Conformational Analysis of *peri*-Interactions in Napththalene Derivatives. Ring Inversion in CH_2–X–CH_2-bridged *peri*-Naphthalenes

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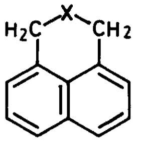
Barriers to ring inversion of the six-membered rings formed by bridging the 1- and 8-position of naphthalene with a CH_2–X–CH_2 chain (X = CH_2, O, S, Se, or Te), are reported and discussed in terms of torsional interactions and bond angle strain present in these inverting molecules.

The conformational interconversion of six-membered rings (ring inversion) has been a continuously intriguing subject since it was first shown in 1960[1,2] that dynamic nuclear magnetic resonance allows a quite direct determination of the barriers to such processes.

Structure (**1**) has a particular interest since the naphthalene nucleus places considerable restraints on internal movements[3] and so in contrast to most six-membered rings, conformational inversion takes place at only one part of the ring (**2**) $\rightleftharpoons$ (**3**).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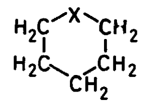
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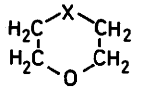
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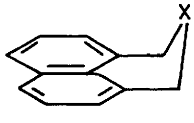
Me — X — Me

(6)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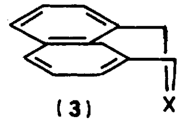
(3)

a; X = CH_2 b; X = O c; X = S d; X = Se e; X = Te

Since X passes through the plane of the naphthalene ring during inversion *via* the limited space between quite rigidly held CH_2 groups, unusual effects might emerge in a series of compounds where the size of X varies. If the strain is great enough, the aromatic nucleus is capable of great distortion,[†] so the rigidity and coplanarity implied by (**2**) and (**3**) should not be considered immutable facts, but a crystal structure determination[4] of (**1c**), and molecular mechanics calculations[‡,5] on (**1a**—**c**) confirm structures like (**2**) and (**3**).

This report concerns ring inversion in the series (**1a**—**e**) as demonstrated by the temperature dependence of their proton n.m.r. spectra. In a later paper[5] we extend our investigations to a series of more diverse groups X, sufficiently different as to add nothing to the present discussion.

The compounds (**1a**—**d**) have previously had their n.m.r. spectra studied at moderately low temperatures[§,¶,6] where no significant changes were observed. A preliminary report of the present results for (**1c**—**e**) only, has appeared.[7]

Results

In the compounds (**1b**—**e**) information on the conformational process is given by the signal of the CH_2 groups which takes the form of a singlet at room temperature. In (**1d**) and (**1e**) this is complicated by weak side bands due to coupling to a minor isotope of the element X (see Experimental section). As the temperature is lowered below about -80 °C, the singlet broadens in each case, and splits to an AB-quartet below about -100 °C (see Table 1). In (**1a**), the corresponding signal is a triplet due to coupling ^3J 6.2 Hz to the X = CH_2 group, which itself appears as a quintet. The α-CH_2 triplet shows no significant changes other than broadening even at -140 °C, but the β-CH_2 quintet broadens and splits to a multiplet just below -100 °C. On irradiation at the α-CH_2 frequency, the appearance of the β-CH_2 signal at -125 °C is an AB-quartet (see Table 1) while the α-CH_2 signal, width 14.5 Hz, on irradiation at the β-CH_2 frequency, is still a singlet with width 9 Hz, when the width of a reference Me_4Si line is 2.5 Hz. In all cases the spectral changes are compatible with the ring inversion process (**2**) $\rightleftharpoons$ (**3**) becoming slow on the n.m.r. timescale. Measurement of coalescence temperatures led to the barriers[‖] indicated along with other spectral data in Table 1.

Discussion

There is an obvious comparison that can be made between the barriers to ring inversion in the series (**1**) and in the series (**4**).[8] Since there is a vast accumulated knowledge of the mechanism of ring inversion of saturated six-membered rings[2] we can show in the following way that the trend in the simple saturated six-membered ring series (**4**) is directly related to mobility of the CH_2–X–CH_2 part of the ring.

The net effect of ring inversion in the series is rotation by about 120 ° around each bond in the carbon skeleton. For any one bond in a substituted cyclohexane, that rotation does not seem to take place continuously during the inversion process, but principally during one of three phases. The first phase is the

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[†] A particularly striking example is the *peri*-substituted 1,3,6,8-tetra-t-butylnaphthalene, see J. Handel, J. G. White, R. W. Franck, Y. H. Yuh, and N. L. Allinger, *J. Am. Chem. Soc.*, 1977, **99**, 3345.

[‡] For n.m.r. spectral data and molecular mechanics calculations for (**1c**), see H. G. Guttenberg, H. J. Bestmann, F. L. Bickert, F. S. Jørgensen, and J. P. Synder, *J. Am. Chem. Soc.*, 1981, **103**, 159.

[§] An upper limit to ring inversion of 6.3 kcal mol^{-1} for (**1b**) and molecular mechanics calculations for (**1a**) and (**1b**) have been determined, see J. E. Anderson and F. S. Jørgensen, *J. Chem. Soc., Perkin Trans. 2*, 1981, 741.

[¶] For results of an n.m.r. investigation of (**1c**) and (**1d**), see A. Biezais-Zirnis and A. Fredga, *Acta Chem. Scand.*, 1971, **25**, 1171.

[‖] 1 cal = 4.184 joules.

Table 1. ^1H N.m.r. spectra[2] of (**1a**—**e**) and barriers to ring inversion

(**1**)	Chemical shift of CH_2 signal at ambient temperature[a]	Relative shifts of A and B components at low temperature T_{10} (p.p.m.)	J_{AB} (Hz)	T_{10} (°C)	Coalescence temperature T_c (°C)	Ring inversion: Rate constant at T_c (s^{-1})	Ring inversion: Free energy of activation at T_c (kcal mol^{-1})
a; X = CH_2 α	3.14	0[b]		−125	—	—	—
β	2.10	0.36	12.2	−125	−101	176	8.2
b; X = O	5.76	0.12	14.0	−145	−137	93	6.4
c; X = S	3.94	0.47	15.5	−136	−118	136[c]	7.4
d; X = Se	4.23	0.57	13.8	−140	−108	262	7.6
e; X = Te	4.49	1.01	13.2	−130	−97.5	455	8.0

[a] In all cases there are additional complex signals in the aromatic region. [b] There is no significant change at low temperature—see Text. [c] This compound was studied at 100 MHz, the others at 200 MHz.

Table 2. Ring inversion barriers in compounds of types (**1**) and (**4**) and rotational barriers and structural parameters for the corresponding dimethyl-element compounds

	Barrier to inversion in the series (**1**) (kcal mol^{-1})	Barrier to inversion in the series (**4**) (kcal mol^{-1})[12,13]	Properties of the compounds Me–X–Me (**6**)*: Barrier to Me–X rotation (kcal mol^{-1})	C–X bond length (m × 10^{-10})	C–X–C angle (°)	C(1) to C(3) distance (m × 10^{-10})
a; X = CH_2	8.4	10.3	2.9	1.54	112.4	2.54
b; X = O	6.5	10.3	2.50	1.41	111.7	2.33
c; X = S	7.4	9.4	2.13	1.80	98.9	2.74
d; X = Se	7.6	8.2	1.50	1.94	96.2	2.89
e; X = Te	8.0	7.3	1.20	2.14	93.6	3.12

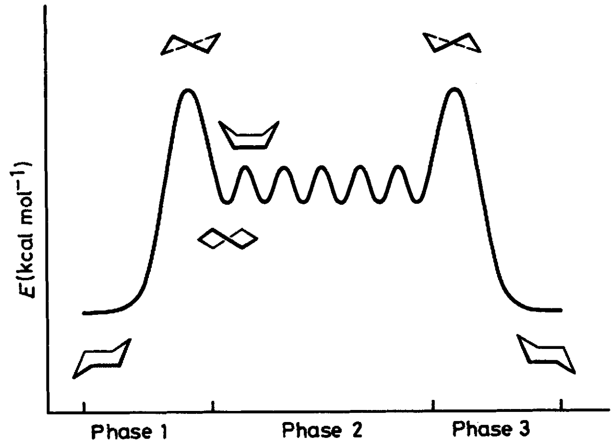

Figure. Rotational barriers in substituted cyclohexane during ring inversion

interconversion of the stable chair and intermediate twist and boat conformations by way of a strained half-chair conformation. The third phase is the reversal of this process to give the ring-inverted chair and the second phase is the pseudorotation among boat and twist conformations (see Figure).

If a substituent is introduced into cyclohexane which produces two bonds with a higher rotational barrier, for example two methyl groups on one of the carbons, rotation about these bonds will usually take place in phase two, with little or no effect on the observed barrier. On the other hand if a substituent is introduced which lowers rotational barriers for two bonds, for example replacement of a CH_2 group by an oxygen atom, rotation about these bonds will for preference be accomplished in phases one or three with some reduction of the observed ring inversion barrier. Thus any simple substitution which could produce a lower barrier will usually do so, while any substitution which could produce a higher barrier may not have this effect. Turning now to the reference series (**4**), the dependence of the ring inversion barriers on X[8,9] follows very closely that of the Me–X rotational barriers in Me–X–Me (**6**)* as Table 2 shows. A similar dependence on X has been demonstrated[10] for barriers in the series (**5**). Several factors are of course important in determining the size of such barriers,[2] but the direct relationship between the two series (**4**) and (**6**), and the importance of torsional interactions in determining the progression of barrier sizes, is clear.

Because of the considerable rigidity of the naphthalene ring, barriers to inversion in the series (**1**) also ought to reflect the conformational properties of the CH_2–X–CH_2 fragment. The striking fact is that the trend in barriers in the naphthalene series is in the opposite sense, so whatever conformational property is involved it is not the Me–X torsional barrier.

Table 2 also lists some geometric information* for the series Me–X–Me on the basis of which it is worth looking more closely at the present results.

The barrier of 8.4 kcal mol^{-1} for compound (**1a**) (X = CH_2) is less than that of cyclohexane (**4a**) (10.3 kcal mol^{-1})[9] but is much greater than in cyclohexene (5.3 kcal mol^{-1}).[11,12] Inspection of models and molecular mechanics calculations indicate that (**1a**) is flatter than both cyclohexane and cyclohexene, and rotation through less than 120° about only three bonds is required yet the barrier is much greater than in cyclohexene, and almost as

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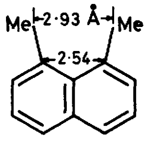
* For compound (**6a**), see D. R. Lide, Jr., *J. Chem. Phys.*, 1960, **33**, 1514; for compound (**6b**), see J. R. Durig and Y. S. Li, *J. Mol. Struct.*, 1972, **13**, 459; U. Blukis, P. H. Kasai, and R. J. Myers, *J. Chem. Phys.*, 1963, **38**, 2573; for compound (**6c**) see, L. Pierce and M. Hayashi, *J. Chem. Phys.*, 1961, **35**, 479; for compound (**6d**) see, J. F. Beecher, *J. Mol. Spectrosc.*, 1966, **21**, 414; for compound (**6e**) see, J. R. Durig, C. M. Plsyer, J. Bragin, and Y. S. Li, *J. Chem. Phys.*, 1971, **55**, 2895; J. M. Freeman and T. Hershell, *J. Mol. Struct.*, 1967, **1**, 31.

large as in cyclohexane with its complicated set of rotations. There is then a decrease in the barrier in moving to (**1b**) (X = O), but it is much greater than expected from differences in torsional barriers. Further down the series, (**1c**—**e**), there are striking increases in ring inversion barriers while torsional barriers decrease.

The crystal structure of 1,8-dimethylnaphthalene (**7**) is known[13] and shows clearly the interaction of the methyl groups. The methyl carbons are 2.93 Å apart while the C(1) to C(8) distance is 2.54 Å. The distance between the methyl atoms in the relevant dimethyl element compounds is shown in Table 2. The fragment with X = CH_2 can best span the *peri* position, while in comparison the ground state of the other compounds is strained in one of two ways.



(**7**)

The oxygen compound must either open the C–O–C bond angle or pull the bonds from C(1) and C(8) towards each other to complete the ring. The sulphur, selenium, and tellurium compounds must increasingly push these bonds apart, or compress the C–X–C bond angle to complete the ring. Thus the compounds with lower barriers than the CH_2-compound owe this in part to a more strained ground state.

There are other considerations however, for the barrier rises down the series oxygen to tellurium (**1b**—**e**), so transition state strain must increase even more down the series than does that of the ground state. Since the transition state for ring inversion is likely to be near to coplanar, the larger CH_2–X–CH_2 fragment will have greater difficulty in fitting into the space at the *peri*-position.

Bond angle opening, particularly at the moving part of the inverting ring, *i.e.*, opening of the naphthalene–C–X angles, is likely to be the least energy-expensive way of approaching a planar transition state. This opening would be greatest for the longest C–X bond, *i.e.*, in the tellurium case, so the increasing barrier down the series can be taken to reflect increasing bond angle deformation necessary for ring inversion.

Experimental

N.m.r. spectra were measured at 200 MHz operating frequency (Varian XL200) and are of *ca.* 0.005M solutions in approximately 1:1 CHF_2Cl–$CHFCl_2$ mixture with about 10% CD_2Cl_2 as lock for (**1a**), (**1b**), (**1d**), and (**1e**). For (**1c**) a similar solution in vinyl chloride was used and examined at 100 MHz operating frequency (Varian HA100).

2,3-Dihydro-1*H*-phenalene (**1a**),[14] 1*H*,3*H*-naphtho[1,8-*cd*]-pyran (**1b**),[15] the corresponding thiopyran (**1c**),* and selenin (**1d**)* were prepared by known literature methods. 1*H*,3*H*-Naphtho[1,8-*cd*]tellurin (**1e**) was prepared analogously to (**1d**),* forming orange needles (hexane), m.p. 107 °C (uncorr.) (Found: C, 51.33; H, 3.54. $C_{12}H_{10}Te$ requires C, 51.14; H, 3.58%).

The CH_2 proton signal of (**1d**) shows two singlet side bands separated by 14.0 Hz, reflecting coupling to the 7% natural abundance ^{77}Se ($I = 1/2$) isotopomer. The CH_2 proton signal of (**1e**) shows two singlet side bands separated by 27.6 Hz reflecting coupling to the 7.7% natural abundance ^{127}Te ($I = 1/2$) isotopomer. These side bands were not observed in the relatively poor quality very-low-temperature spectra.

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* See footnote ¶ on p. 469.