A Lower Limit to the Barrier to Pyramidal Inversion in Stibines Determined by Nuclear Magnetic Resonance Spectroscopy

By JOHN JACOBUS

(*Department of Chemistry, Clemson University, Clemson, South Carolina* 29631)

Summary A lower limit (26 kcal mol^{-1}) for the barrier to pyramidal inversion of stibines is established and indicates that the direct measurement of such barriers is probably not amenable to either classical or n.m.r. techniques.

CURRENT interest in pyramidal inversion of trico-ordinate species, *e.g.*, sulphoxides,[1] sulphonium salts,[2] amines,[3] and phosphines,[4] has mainly been limited to second- and third-row elements.[5] We report here a lower limit for the barrier to pyramidal inversion of a dialkyl aryl stibine, di-isopropyl-*p*-tolylstibine (**1**).†

The n.m.r. spectrum of (**1**) in $CDCl_3$ and in 1-methylnaphthalene exhibits the expected diastereotopicity of the isopropyl methyl groups (Table). In $CDCl_3$ two of the isopropyl methyl resonances are overlapping, while in 1-methylnaphthalene all four expected methyl signals are observed. In 1-methylnaphthalene the chemical shift difference for the isopropyl methyl resonances is 0·06 p.p.m. The diastereotopic methyl resonances of (**1**) in 1-methylnaphthalene do not coalesce at temperatures up to 200°, and, further, no evidence of even the beginning of collapse is noted. Application of the approximate line-shape relationships and the Eyring equation yields a lower limit of 26 kcal mol^{-1} for the barrier to pyramidal inversion of tri-*C*-substituted stibines.

TABLE

N.m.r. spectral parameters of (**1**)[a]

	Solvent	
Resonance	$CDCl_3$	1-methylnaphthalene
Me_2CH	8·80 (d)[b] J 6 Hz	8·80 (d) J 6 Hz
	8·69 (d) J 6 Hz	8·74 (d) J 6 Hz
$Me_2C\mathit{H}$	8·33—7·58 (m)	c
$\mathit{Me}C_6H_4$	7·17 (s)	7·90 (s)
Ar	2·74 (q)	d

[a] Relative to internal Me_4Si, room temperature spectra at 60 MHz. [b] Multiplicity; s = singlet, d = doublet, q = quartet, m = multiplet. [c] Partially obscured by tolyl resonance. [d] Obscured by solvent.

Numerous calculations of barriers to pyramidal inversion, generally based on the Kincaid–Henriques method,[6] have appeared.[7–9] The calculations of both Weston[8] and Koeppl *et al.*[9] indicate that the maximum barrier to pyramidal inversion for trisubstituted Group V compounds should be for arsenic, with a slight decrease for antimony. Thus, it was thought that the barrier to stibines might be measurable since the most recently calculated barrier to pyramidal inversion about antimony is that for trimethylstibine, *ca.* 25 kcal mol^{-1}.[9] These calculations have yielded low values for pyramidal inversion barriers for trivalent phosphorous and arsenic compounds also.

It has previously been noted[10] that optically active *p*-carboxyphenyl-1-naphthylphenylstibine, upon being heated in *p*-xylene, is not racemized during 2 h; granted that the half-life for racemization is greater than 2 h, a minimum barrier of *ca.* 30 kcal mol^{-1} can be estimated‡ for the pyramidal inversion. It thus appears highly unlikely that either n.m.r. or classical techniques can be used in the determination of barriers to pyramidal inversion of tri-carbon substituted stibines.

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† Prepared by the action of Pr^iMgBr on *p*-tolyldichlorostibine, b.p. 110° at 0·8 mmHg (kugelrohr).

‡ Decomposition of the sample was observed. In the present work, samples of (**1**) which were heated above 200° for long periods were observed to undergo partial decomposition.

The author thanks the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support.

(*Received, June 21st*, 1971; *Com.* 1007.)

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