Barrier to Internal Rotation around the Isopropyl-Nitrogen Bond of Some *N,N*-Diisopropyl-1,3-dithia- and 1,3-diselenacycloalkan-2-iminium Salts, $[\overline{X(CH_2)_nXCN(i\text{-}Pr)_2}]^+Y^-$ (X=S, Se; Y=Br, PF_6; *n*=2,3)

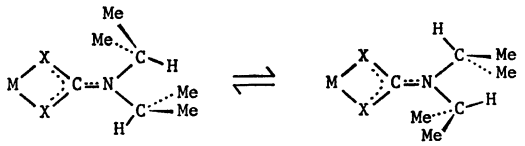
Yu-ichi TAKEDA, Tsuneo MATSUDA, and Toshio TANAKA

Department of Applied Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka 565

(Received July 4, 1977)

Activation parameters for rotation around the isopropyl-nitrogen bond of the title compounds were determined by the line shape analysis of ^1H NMR spectra. The E_a values lie in the ranges of 58—60 kJ/mol for X=S and 52—54 kJ/mol for X=Se. The activation parameters are little influenced by the ring size of the 1,3-diheteracycloalkane moiety and the counter anions.

Internal rotation around the isopropyl-nitrogen bond in metal complexes of diisopropyldichalcogenocarbamate is well known to cause interconversion between two stable equivalent rotamers as follows.[1-3]



X=S, Se

The barriers (E_a) to rotation of this kind have been reported for some metal complexes of diisopropyldithiocarbamate (dtc) and diisopropyldiselenocarbamate (dsc). The E_a values obtained so far, however, are rather scattered; $Ni(dtc)_2$, 19;[1] $Co(dtc)_3$, 21;[1] $Ti(dtc)_nCl_{4-n}$, 42.3 for n=2 and 41.0 for n=3, 4;[2] $R_2Sn(dtc)_2$, 76.6 for R=Cl and 68.6 for R=Me;[3] and $R_2Sn(dsc)_2$, 69.0 for R=Cl and 58.2 for R=Me[3] (the values in kJ/mol). The values for the Ni(II) and Co(III) complexes were obtained by line shape analysis of the methine proton signal, and those for the other complexes by the same analysis of the isopropyl-methyl proton signal. A similar interconversion between two equivalent rotamers has been proposed for (diisopropylamino)bis(methylthio)methylium perchlorate, $[(MeS)_2CN(i\text{-}Pr)_2]^+ClO_4^-$, only $\Delta G^{\neq}$ value being obtained.[4]

This paper reports the results of line shape analysis of the isopropyl-methyl proton signal of *N,N*-diisopropyl-1,3-dithia- and 1,3-diselenacycloalkan-2-iminium bromides and hexafluorophosphates, $[\overline{X(CH_2)_nXCN(i\text{-}Pr)_2}]^+Y^-$ (X=S, Se; Y=Br, PF_6; n=2, 3). The purpose of this work is to elucidate both effects of the hetero atoms in the 1,3-dichalcogenacycloalkane ring and the ring size on the activation parameters for rotation around the isopropyl-nitrogen bond.

Experimental

N,N-Diisopropyl-1,3,-dithiacyclohexane- and -cyclopentan-2-iminium bromides and their diselena analogs, $[\overline{X(CH_2)_nXCN(i\text{-}Pr)_2}]^+Br^-$ (n=3, X=S (**1a**); n=2, X=S (**2a**); n=3, X=Se (**3a**); n=2, X=Se (**4**)), were prepared by the reaction of 1,3-dibromopropane or 1,2-dibromoethane with Na(dtc) or $Me_2Sn(dsc)_2$ according to the method described for the *N,N*-dimethyl derivatives.[5] The corresponding hexafluorophosphates, $[\overline{X(CH_2)_nXCN(i\text{-}Pr)_2}]^+PF_6^-$ (n=3, X=S (**1b**); n=2, X=S (**2b**); n=3, X=Se (**3b**)), were obtained by the addition of an ethanol solution of NH_4PF_6 to the bromide salts in ethanol.

All the compounds were recrystallized from a mixture of CH_2Cl_2 and petroleum ether. The elemental analysis and properties are summarized in Table 1.

Measurement of ^1H NMR spectra in dichloromethane (0.01—0.1 M) and line shape analysis were carried out as described previously.[3] The ^1H chemical shift data of **1a**—**3a**, **4**, and **1b**—**3b** are given in Table 2.

Results and Discussion

Figure 1a depicts variable temperature ^1H NMR spectra of **1a** in dichloromethane. At room temperature **1a** exhibits a doublet signal due to the isopropyl-methyl

Table 1. Properties and analytical data of $[\overline{X(CH_2)_nXCN(i\text{-}Pr)_2}]^+Y^-$

Compound	X	Y	*n*	Mp, °C	Found %			Calcd %			*M.W.*[a]	
					C	H	N	C	H	N	Found	Calcd
1a	S	Br	3	176—177	39.83	6.82	4.71	40.26	6.76	4.70	295	298
2a	S	Br	2	189—191	37.68	6.50	4.92	38.03	6.38	4.93	272	284
3a	Se	Br	3	152—153	30.41	5.09	3.51	30.63	5.14	3.57	394	392
4	Se	Br	2	170—172	28.41	4.74	3.65	28.59	4.80	3.70	386	378
1b	S	PF_6	3	194—195	26.37	4.54	3.17	26.27	4.51	3.06	368	363
2b	S	PF_6	2	196—198	31.64	5.39	4.00	31.44	5.19	4.01	377	349
3b	Se	PF_6	3	200—203	26.73	4.54	3.17	26.27	4.41	3.06	423	457

a) Measured in CH_2Cl_2 at 25 °C by vapor pressure osmometry.

Table 2. Proton chemical shifts (δ) in CH_2Cl_2, 0.05 M

Compound	$\delta(CH_3)$[a]	$\delta(C\text{-}CH_2\text{-}C)$[b]	$\delta(S\text{-}CH_2)$[b]
1a	1.47, 1.67	2.50	3.48
2a	1.48, 1.58	—	4.18
3a	1.47, 1.67	2.49	3.49
4	1.49, 1.60	—	4.31
1b	1.44, 1.64	2.43	3.35
2b	1.48, 1.57	—	3.95
3b	1.48, 1.68	2.45	3.39

a) At −30 °C, $J(CH_3\text{-}CH)=7.2\pm0.2$ Hz. b) At room temperature.

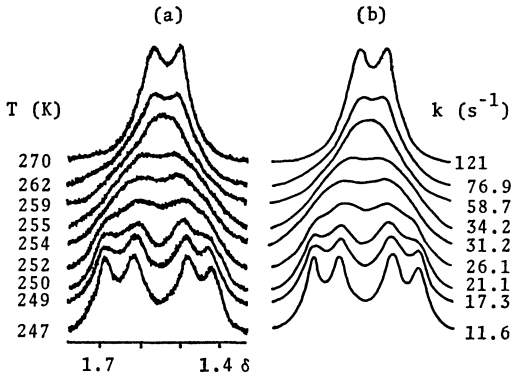
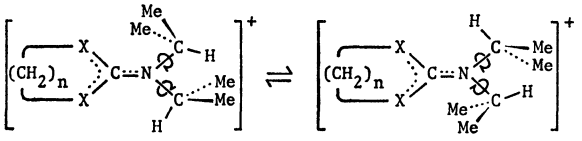


Fig. 1. Observed (a) and calculated (b) spectra of the isopropyl-methyl protons of $[\overline{S(CH_2)_3SCN(i\text{-}Pr)_2}]^+Br^-$.

protons (not shown in Fig. 1a). With fall in temperature, the signal coalesces into a broad one, splitting into two broad signals at about −18 °C. On further fall in temperature, the methyl protons appear as two doublets with identical intensities. A similar temperature dependence was also observed in the ^1H NMR spectra of all the other compounds. The spectra show no concentration dependence for solutions in the range 0.1—0.01 M. The spectral patterns of all the compounds in the range from room temperature to −30 °C are very similar to those of some diisopropyldithiocarbamato and -diselenocarbamato complexes of tin(IV), $R_2Sn(dtc)_2$ and $R_2Sn(dsc)_2$ (R=Me and Cl).[3] It is therefore suggested that the rotation around the isopropyl-nitrogen bond is restricted at relatively low temperatures, while that near room temperature occurs rapidly on the NMR time scale, resulting in interconversion between two identical rotamers as shown below.



X=S, Se; n=3, 2

The rate constants of the interconversion, k, were determined by line shape analysis of the isopropyl-methyl signal. Figure 1 shows an example of the best fits between the observed and calculated spectra of **1a**. The plots of ln k *vs.* $1/T$ and ln (k/T) *vs.* $1/T$ of **1a**, **2a**, **3a**, and **4** are given in Figs. 2 and 3 respectively, from

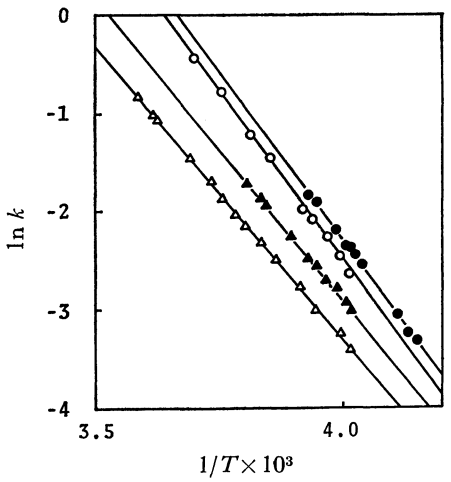


Fig. 2. Arrhenius plots for exchange of the isopropyl-methyl group in $[\overline{X(CH_2)_nXCN(i\text{-}Pr)_2}]^+Br^-$: X=S, n=3 (○); X=S, n=2 (●); X=Se, n=3 (△); X=Se, n=2 (▲).

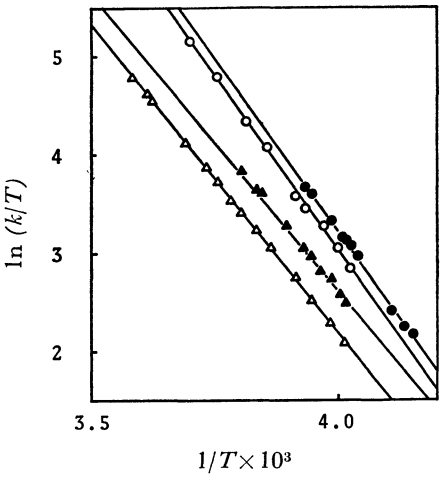


Fig. 3. Eyring plots for exchange of the isopropyl-methyl group in $[\overline{X(CH_2)_nXCN(i\text{-}Pr)_2}]^+Br^-$: X=S, n=3 (○); X=S, n=2 (●); X=Se, n=3 (△); X=Se, n=2 (▲).

Table 3. Thermodynamic data[a] for internal rotation around the isopropyl-nitrogen bond

Compound	E_a (kJ/mol)	ΔH^* (kJ/mol)	ΔS^* (J/(K mol))	ΔG^*_{298} (kJ/mol)
1a	59.9±1.7	57.7±1.7	12.4±6.6	54.0±2.6
2a	59.3±1.8	57.3±1.8	12.4±7.5	53.6±2.9
3a	52.2±0.5	50.0±0.5	−25.3±2.1	57.5±0.7
4	53.8±1.4	51.6±1.4	−15.3±5.5	56.2±2.2
1b	58.8±1.3	56.7±1.3	6.3±5.0	54.8±2.0
2b	58.7±2.4	56.6±2.4	7.8±9.8	54.3±3.8
3b	52.1±0.4	49.9±0.4	−27.5±1.7	58.1±0.7

a) Errors were estimated at the 95% confidence level.

which the Arrhenius and Eyring activation parameters, E_a, ΔH^*, and ΔS^*, were calculated by the least-squares method. The results together with the ΔG^* value are summarized in Table 3.

The barriers to the rotation around the isopropyl-nitrogen bond, E_a (52—60 kJ/mol) are close to those in $PhC(S)N(i\text{-}Pr)_2$ and $PhCH_2C(S)N(i\text{-}Pr)_2$ (51.0 and 59.4 kJ/mol at −25 °C, respectively).[6] This seems to indicate that the 1,3-dichalcogenacycloalkane moiety of the present compounds does not appreciably influence the barrier to rotation around the isopropyl-nitrogen bond. In fact, there is little difference in the E_a value between any of the pairs of cyclohexane and cyclopentane compounds, **1a**—**2a**, **3a**—**4**, and **1b**—**2b**. The E_a values of the bromide salts, **1a**, **2a**, and **3a**, are essentially the same as those of the hexafluorophosphate salts, **1b**, **2b**, and **3b**, respectively (Table 3). On the other hand, the dithia compounds, **1a**—**3a** and **4** give E_a values larger by 5—8 kJ/mol than the diselena analogs, **1b**—**3b**. The difference is compared with that between the E_a values of $R_2Sn(dtc)_2$ and $R_2Sn(dsc)_2$ (7.5 and 10.4 kJ/mol when R=Cl and Me, respectively)[3] where the steric repulsion of the isopropyl group with the sulfur atoms has been suggested to be larger than that with the selenium atom owing to the shorter length of the C–S bond than that of the C–Se bond. The absolute values of ΔS^* obtained are not so large (less than 28 J/(K mol)), suggesting the occurrence of an intramolecular process in solution.

References

1) R. M. Golding, P. C. Healy, P. W. G. Newman, E. Sinn, and A. H. White, *Inorg. Chem.*, **11**, 2435 (1972).
2) A. N. Bhat, R. C. Fay, D. F. Lewis, A. F. Lindmark, and S. H. Strauss, *Inorg. Chem.*, **13**, 886 (1974).
3) Y. Takeda, N. Watanabe, and T. Tanaka, *Spectrochim. Acta, Part A*, **32**, 1553 (1976).
4) A. Lindén, C. Roussel, T. Liljefors, M. Chanon, R. E. Carter, J. Metzger, and J. Sandström, *J. Am. Chem. Soc.*, **98**, 2853 (1976).
5) K. Tanaka and T. Tanaka, *Bull. Chem. Soc. Jpn.*, **45**, 489 (1972).
6) K. C. Ramey, D. J. Louick, P. W. Whitehurst, W. B. Wise, R. Mukherjee, J. F. Rosen, and R. M. Moriarty, *Org. Magn. Reson.*, **3**, 767 (1971).