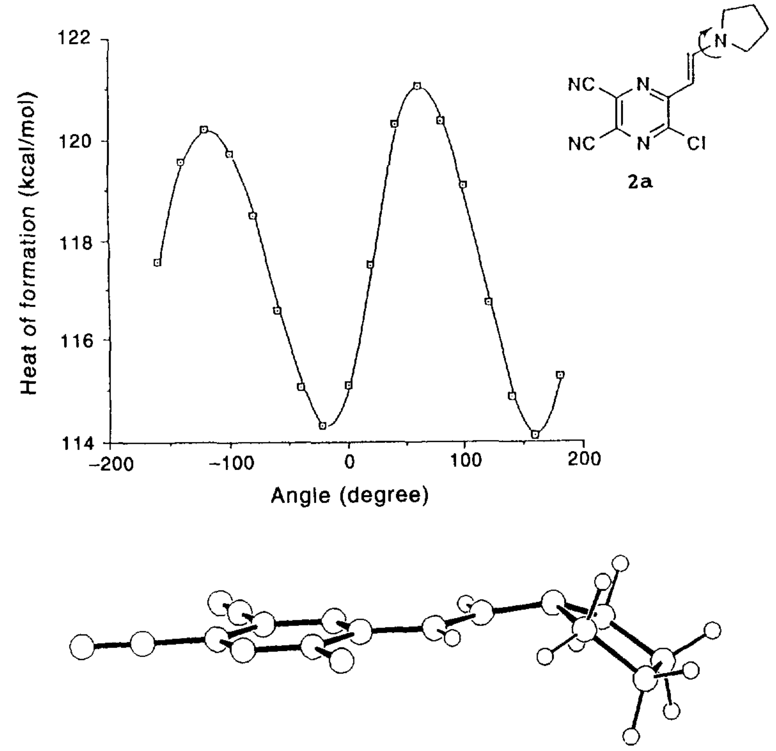


Fig. 3. The calculated energy profile of **2a** by MOPAC version 6 with PM3 (top) and the most stable conformation of **2a** (bottom).

group. The results of AM1 are shown in Fig. 2 (top). The most stable conformer of **2a** was presented by the ORTEP structure in Fig. 2 (bottom), in which a planar π-system through the nitrogen atom of pyrrolidine ring to the pyrazine ring was observed. The intramolecular charge-transfer chromophoric system of **2a** was confirmed by the PPP method. The most stable conformer was observed at 0 and 180°. On the other hand, the PM3 calculation also gave similar figures, as shown in Fig. 3 (top), but some displacement of the pyrrolidine ring against the π-plane was observed in the most stable conformer (Fig. 3, bottom).

The Arrhenius plot of **2** was obtained from the ^{1}H-NMR spectra, which is shown in Fig. 4. The heat of activation was obtained from the slope and determined to be 8.0 kcal/mol, a value which was well reproduced by the MOPAC calculations of 8.7 kcal/mol by the AM1 and 6.8 kcal/mol by PM3 method, respectively. From these results, it was found that compound **2** has a planar structure with intramolecular charge-transfer character in the π-system, but has rotational conformer at higher temperature.

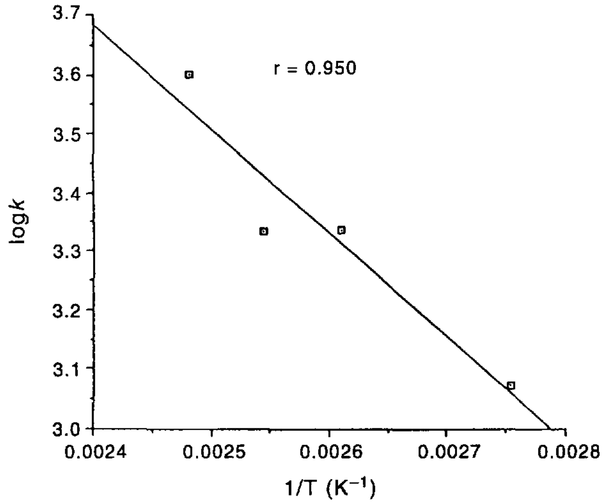


Fig. 4. Arrhenius plots of **2**.

CALCULATIONS AND EXPERIMENTAL

Geometry optimizations of the pyrazine **2** were performed with the MOPAC 6.01 program[9] on the DEC3000 at Osaka Prefectural Industrial Technology Research Institute. The parameter sets of AM1 and PM3 were used with the keyword PRECISE. The ^{1}H-NMR spectra of **2** were taken on a JEOL ALPHA-500 (500 MHz) spectrometers.

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REFERENCES

1. Dow Chemical Co., *US Patent* 3, 879, 394 (1975).
2. Dow Chemical Co., *US Patent* 4, 199, 581 (1978).
3. Nakamura, A., Ataka, T., Segawa, H., Takeuchi, Y. & Takematsu, T., *Agric. Biol. Chem.*, **47** (1983), 1555 and 1561.
4. Nakamura, A., Ikeda, O., Segawa, H., Takeuchi, Y. & Takematsu, T., *Agric. Biol. Chem.*, **47** (1983) 2923.
5. Kawada, H. *et al.*, Hodogaya Chemicals, EP 0,308,895 (1989).

6. Hou, D. & Matsuoka, M., *Dyes and Pigments*, **22** (1993) 57.
7. Hou, D., Oshida, A. & Matsuoka, A., *J. Heterocyclic Chem.*, **30** (1993) 1571.
8. Jaung, J. Y., Matsuoka, M. & Fukunishi, K., *Dyes and Pigments*, **31** (1996) 141.
9. MOPAC version 6, Stewart, J. J. P. QCPE #455; Revised as Version 6.01 by Hirano, T., *JCPE Newsletter*, **2** (1991) 26.