Tetrahedron Letters, Vol.31, No.11, pp 1605-1608, 1990
Printed in Great Britain

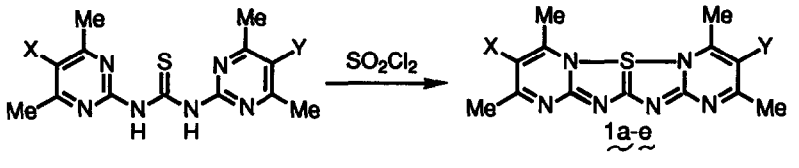
0040-4039/90 $3.00 + .00
Pergamon Press plc

RESTRICTED ROTATION OF PYRIMIDINE RING IN SYMMETRICAL 10-S-3 SULFURANES: EVALUATION OF HYPERVALENT N-S-N BOND ENERGY

Katsuo OHKATA, Minoru OHSUGI, Tetsuo KUWAKI, Kazuhiro YAMAMOTO, and Kin-ya AKIBA*
Department of Chemistry, Faculty of Science, Hiroshima University
Higashisenda-machi, Nakaku, Hiroshima 730, Japan

Abstract: Symmetrical 10-S-3 sulfuranes (1a-c) fused with two pyrimidine rings and their unsymmetrically substituted ones (1d,e) were synthesized by oxidation of the corresponding thioureas. Substituent effect on the kinetic data of the restricted rotation was explained in terms of the balance of electron-withdrawing ability of the ligand in the N-S-N hypervalent bond.

In the last decade, several examples of ring-transformation ("bond switching") via hypervalent sulfurane (10-S-3) have been investigated.[1] Especially, degenerate rearrangements of heterocycles, which took place via 10-S-3 sulfuranes were also observed. In a preceding communication, we showed that restricted rotation of pyrimidine ring in unsymmetrical cyclic 10-S-3 sulfuranes fused with pyridine and pyrimidine rings could reflect hypervalent N-S-N bond energy of trithiapentalene analogues.[2] We now report synthesis and ^{1}H NMR spectral behaviors of symmetrical 10-S-3 sulfurane, bis(4,6-dimethylpyrimido)[1,2-a:2',1'-f]-1,3,4,6,6aλ^4-tetraza-thiapentalene (1a) and its halogenated derivatives (1b-e).



	X	Y
1a	H	H
1b	Cl	Cl
1c	Br	Br
1d	Cl	H
1e	Br	H

Each compound (1a-e, mp > 300 °C) was prepared from the corresponding thiourea by oxidation with sulfuryl chloride or N-bromosuccinimide in dichloromethane solution at room temperature.[3] ^{1}H NMR spectral data are

summarized in Table 1. In the NMR spectra at 0 °C ($CDCl_3$), 1a shows a singlet at δ 2.53 and a doublet at δ 2.66 (integral ratio 1 : 1 separated by 10.3 Hz at 90 MHz) for the two nonequivalent methyls of the two pyrimidine rings together with a quartet at δ 6.62 with J = 0.66 Hz for the pyrimidine proton. Compounds (1b,c) show two singlets for methyl groups with slightly lowered chemical shifts. On the other hand, ^{1}H NMR spectra of monohalogenated substrates (1d,e) show four signals corresponding to each methyl group. One of them coupled with the pyrimidine ring proton appears as a clear doublet at δ 2.76 with J = 0.44 Hz (1e). According to the coupling with heterocyclic proton (Y = H) and coalescence temperature of each pair of methyl signals, the doublet signal and its counterpart were assigned to the methyl groups of unhalogenated pyrimidine ring.

Table 1. ^{1}H NMR Spectral Data of 1a-e at 0 °C in $CDCl_3$.

Compd.	^{1}H NMR (δ)		
	Methyl		Heterocyclic (X, Y)
1a	2.53 (s, 6H)	2.66 (d, J=0.66 Hz, 6H)	6.62 (q, J=0.66 Hz, 2H)
1b	2.68 (s, 6H)	2.81 (s, 6H)	
1c	2.74 (s, 6H)	2.86 (s, 6H)	
1d H-side	2.56 (s, 3H)		6.63 (q, J=0.44 Hz, 1H)
Cl-side	2.68 (s, 3H)		
1e H-side	2.57 (s, 3H)	2.76 (d, J=0.44 Hz, 3H)	6.62 (q, J=0.44 Hz, 1H)
Br-side	2.69 (s, 3H)	2.79 (s, 3H)	

The two methyl signals of 1a, 1b, and 1c coalesced at 45, 47, 48 °C, respectively (in CD_2Cl_2). The exchange rate at the coalescence temperature was calculated by using the Gutowsky-Holm approximation ($k_c = \pi\Delta\nu/\sqrt{2}$) and the $\Delta G_c^{\neq}$ value by using the Eyring equation, assuming a transmission coefficient of unity.[4] The $\Delta G_c^{\neq}$ values for the process of 1a-c were the same each other within the experimental error. The barrier for the coalescence of the exchange was also calculated by a total line-shape analysis. Table 2 summarized the kinetic data. There were observed two coalescence processes in monohalogenated 10-S-3 sulfuranes (1d,e). The coalescence at 21, 24 °C in 1d,e was assigned to the exchange process of the methyl groups in 5-halogenated pyrimidine ring and the other coalescence at 74, 75 °C was assigned to that in nonhalogenated pyrimidine ring on the basis of spectral assignment of each pair of signals as described above.

Table 2. Kinetic Data for Restricted Rotation of 1a-e in CD_2Cl_2

Compound		Tc (°C)	k_c (sec^{-1})	$\Delta G_c^{\neq}$ (kcal/mol)	$\Delta G_{298}^{\neq}$ (kcal/mol)	$\Delta H_{298}^{\neq}$ (kcal/mol)	$\Delta S_{298}^{\neq}$ (eu)
1a		45	22.9	16.7	16.9	15.9±1.1	-2.4±3.4
1b		47	26.6	16.7	16.7	16.9±0.5	0.5±1.6
1c		48	24.4	16.8	16.8	16.7±0.6	-0.3±1.8
1d	H-Side	74	27.8	18.1			
	Cl-Side	21	21.1	15.4	15.5	15.1±0.6	-1.4±1.9
1e	H-Side	75	26.6	18.2	18.3	18.8±0.3	1.8±1.0
	Br-Side	24	18.9	15.6	15.5	16.1±0.3	2.2±0.9

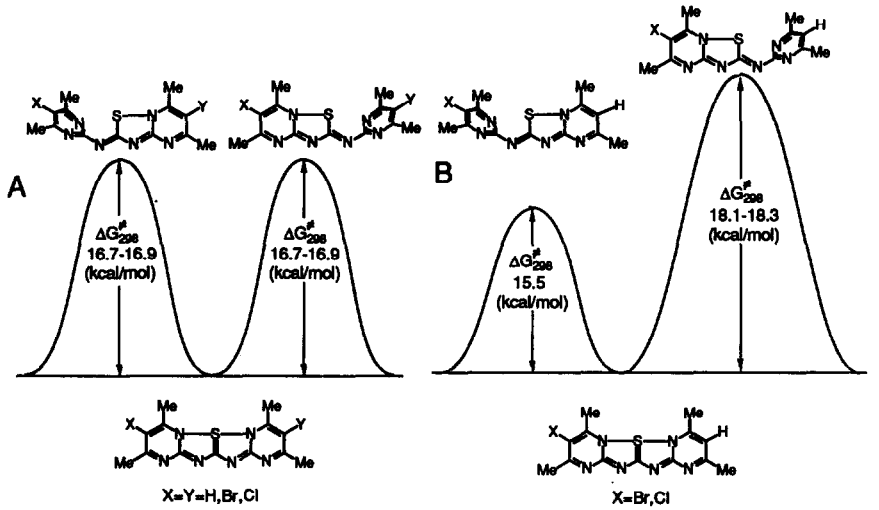
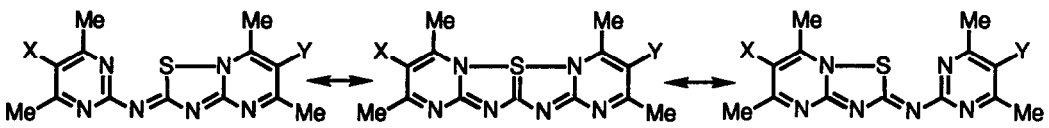


Figure 1. Schematic potential energy diagram for the rotation of pyrimidine ring in 1a-c (A) and 1d,e (B).

The coalescence process can be explained by the restricted rotation of one of pyrimidine rings in the 10-S-3 sulfurane as illustrated in Figure 1. The rotational potential curve (A) of 1a-c is understandable in terms of degenerate process in which the left and right barriers are the same each other. On the other hand, the rotational barrieres (B) in 1d,e are different between each side. The rotation of the halogenated pyrimidine ring is faster than that of nonhalogenated ring in the monohalogenated substrate (1d,e) at the same temperature. The results can be attributed to the balance of the electron-withdrawing ability between both nitrogens in the hypervalent N-S-N bond. These can be visualized by difference of

contribution of resonance structures (Scheme 1). As the electron-withdrawing property of halogenated ring increases compared with the other nonhalogenated one, the contribution of resonance structure (1-i; X = Cl, Br, and Y = H) will increase relatively and therefore the S-N bond in halogenated pyrimidine side is weakened. In contrast, the S-N bond of the other side is strengthened. It is noticable that the average of both rotational barriers ($\Delta G^{\ddagger}$) is almost equal to that of the symmetrical system (1a-c). These facts imply that the sulfur atom in 1d,e is slightly deviated away from the center of the two nitrogen atoms to the unhalogenated ring in the N-S-N hypervalent bond while total length of the hypervalent N-S-N bond is retained almost constant due to considerable rigidity of the tridentate ligand on the sulfur atom.

Scheme 1



References and Notes

1) (a) K-y. Akiba, T. Kobayashi, S. Arai, J. Am. Chem. Soc., 101, 5857 (1979). (b) K-y. Akiba, A. Noda, K. Ohkata, Phosphorus and Sulfur, 16, 111 (1983). (c) Y. Yamamoto, K-y. Akiba, J. Am. Chem. Soc., 106, 2713 (1984). (d) K-y. Akiba, K. Kashiwagi, Y. Ohyama, Y. Yamamoto, K. Ohkata, J. Am. Chem. Soc., 107, 2721 (1985).

2) K-y. Akiba, M. Ohsugi, H. Iwasaki, K. Ohkata, J. Am. Chem. Soc., 110, 5576 (1988).

3) (a) Analytical and spectral data for all new compounds were fully compatible with the given assignment. (b) On the basis of the UV and the other spectral features, 1a-e are considered to be planar.[2] (c) UV, λ_{max} (ε_{max}, $CHCl_3$) 1a; 335 nm (31500): 1b; 345 nm (33600): 1d; 340 nm (26900).

4) H. S. Gutowsky, C. H. Holm, J. Chem. Phys., 25, 1228 (1956). G. Binsch, Top. Stereochem., 3, 97 (1968).

5) Partial support of this work was provided by a grant under the Monbusho International Scientific Research Program (Nos. 01540427 and 01648001) administered by the Ministry of Education, Science and Culture of Japanese Government.

(Received in Japan 16 January 1990)