

Ring Inversion of CH₂-X-CH₂-bridged *peri*-Naphthalenes. A Dynamic N.M.R. Study

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Barriers to the inversion of the six-membered rings formed by bridging the 1- and 8-positions of naphthalene with a CH₂-X-CH₂ chain (X = O, S, Se, or Te) increase along the series, O < S < Se < Te, in marked contrast with the corresponding pentamethylene heterocycles, reflecting the importance of bond angle strain during inversion.

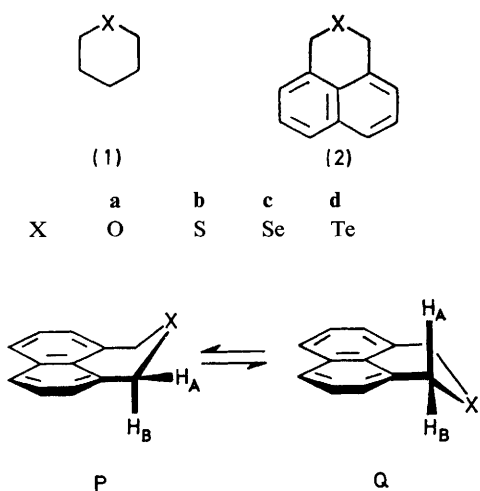
Torsional strain greatly contributes to the barrier to ring inversion of six-membered rings, as has been shown both by

calculation and by experiment.¹ Perhaps the most convincing demonstration is the close parallel found by Lambert and his

Table 1. Conformational barriers^a and n.m.r. parameters.

	X	Barriers ^a /kcal mol ⁻¹ †		Ring inversion in (2)	N.m.r. parameters ^b for (2)			
		Ring inversion in (1)	Rotation in CH ₃ -X-CH ₃		δ	δ _{AB}	² J _{AB}	T _c
a	O	10.3	2.50	<6.3	5.76	—	—	—
b	S	9.4	2.13	7.4	3.94	0.47	15.5	-118
c	Se	8.2	1.50	7.6	4.23	0.57	13.8	-108
d	Te	7.3	1.2	8.0	4.49	1.01	13.2	-97.5

^a Those for series (1) and for CH₃-X-CH₃ are from reference 2. ^b Coupling constants in Hz. A and B are the two methylene hydrogen atoms. T_c is the coalescence temperature in the 100 MHz spectrum of (2b), and the 200 MHz spectra of (2c) and (2d).



co-workers² between the barrier to ring inversion in the series (1a—d) and the barrier to rotation in the corresponding acyclic compound CH₃-X-CH₃ (see Table 1).

Bond angle strain is of lesser importance, and is difficult to demonstrate experimentally, since any substitution to change bond angle strain inevitably affects the torsional strain to some extent. We report a six-membered ring where bond angle strain is demonstrably the most important factor affecting the ring inversion.

When naphthalene has a three-atom chain bridging the *peri*-position as in (2), the naphthalene framework tends to constrain the resultant six-membered ring to a conformation with five atoms coplanar, *i.e.* as P or Q, with only the central X-atom of the three-atom chain out of the plane. Ring inversion P ⇌ Q may therefore be easy and the barrier in (2a) is known to be less than 6.3 kcal mol⁻¹.³† Higher barriers may be expected however, when the covalent radius of X is large because the resultant longer C-X bonds can best be accommodated by X being further out of the plane, and with such long bonds it is particularly difficult for X to pass between the relatively rigidly held 1- and 8-substituents. There must be great distortion of the bond angles C-C-X and C-X-C in a planar or near planar transition state, yet the longer the C-X bond, the *smaller* the torsional interactions will be. We therefore chose to examine the compounds (2b), (2c), and (2d)‡ because

the sum of the carbon and X covalent radii⁵ in these cases is 1.81, 1.94, and 2.14 Å respectively compared with 1.43 Å for (2a).

In the ¹H n.m.r. spectrum of (2b), (2c), and (2d) the CH₂ signal appears as a single line§ at ambient temperature, but at temperatures somewhat below -100 °C in each case¶ this has changed to an AB-quartet, showing that the geminal hydrogen atoms are non-equivalent, and thus the ring inversion P ⇌ Q has become slow on the n.m.r. time-scale. In each case, from a knowledge of the chemical shift and coupling of the geminal hydrogen atoms and the temperature of coalescence of their signals, a barrier to ring inversion P ⇌ Q was calculated (see Table 1).

The barrier in (2b) is indeed markedly larger than in (2a) and there is a further small rise for (2c) and then for (2d). Thus while torsional interactions during ring inversion no doubt diminish down the series (2a)—(2d), the barrier rises.

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§ For (2c), these are small side bands, separated by 14.0 Hz, due to coupling of the CH₂ protons with the 7% natural abundance ⁷⁷Se (*I* = $\frac{1}{2}$). For (2d), there are small side bands separated by 27.6 Hz due to coupling of the CH₂ protons with the 7.7% natural abundance ¹²⁷Te (*I* = $\frac{1}{2}$).

† 1 cal = 4.184 joules.

‡ Compounds (2b) and (2c) have been reported previously, see for example ref. 4. Satisfactory analysis has been obtained for (2d) (m.p. 107 °C), which was prepared analogously to (2c).

¶ Two previous dynamic n.m.r. investigations^{4,6} failed to measure a barrier to ring inversion for (2b) and for (2c), noting only that the process is still fast on the n.m.r. time-scale at *ca.* -100 °C.