Energy Barriers for the Enantiotopomerization of Tetrahedral Boron Chelates
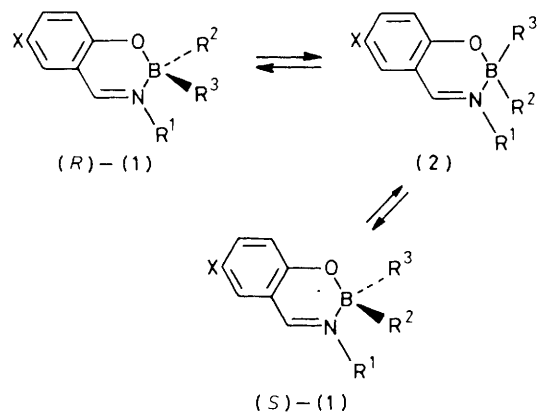
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The enantiotopomerization of diarylboron salicylideneaminato-chelates proceeding *via* a transition state with planar tetraco-ordinate boron is associated with thermally accessible energy barriers which have been determined by use of dynamic n.m.r. spectroscopy.

The inversion of the tetrahedral bond configuration, if it proceeds during an intramolecular rearrangement without bond scission, has been shown by structural correlations[1] and MO calculations[2] to involve planar and square-pyramidal species as transition-state or intermediate structures. The energies of the latter species relative to the stable tetrahedral form depend strongly on the nature of both the central four-co-ordinate atom and the attached ligands.[3,4] While the energy barriers for enantiomerization (enantiotopomerization) for tetrahedral transition-metal (*e.g.* Ni^{II}) complexes are extremely low (7—75 kJ mol^{-1}),[5] the corresponding values for compounds of carbon and other first-row elements, have been estimated by *ab initio* MO calculations[2—4,6] to amount to 600—800 kJ mol^{-1}. However, an effective structural strategy for decreasing the tetrahedral inversion barriers based on frontier orbital analysis has proved to be useful in predicting those compounds which would have a small planar–tetrahedral gap.[3,4] In particular, it has been deduced that strong π-donor and σ-acceptor groups (with O, N, or S atoms attached to the central atom) would significantly decrease the energy difference between planar and tetrahedral structures in four-co-ordinate compounds of non-transition elements less electronegative than carbon.[4,7]

We report here experimental evidence for this deduction in the boron chelate systems (1) where tetrahedral inversion at the four-co-ordinate boron atom (enantiomerization) can be effected thermally in solution and energy barriers for the enantiomerization can easily be determined by dynamic n.m.r. spectroscopy.

The chelates (1a—f) were obtained by refluxing methanolic solutions of equimolar quantities of the diarylborinic acid aminoethanol esters[8] and *N*-isopropyl- (or benzyl-) salicyl-ideneamine during 1—3 h. Owing to the presence of the prochiral group R^1 in (1) the kinetics of the (*R*)-(1) $\rightleftharpoons$ (*S*)-(1) interconversion can be measured without separation of the enantiomers by direct observation of the ^1H n.m.r. spectra of compounds (1a—f) at different temperatures. Computer

	X	R^1	R^2	R^3	M.p. of (1) $(t/°C)$
a	H	Pr^i	o-$MeOC_6H_4$	Ph	100
b	H	Pr^i	α-naphthyl	Ph	221
c	H	Pr^i	α-naphthyl	o-$MeOC_6H_4$	196
d	Br	Pr^i	o-$MeOC_6H_4$	Ph	116
e	NO_2	Pr^i	α-naphthyl	Ph	125
f	H	CH_2Ph	α-naphthyl	o-$MeOC_6H_4$	172

simulations of the temperature-dependent spectra were obtained using a version of the program in ref. 9 in order to obtain rate constants and activation parameters for the enantiomerization which results in an averaging of the signals from diastereotopic groups at elevated temperatures. These results are given in Table 1.

The rates and the energy barriers of the (*R*)-(1) $\rightleftharpoons$ (*S*)-(1) interconversion are independent of the concentration of (1) (within the range 0·1—3·0 M studied) and also of the solvent (*o*-dichlorobenzene, nitrobenzene, or benzonitrile). Addition of different amounts of the salicylideneaminato-ligands to the

Table 1. Chemical shifts (100 MHz) of the diastereotopic groups, rate constants (25 °C), and activation parameters for the (R)-(1) $\rightleftharpoons$ (S)-(1) interconversion (o-dichlorobenzene).

Compound	$\Delta\nu/$ Hz	$10^3\,k/$ s^{-1}	$\Delta H^{\ddagger}/$ kJ mol^{-1}	$\Delta S^{\ddagger}/$ J mol^{-1} K^{-1}	$\Delta G^{\ddagger}_{25}/$ kJ mol^{-1}
(1a)	36	8.7	85.8 ± 1.7	4.6 ± 2.5	84.5
(1b)	38	4.3	94.1 ± 1.3	26.4 ± 3.3	84.0
(1c)	33	11.0	93.7 ± 1.2	31.8 ± 2.9	84.0
(1d)	15	13.3	90.4 ± 1.6	23.2 ± 2.8	83.7
(1e)	43	1.7	99.6 ± 1.3	36.0 ± 2.9	88.7
(1f)	29	0.9	98.7 ± 1.6	28.4 ± 3.7	90.3

solutions of (1) did not influence the rate of the interconversion either. The ligand-exchange process was found, by investigating the spectral behaviour of a mixture of two distinct types of complex (1), to occur with an appreciable rate only at 90—100 °C, conditions under which the enantiomerization is already fairly rapid.

Therefore we conclude that the energy barriers for the enantiomerization in Table 1 should be regarded as the barriers to the intramolecular digonal twist rearrangement (R)-(1) $\rightleftharpoons$ (2) $\rightleftharpoons$ (S)-(1) and serve thereby as an experimental measure of the energy difference between tetrahedral and planar (probably slightly pyramidalized) bond configurations of the four-co-ordinate boron atom in compounds (1).

The energy barriers thus obtained are 10—20 kJ mol^{-1} lower than those for tetrahedral beryllium(II) bis-salicylideneaminato-complexes[10] but substantially higher than for tetrahedral zinc(II), cadmium(II), and mercury(II) bis-chelates.[9,11,12] For the latter compounds, however, clear evidence in favour of the intramolecular mechanism of the enantiomerization has been presented only for the cadmium(II) complexes.[12]

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References

1 E. L. Muetterties, *Tetrahedron*, 1974, **30**, 1595.
2 V. I. Minkin, R. M. Minyaev, and I. I. Zacharov, *J. Chem. Soc., Chem. Commun.*, 1977, 213; V. I. Minkin, R. M. Minyaev, I. I. Zacharov, and V. I. Avdeev, *Zh. Org. Khim.*, 1978, **14**, 3.
3 R. Hoffmann, R. W. Alder, and C. F. Wilcox, *J. Am. Chem. Soc.*, 1970, **92**, 4492; J. B. Collins, J. B. Dill, E. D. Jemmis, P. v. R. Schleyer, R. Seeger, and J. A. Pople, *ibid.*, 1976, **98**, 5419; J. Chandrasekhar and P. v. R. Schleyer, *J. Chem Soc., Chem. Commun.*, 1981, 260.
4 M. B. Krogh-Jespersen, J. Chandrasekhar, E.-U. Würthwein, J. B. Collins, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, 1980, **102**, 2263.
5 L. H. Pignolet, W. D. Horrocks, and R. H. Holm, *J. Am. Chem. Soc.*, 1970, **92**, 1855; J. J. McGarvey and J. Wilson, *ibid.*, 1975, **97**, 2531; R. Knorr, A. Weiss, H. Polzer, and E. Räpple, *ibid.*, 1977, **99**, 650; R. Knorr and A. Weiss, *Chem. Ber.*, 1981, **114**, 2104; L. E. Nivorozhkin, L. E. Konstantinovsky, M. S. Korobov, A. L. Nivirozhkin, and V. I. Minkin, *Zh. Obsch. Khim.*, 1982, **52**, 186.
6 K. B. Wiberg, G. B. Ellison, and J. J. Wendoloski, *J. Am. Chem. Soc.*, 1976, **98**, 1212.
7 E.-U. Würthwein and P. v. R. Schleyer, *Angew. Chem.*, 1979, **91**, 588.
8 I. Bally, E. Giorley, and A. T. Balaban, *Rev. Roum. Chim.*, 1968, **13**, 1507.
9 V. I. Minkin, L. E. Nivorozhkin, L. E. Konstantinovsky, and M. S. Korobov, *Koord. Khim.*, 1977, **3**, 174.
10 L. E. Nivorozhkin, L. E. Konstantinovsky, M. S. Korobov, and V. I. Minkin, *Koord. Khim.*, 1979, **5**, 508; F. A. Bottino, A. Recca, and P. Finocchiaro, *J. Organomet. Chem.*, 1978, **160**, 373.
11 S. S. Eaton and R. H. Holm, *Inorg. Chem.*, 1971, **10**, 1446.
12 L. E. Nivorozhkin, V. I. Minkin, L. E. Konstantinovsky, N. I. Borisenko, and M. S. Korobov, *Dokl. Akad. Nauk, SSSR*, 1981, **261**, N5.