Determination of Ring Inversion Barriers for 1*H*,3*H*-Naphtho[1,8-*cd*]-pyran and its Methyl Substituted Derivatives by Molecular Mechanics Calculations and Dynamic Nuclear Magnetic Resonance Spectroscopy

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Molecular mechanics calculations with Allinger's MMPI program indicate that substitution of the methylene hydrogens in 1*H*,3*H*-naphtho[1,8-*cd*]pyran with methyl groups lowers the barrier to ring inversion. This seems to arise from increasing steric interactions in the ground state, whereas the energy of the transition state is less affected. The transition state for the inversion process has been calculated to possess C_{2v} symmetry. Increased steric interactions on the introduction of methyl groups result in a more planar (*i.e* less puckered) ground state with an increased C–O–C bond angle. Dynamic ^{1}H n.m.r. spectroscopy of 2,2-dimethyl-1*H*,3*H*-naphtho[1,8-*cd*]pyran reveals a $\Delta G^{\dagger}$ value for ring inversion of 6.9 kcal mol^{-1} at −133°. For the four other naphthopyrans studied by dynamic n.m.r. only upper limits for the inversion barrier are obtained.

NAPHTHALENES substituted in the 1 and 8 positions (*peri*-substituted) have attracted much attention in the last two decades.[1] The close proximity of the *peri*-substituents is responsible for several unique properties.[2-5] *X*-Ray crystallography,[3,4,6-9] n.m.r.,[2,5,10-12] e.s.r.,[12-14] and photoelectron spectroscopy,[5,15-17] and both molecular orbital [5,16,17] and molecular mechanics [3,5,9,13] calculations have been applied to the study of such *peri*-substituted naphthalenes.

Little information is available on the conformational mobility of compounds with a six-membered ring *peri*-fused to a naphthalene system.[5,10] To gain further insight on this subject we have investigated the 1*H*,3*H*-naphtho[1,8-*cd*]pyran system (1). We have performed molecular mechanics calculations with full geometry optimization of the ground state structures and studied the process of ring inversion *via* a planar transition state of (1) and its methyl substituted derivatives. The force field used was Allinger's MMPI (1973 version) [18] which has recently been applied to *peri*-substituted naphthalenes with good results.[3,5] The conformational behaviour of the compounds has been studied by dynamic ^{1}H n.m.r. spectroscopy.

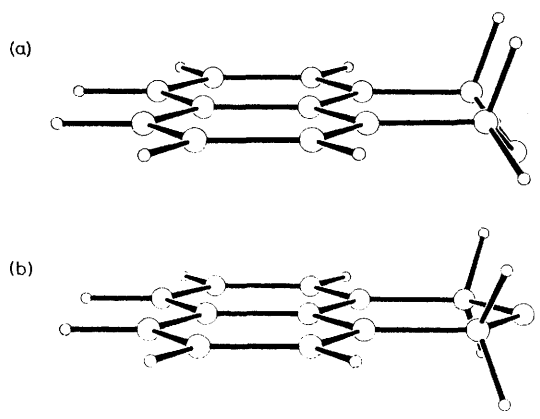
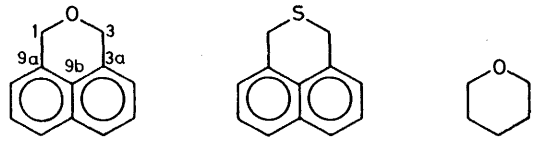


FIGURE 1 ORTEP representation of the MMPI-calculated structures of 1*H*,3*H*-naphtho[1,8-*cd*]pyran (1): (a) ground state structure (C_s symmetry); (b) transition state structure (C_{2v} symmetry)

Molecular Mechanics Calculations.—The structure of naphthopyran (1) has been fully geometry-optimized with MMPI, giving for the ground state a C_s conformation with the oxygen atom of the pyran ring located out of the main plane of the molecule (see Figure 1). The optimized geometries and strain energies are shown in Table 1. The molecular structure of naphthopyran (1) has not been determined experimentally, but the structure of the related compound, 1*H*,3*H*-naphtho-[1,8-*cd*]thiopyran (2) has been shown by *X*-ray crystallography to possess C_s symmetry with the thiopyran ring folded.[6] For this compound the MMPI-calculated and the *X*-ray determined structures showed good agreement.[5] The C_s form of naphthopyran (1) seems to



(1) (2) (3)

be almost strainless as the MMPI structural values for the pyran ring are nearly identical with the corresponding electron-diffraction-determined values for tetrahydropyran (3): [19] *r*(CO) 1.412/1.420 Å, $\hat{COC}$ 111.3/111.5°, $\hat{OCC}$ 112.4/111.8°, $\hat{COCC}$ 58.3/59.9° for naphthopyran (1) tetrahydropyran (3), respectively. Furthermore, the bond angles at the C(3a), C(9a), and C(9b) positions are nearly 120° showing no sign of *peri*-deformations.

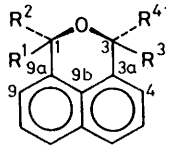
We then studied naphthopyrans where the hydrogens of the methylene groups in (1) were replaced successively by methyl groups (Table 1). The replacement of a single hydrogen atom with a methyl group gives rise to two different ground state conformations, one with the methyl group equatorial (4e) and one with the methyl group axial (4a), the latter being the more stable by 0.5 kcal mol^{-1}. Inspection of Newman-type projections of (4e and a) (Figure 2) reveals that an equatorial methyl group will possess a torsional angle of 34° relative to the

TABLE 1

Molecular mechanics calculated data for 1*H*,2*H*-naphtho[1,8-*cd*]pyran and its methyl-substituted derivatives

	Compound									
	(1)	(4e)	(4a)	(5ee)	(5aa)	(6)	(7)	(8eea)	(8aae)	(9)
R^1	H	Me	H	Me	H	Me	Me	Me	Me	Me
R^2	H	H	Me	H	Me	H	Me	Me	Me	Me
R^3	H	H	H	Me	H	H	H	Me	H	Me
R^4	H	H	H	H	Me	Me	H	H	Me	Me
Strain energy [a] (kcal mol^{-1})	0.0	1.7	1.2	3.4	4.4	3.0	3.7	5.4	7.0	9.6
Ring inversion barrier [b]	7.4	7.0	7.5	6.4	5.3	7.0	6.6	5.6	4.0	2.4
Bond lengths (Å)										
O-C(1) O-C(3)	1.412	1.409 1.409	1.409 1.410	1.407	1.407	1.407 1.406	1.406 1.406	1.403 1.404	1.404 1.404	1.400
C(9a)-C(1) C(3a)-C(3)	1.508	1.515 1.505	1.510 1.506	1.512	1.508	1.514 1.507	1.522 1.503	1.519 1.511	1.520 1.505	1.516
Bond angles (°)										
C(1)-O-C(3)	111.3	112.8	112.8	114.4	115.8	114.6	114.8	116.7	118.3	121.0
O-C(1)-C(9a) O-C(3)-C(3a)	112.4	111.0 111.8	112.1 113.0	110.5	113.4	111.5 111.6	111.4 112.6	110.8 111.1	112.7 113.2	112.5
C(1)-C(9a)-C(9b)										
C(3)-C(3a)-C(9b)	118.2	118.5 118.0	118.6 118.3	118.3	119.1	118.7 118.4	118.8 118.3	118.8 118.8	119.5 119.1	119.5
C(9a)-C(9b)-(3a)	118.9	119.3	119.0	119.5	119.5	119.3	119.4	119.7	119.5	119.8
Torsional angles (°)										
C(3)-O-C(1)-C(9a)										
C(1)-O-C(3)-C(3a)	58.3	58.4 59.2	56.5 55.9	59.1	49.9	55.5 57.1	54.6 55.7	55.2 55.4	46.5 48.7	44.9
O-C(1)-C(9a)-C(9b)										
O-C(3)-C(3a)-C(9b)	28.7	27.8 28.6	28.3 26.5	27.6	24.0	25.3 28.1	25.6 26.8	25.7 25.2	20.3 24.2	20.3
C(9)-C(9a)-C(1)-R^1										
C(4)-C(3a)-C(3)-R^3	34.2	33.9 34.7	40.0 36.5	34.6	45.0	36.6 40.6	41.5 37.1	41.8 37.5	47.3 45.9	47.8
C(9)-C(9a)-C(1)-R^3										
C(4)-C(3a)-C(3)-R^4	85.3	87.8 85.1	78.7 81.7	87.4	71.4	84.5 78.2	79.3 82.8	79.3 83.8	72.4 70.4	72.1
C(9b)-C(9a)-C(1)-R^2										
C(9b)-C(3a)-C(3)-R^4	94.0	90.7 94.3	100.3 98.0	91.1	107.9	94.3 100.7	98.6 98.0	98.7 94.7	105.9 108.2	106.2
Puckering angle [c] (°)	52.0	52.8	50.1	53.5	44.5	50.7	49.6	45.4	42.9	40.8

[a] The strain energy of the ground state conformation relative to the minimum energy conformation of (1) (kcal mol^{-1}). [b] The energy difference between the planar transition state structure and the fully optimized ground state structure (kcal mol^{-1}). [c] This value corresponds to the angle between the C(1)-O-C(3) plane and the average C(9a)-C(3a)-C(1)-C(3) plane.



naphthalene ring, whereas an axial methyl group will have a torsional angle with the naphthalene ring of 79°.

There are three structural isomers of dimethyl-

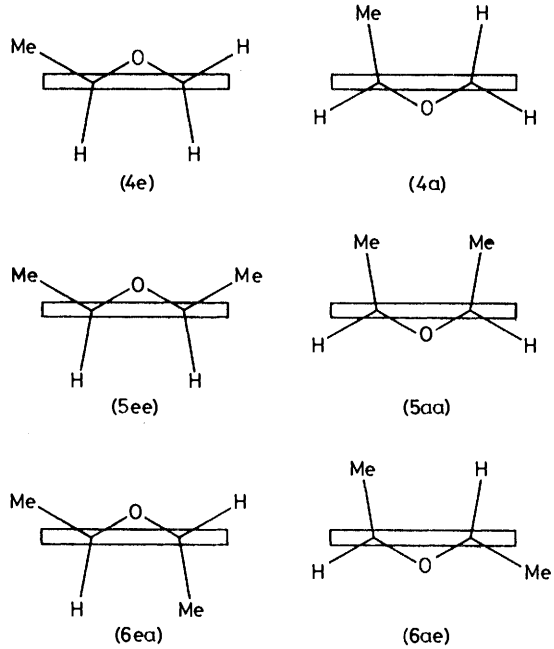
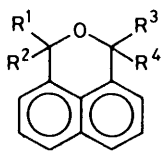


FIGURE 2 Newman-type projections of the methyl-substituted naphthopyrans (4)—(6)

1*H*,3*H*-naphtho[1,8-*cd*]pyran, the *cis* (5), the *trans* (6), and the *gem* (7). For the *cis*-isomer the conformation with two equatorial methyl groups (5ee) is 1.0 kcal mol^{-1} more stable than the conformation with two axial methyl groups (5aa) (Figure 2). Both the *trans*- (6) and the *gem*-dimethylnaphthopyran (7) exist in a conformation with one equatorial and one axial methyl group.

The trimethylnaphthopyran (8) can exist in conformations with either one equatorial and two axial or one axial and two equatorial methyl groups (Figure 2), calculations suggesting that the latter is favoured by 1.6 kcal mol^{-1}. For the tetramethylnaphthopyran (9) the ground state is concluded to be a C_s conformation analogous to that of the parent compound (1).



(1) $R^1-R^4=H$
(4) $R^1=Me, R^2-R^4=H$
(5) $R^1=R^3=Me, R^2=R^4=H$
(6) $R^1=R^4=Me, R^2=R^3=H$
(7) $R^1=R^2=Me, R^3=R^4=H$
(8) $R^1-R^3=Me, R^4=H$
(9) $R^1-R^4=Me$

The transition state for the interconversion of the degenerate C_s forms of naphthopyran (1) and (1′) has previously been assumed to possess C_{2v} symmetry (10) [13] (see Figure 1). The energy calculated for the C_{2v} form is 7.4 kcal mol^{-1} above that of the C_s form. A possible non-planar transition state with C_2 symmetry (11) was investigated by optimising the geometry with C_2 restrictions, but was ruled out as the resulting structure proved to be identical to the C_{2v} form. Optimization

TABLE 2

^{1}H N.m.r. spectroscopic data for naphthopyran and related compounds at room temperature [a]

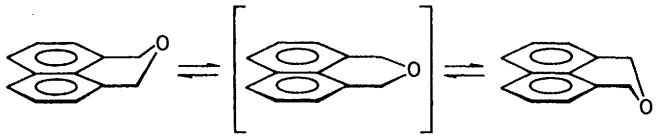
	Methyl signals [b]	Benzylic hydrogen signals [b]	OH signals [b]	Methyl–methine coupling (Hz)
(1)		5.76		
(5)	1.76 (d)	5.20 (q)		6.33
(6)	1.69 (d)	5.38 (q)		6.55
(7)	1.83	5.14		
(9)	1.66			
(16)	1.57 (d)	5.88 (q)	2.9br	6.6
(17)	1.57 (d)	5.75 (q)	2.9br	6.6
(18)	1.60		2.2br	
(20) [c]	2.17 (m)	4.73 (m)	1.96br	
		5.10 (m)		

All compounds show complex aromatic signals in addition to those quoted here. Solvent is deuteriochloroform except for (7) (vinyl chloride) and (20) (carbon tetrachloride). Signals are singlets except where otherwise indicated; thus d = doublet, q = quartet, m = multiplet, br = broad. [b] Chemical shift downfield relative to Me_4Si (in p.p.m.). [c] Vinylic hydrogens: δ 4.98 (m) and 5.19 (m).

without restrictions leads to the C_s ground state conformation.

Dynamic N.m.r. Spectroscopy.—Details of chemical shifts and coupling constants are given in Table 2. Vinyl chloride solutions were used for n.m.r. spectra at low temperatures.

The methyl singlet signal in the ^{1}H n.m.r. spectrum of the *gem*-dimethylnaphthopyran (7) splits below −133° to a symmetrical doublet of relative chemical shift 22 Hz at 100 MHz as seen at −145°. At the latter temperature the CH_2 signal appears as an AB quartet with δ_{AB} *ca.* 12 Hz and J_{AB} *ca.* 15 Hz. From the coalescence of the methyl signal, the barrier to the conformational exchange process is 6.9 kcal mol^{-1} at −133°.



(1) (10) (1′)

(11)

In the n.m.r. spectrum of the parent naphthopyran (1) the methylene hydrogen signal remains a single absorption down to −151°. Similarly in the n.m.r. spectrum of the tetramethylnaphthopyran (9), the methyl signal remains a singlet down to −166°. The spectra of the *cis*- and *trans*-dimethylnaphthopyrans (5) and (6), respectively, remain substantially unaltered at temperatures as low as −147°, the methyl signal a doublet, the methine signal a quartet. Unfortunately, as in all cases at such low temperatures, there is a great deal of broadening due to fast relaxation in viscous solutions, but it is noticeable that the *trans*-isomer (6) shows broadening at higher temperatures than the *cis*-isomer (5). This might be attributed to the onset of kinetic broadening in (6) rather than viscosity broadening, which presumably is similar in these isomeric compounds.

However, for (1), (5), (6), and (9) the most that can be concluded is that if signals are not accidentally coincident [relative chemical shifts in the dimethylnaphthopyrans (5)—(7) suggest that this is a reasonable assumption], the barrier to conformational isomerism in (1) and (5) is not greater than 6.3 kcal mol^{-1}, and in the case of (6) may be close to 6.3 kcal mol^{-1}. In (9) the barriers appears to be less than 5.6 kcal mol^{-1}.

DISCUSSION

The increased ground state strain introduced on substitution by methyl groups (*cf.* Table 1 and Figure 3) can be explained as arising from two effects. The first is the repulsion between an equatorial methyl group and the *ortho*-hydrogens on the naphthalene ring, favouring (4a) over (4e). The second effect is the repulsion between 1,3-diaxial methyl groups, which tends to destabilize conformers (5aa) and (8aae). The strain seems to be accommodated by the molecule in at least two ways. Introducing equatorial methyl groups tends to increase the puckering [*i.e.* (1) ⟶ (4e) ⟶ (5ee) and (4a) ⟶ (6)], whereas axial methyl groups tend to decrease the puckering, *i.e.* flatten the pyran ring [*i.e.* (1) ⟶ (4a) ⟶ (5aa) and (4e) ⟶ (6)]. When both types of methyl groups are introduced the pattern becomes more complex, but the flattening dominates. As the molecule gets more planar it moves towards the transition state for ring inversion and the barrier is lowered. The introduction of methyl groups, axial as well as equatorial, leads to an increase of the C–O–C bond angle [(1) ⟶ (4) ⟶ (5) ⟶ (6) and (7) ⟶ (8) ⟶ (9)].

On moving from the ground state (1) or (1′)′ to the C_{2v} transition state (10) the largest distortions are calculated for the C–O–C and O–C–C bond angles, which are increased by 7.3 and 8.4°, respectively, suggesting that the barrier to inversion arises mainly from bond angle deformation. The repulsion between the *ortho*-hydrogens on the naphthalene ring and the equatorially placed hydrogens of the methylene groups, and the

repulsion between the two 1,3-diaxially placed hydrogens, decrease on moving from the C_s form to the planar C_{2v} transition state; thus these two effects seem to be of minor importance.

We have assumed that the transition state for ring inversion in the methyl-substituted naphthopyrans is planar, as found for the parent compound (1). This assumption may introduce an error for the unsymmetrically substituted compounds [*i.e.* (4), (5), and (8)], as the transition state for the transformation of, for example,

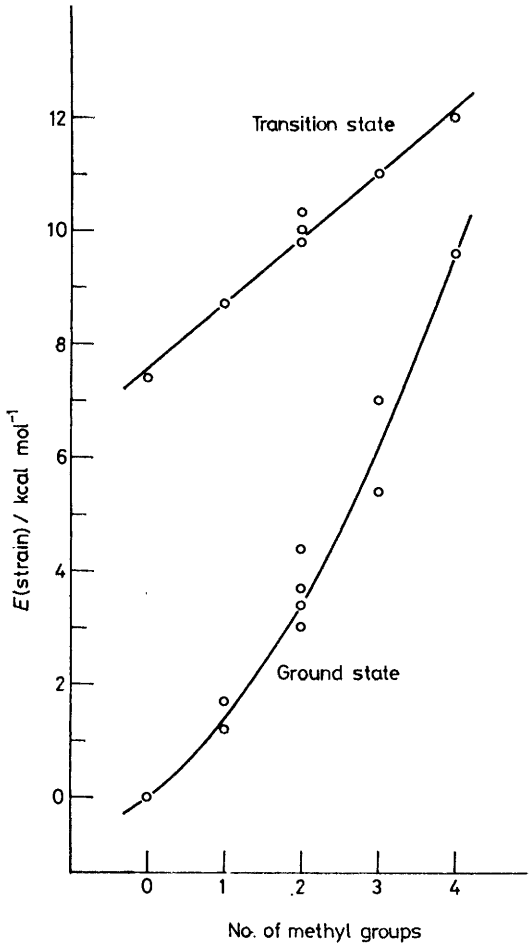


FIGURE 3 The strain energy of the ground state and transition state conformations of the naphthopyrans relative to the minimum energy conformation of (1). The inversion barrier is the difference between the strain of the transition state and the ground state

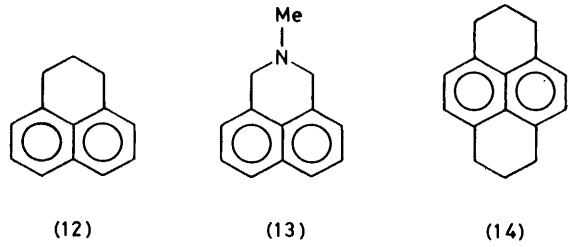
(5aa) to (5ee) (see Figure 2) may be supposed to appear slightly before the planar form. There may therefore be small errors in the calculated values of the barriers.

The strain of the transition state tends to increase by the constant amount of 1.2—1.3 kcal mol^{-1} per methyl group (*cf.* Table 1 and Figure 3). This suggests that the introduction of methyl groups affects the strain of the transition state only by the interactions between the methyl group and the rest of the molecule, and that interactions between the methyl groups are negligible.

The barrier to ring inversion (*cf.* Table 1) decreases from 7.4—7.5 kcal mol^{-1} for the unsubstituted (1) and the monomethyl (4) naphthopyran, to 6.4—7.0 kcal mol^{-1} for the dimethyl naphthopyrans (5)—(7) and then drops considerably to 4.0 kcal mol^{-1} and further to 2.4 kcal mol^{-1} for the trimethyl- (8) and tetramethylnaphthopyran (9), respectively.

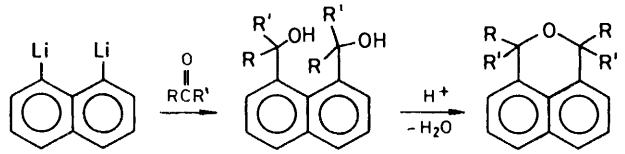
From Figure 3 it is evident that the decrease of the barrier height for ring inversion by introduction of methyl groups in 1*H*,3*H*-naphtho[1,8-*cd*]pyran is determined by increasing strain in the ground state.

For the *gem*-dimethylnaphthopyran (7), the only compound for which the barrier has been firmly determined by n.m.r., the agreement between the experi-

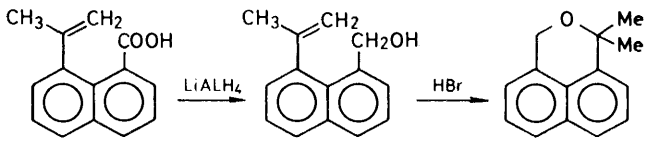


(12) (13) (14)

mental (6.9 kcal mol^{-1}) and the calculated (6.6 kcal mol^{-1}) value is good. For the remaining compounds studied by n.m.r. [*i.e.* (1), (5), (6), and (9)] only upper limits to the ring inversion barrier have been determined. These upper limits give no support to the relatively high calculated barriers of 7.4 and 7.0 kcal mol^{-1} for (1) and (6), and are not discordant with the calculated barriers of 6.4 and 2.4 kcal mol^{-1} for (5) and (9). The limited n.m.r. results can hardly be construed as supporting the trend shown by the calculations.



(15) (16) – (18) (5),(6),(9)



(19) (20) (7)

SCHEME

For the radical anion derived from the unsubstituted naphthopyran (1) the barrier to ring inversion has been determined by e.s.r. spectroscopy to be E_a 5.47 kcal mol^{-1} [13] which accords with our n.m.r. result for the neutral (1), that $\Delta G^{\dagger} < 6.3$ kcal mol^{-1}. The comparison of n.m.r. and e.s.r. barriers may be misleading for some systems, but perhaps not for *peri*-substituted naphthalenes where the extra electron (in the e.s.r. experi-

ment) is localized in the naphthalene moiety, and should have only a small effect on the height of the barrier.[13,15]

The barriers for the related compounds, the 1*H*,3*H*-naphtho[1,8-*cd*]thiopyran (2) and 2,3-dihydrophenalene (12) have been calculated by MMPI to 5.3 [5] and 7.5 kcal mol^{-1},[20] respectively. The former compound (2) as well as the *N*-methyl-1*H*,3*H*-naphtho[1,8-*cd*]pyridine (13) have been studied by n.m.r. For the sulphur compound (2) the barrier is 7.4 kcal mol^{-1} [21] and for the nitrogen compound (13) a barrier of 9.7 kcal mol^{-1} was measured,[10a] but the high energy point in the conformational exchange for (13) corresponds to nitrogen inversion. The barrier for ring inversion in the radical anion derived from hexahydropyrene (14) has been determined by e.s.r. to be either 6.4 or 8.1 kcal mol^{-1}.[14]

EXPERIMENTAL

The preparation of the compounds studied is outlined in the Scheme. 1*H*,3*H*-Naphtho[1,8-*cd*]pyran (1),[22] its dimethyl derivatives (5) and (6),[23] as well as the tetramethyl derivative (9) were prepared from the corresponding diols by brief treatment with toluene-*p*-sulphonic acid in benzene solution. The dimethylnaphthopyrans (5) and (6), which are the two products of the treatment of 1,8-dilithionaphthalene (15) [24] with acetaldehyde followed by dehydration, can be separated by repeated crystallization,[23] or in our hands, by column chromatography on silica gel. The compounds so obtained, *A* and *B*, melt at 91—93 and 80—82°, respectively, the former being present in greater amount and moving faster down the chromatographic column.

The assignment of the structures of *A* and *B* was based on their ^{1}H n.m.r. spectra. *A* has its methyl signal downfield to the of *B*, and its methine signal upfield (see Table 2). The above molecular mechanics calculations suggest that the *cis*-isomer will exist predominantly in the conformation (5ee) rather than (5aa) and that the *trans*-isomer will exist as an equilibrium between the enantiomeric forms (6ea) and (6ae). On the basis of the general rule that the closer a proton is to the plane of the aromatic system, the further downfield its signal will be,[25] *A* with its methyl signal downfield can be assigned to the isomer with two equatorial methyl groups (5ee), and *B* is the *trans*-isomer (6ea) ⇌ (6ae).

This assignment is supported by the spin–spin coupling between the methine proton and the aromatic protons in the *ortho*- and *para*-positions. It has been shown that this coupling is greater the more the methine proton is orthogonal to the mean plane of the aromatic ring.[25] In the present case for the isomer *A*, the quartet for the methine hydrogens (coupled to methyl, *J* 6.33 Hz) shows further splitting of each peak in the quartet into approximately 1 : 2 : 1 triplets (*J ca.* 1.0 Hz, coupling to one *ortho*- and one *para*-hydrogen), the average width of the peaks of the quartet being 2.9 Hz. In agreement, the signals for the *ortho*- and *para*-aromatic hydrogens show splittings of 1.37 and 1.15 Hz owing to coupling with the methine protons.

For the isomer *B*, the methine proton signal shows no resolved coupling to aromatic hydrogens, and though broadened to 2.1 Hz, it is not as broad as the methine signal in *A*. The *ortho*-hydrogen shows a splitting of 1.15 Hz owing to coupling with the methine hydrogen, but the *para*-hydrogen shows no resolved coupling.

Thus, on the basis of both chemical shift and coupling information, the isomer *A* is assigned the *cis*-structure (5ee), and the isomer *B* is assigned the *trans*-structure (6), *i.e.* (6ea) ⇌ (6ae).

The *gem*-dimethylnaphthopyran (7) was prepared by lithium aluminium hydride reduction of 8-isopropenyl-1-naphthoic acid (19) [26] affording 1-hydroxymethyl-8-isopropenylnaphthalene (20), which on treatment with hydrobromic acid gave (7).[27]

The ^{1}H n.m.r. spectra were measured on a Varian HA-100 spectrometer as described previously.[28]

2,2,6,6-*Tetramethyl*-1H,3H-*naphtho*[1,8-cd]*pyran* (9) had m.p. 103—104° (Found: C, 85.2; H, 8.2. $C_{16}H_{18}O$ requires C, 84.9; H, 8.0%).

2,2-*Dimethyl*-1H,3H-*naphtho*[1,8-cd]*pyran* (7) had b.p. 79—90° at 0.3 mmHg (Found: C, 84.35; H, 7.1. $C_{14}H_{14}O$ requires C, 84.7; H, 7.2%).

1-*Hydroxymethyl*-8-*isopropenylnaphthalene* (20) had m.p. 61—62° (Found: C, 84.45; H, 7.25. $C_{14}H_{14}O$ requires C, 84.7; H, 7.2%).

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