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DYNAMIC STEREOCHEMISTRY OF BIS(*N*-ISOPROPYLSALICYLALDIMINATO) BERYLLIUM(II): ENANTIOMERIZATION PROCESS

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Summary

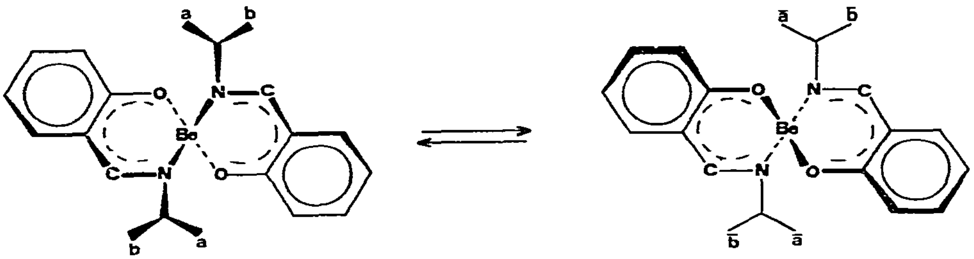
Bis(*N*-isopropylsalicylaldiminato)beryllium has been prepared. Its variable temperature ^{1}H NMR spectrum has been investigated in 1,2-dichlorobenzene, and the free energy of activation (22.1 kcal/mole at 139°C) thus determined for enantiomerization (inversion at the beryllium tetrahedral atom) without prior separation of the optical antipodes.

Introduction

It is well established that β-diketonate complexes of beryllium(II) assume a tetrahedral idealized D_{2h} structure in solution [1] and in the solid state [2]. In such a conformation bis-chelate complexes derived from unsymmetrically substituted ligands can exist as only one *dl* pair. Resolution of optical antipodes of Be(chel)$_2$ complexes has been accomplished in the past [3—7], and these experiments confirmed the tetrahedral structure of these complexes in solution.

However, no information was obtained on the nature of the racemization process.

In order to obtain a direct measure of the inversion barrier at the tetrahedral beryllium center we investigated the D NMR behaviour of bis(*N*-isopropylsalicylaldiminato)beryllium (I) under conditions in which the molecular interactions are weak and, more important, in which the reversibility of the process can be readily ascertained. In compound I, as can be seen from Fig. 1, the isopropyl group functions as a diastereotopic probe, in the sense that under conditions in which the chirality of the structure is preserved the two methyl groups within each isopropyl moiety (labeled a and b) are magnetically nonequivalent, giving rise to two doublets in the methyl region of the ^{1}H NMR spectrum. Any process



(I a) (I b)

Fig. 1. The two enantiomers of compound I. Barred letters denote enantiomeric relationships.

which destroys the chirality of the structure or results in an averaging of the two enantiomers will render the two methyl groups equivalent on the NMR timescale, and the two doublets will collapse to a single doublet.

Experimental

Compound I was prepared by treating *N*-isopropylsalicylaldimine (obtained from *N*-isopropylamine and salicylaldehyde) with $Be(OH)_2$ [8]; recrystallization from $EtOH/H_2O$ gave material of m.p. 187—188°C with an ^1H NMR spectrum in C_6D_6 showing absorptions at δ (ppm): 0.92, 0.98 (6 H, two doublets, $^3J(HH)$ 6.6 Hz, $CH(\underline{CH_3})_2$), 3.32 (1 H, m, $\underline{CH}(CH_3)_2$), 6.63, 7.10 (4 H, m, ArH), and 7.75 (1 H, s, CH). Found: C, 71.99; H, 7.20; Be, 2.65. $C_{20}H_{24}N_2O_2Be$ calcd.: C, 72.05; H, 7.26; Be, 2.70%.

The ^1H NMR spectra were recorded on a Varian A-60D spectrometer equipped with variable-temperature accessories. Temperature measurements were based on the chemical shift separation of the protons of an ethylene-glycol sample, and utilized the temperature-shift correlation of Van Geet [9]. Temperatures are considered to be accurate to ±2°C, although within a given series of measurements smaller differences (ca. ±0.5°) were considered significant. Saturation of the NMR signals was avoided. NMR samples were ca. 15% v/v solutions with ca. 5% Me_4Si and chemical shifts are reported in parts per million on the δ scale.

Results and discussion

The ^1H NMR spectrum of I in C_6D_6 shows two doublets in the methyl region corresponding to the two diastereotopic methyl groups within each isopropyl moiety. This spectrum is consistent with a tetrahedral conformation of I in solution and with slow interconversion between the two configurational enantiomers (Ia and Ib) on the NMR time scale at ca. 38°C. (Chirality is preserved at this temperature). For work at higher temperatures 1,2-dichlorobenzene was used as solvent; in this solvent, as can be seen from Fig. 1, accidental isochronies are present in the 38°C spectrum, but are absent from the higher temperature spectrum (126°C), so variable-temperature experiments are significant in this

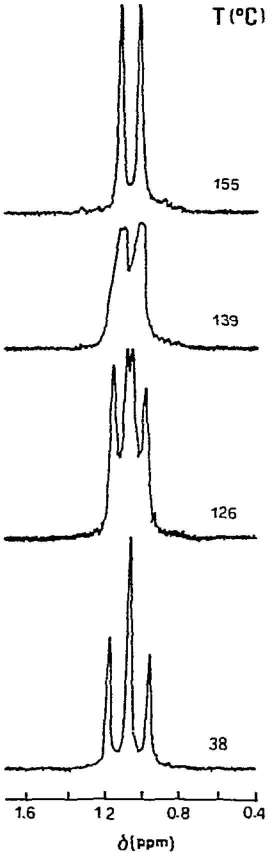


Fig. 2. Temperature-dependent 60 MHz ^{1}H NMR spectrum of I (methyl region) in 1,2-dichlorobenzene and TMS as internal reference.

TABLE 1

FREE ENERGY OF ACTIVATION FOR THE RACEMIZATION OF β-DIKETONATE BERYLLIUM COMPLEXES

Compound	Solvent	$\Delta G^{\neq}$(kcal/mol)/T(°C)
Ia, Ib	1.2-Dichlorobenzene	22.10/139 [a]
Bis(benzoylpyruvato)beryllium (brucine salt)	$CHCl_3$	21.26/20 [b]
Bis(benzoylpyruvato)beryllium (brucine salt)	EtOH	22.24/20 [b]
Bis(benzoylpyruvato)beryllium	EtOH	20.70/20 [b,c]
Bis(benzoylcamphor)beryllium	C_6H_6	24.90/20 [d]
Bis(benzoylcamphor)beryllium	C_6H_6 + 0.18% piperidine	21.90/20 [d]
Bis(benzoylcamphor)beryllium	$CHCl_3$	21.70/20 [d]

[a] This work. [b] Calculated from the Eyring equation (transmission coefficient assumed to be unity) from the kinetic data reported in ref. 4. [c] Mean value calculated from kinetic data obtained [4] on the dextro- and levo-rotatory derivative. [d] Calculated from the Eyring equation from the kinetic data reported by ref. 3.

solvent. As the temperature of the sample is raised the two isopropyl-methyl groups coalesce to a single doublet at 139°C (Fig. 2), and further heating sharpens the doublet, as expected. The Gutowsky—Holm equation [10] was used to give a rate constant at the coalescence temperature, and this was used to calculate an Eyring free energy of activation for the enantiomerization of $\Delta G^{\neq}_{139}$ 22.10 kcal/mol. Cooling the sample restores the original spectrum, indicating that the process is reversible and that no decomposition or bond rupture process occurs.

It is of interest to compare our $\Delta G^{\neq}$ value with those which can be calculated from reported values of the rate constants for the enantiomerization of bis-(benzoylpyruvato)beryllium [4] and beryllium bis-benzoylcamphor [3], and the data are given in Table 1. It will be seen that the $\Delta G^{\neq}$ values are very close to each other for all the complexes listed, even though various solvents and temperatures were employed.

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