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RESTRICTED CONFORMATIONAL INVERSION IN 1,8-(1',8'-NAPHTHYLDIMETHYL)NAPHTHALENE

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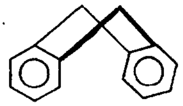
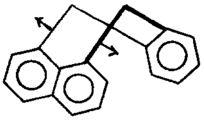
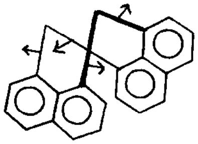
As part of our continuing studies of 7,12-dihydropleiadene chemistry[1], we have studied ring inversion in the 1,8-(1',8'-naphthyldimethyl)naphthalene system (C). It has already been amply demonstrated[1] that simple 7,12-dihydropleiadenes (B) have substantially higher ΔF^* inversion (~13-16 kcal/mole) than similarly substituted 9,10-dihydroanthracenes (A) which flip too rapidly, on the n.m.r. time scale, for determination of the inversion barrier[2] separating the folded conformers. Examination of models reveals that structure B will suffer greater bond angle strain during inversion than A and that the corresponding strain in the flattened transition state for the highly folded eight-membered analog (C) will be even greater (see arrows below).


A


B


C

The angle strain contribution to raising ΔF_* inversion was also noted by Agosta[3], who succeeded in preparing optically active 4-nitro-1,8-(1',8'-naphthalyl)naphthalene and found its conformational stability such that

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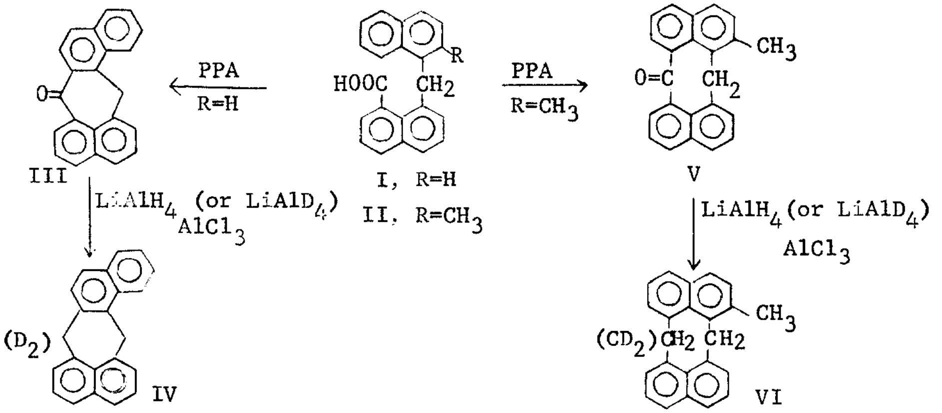
$\Delta F^{\neq}_{293°}$ = 22.9 kcal/mole, corresponding to $t_{1/2}$ ~102 minutes at 25.5°. We now report on a methyl 1,8-(1',8'-naphthyldimethyl)naphthalene whose inversion barrier is at least 10 kcal/mole higher than the related 1-methyl-7,12-dihydropleiadene.[4]

The 8-aroyl-1-naphthoic acid (mp 242-3° $\lambda_{>C=O}$ 5.94, 6.06 μ) obtained from the Grignard reagent derived from 2-methyl-1-bromo-naphthalene and 1,8-naphthalic anhydride[5] was converted to methylene acid II (mp 155-160°, $\lambda_{>C=O}$ 5.95 μ (nujol)) by Huang-Minlon reduction.[5] Polyphosphoric acid cyclization[5] of II afforded V[6] (m.p. 238-239°, $\lambda_{>C=O}$ 6.04 μ) in low yield, which gave 2-methyl-1,8-(1',8'-naphthyldimethyl)naphthalene[6] (VI), mp 202-4°, upon mixed hydride reduction.[5] These transformations are summarized below together with the alternative results obtained when seeking the <u>des</u>-methyl compound[7] (from I)



The inversion barrier for IV-12,12-d_2 (deuterated to avoid two overlapping AB spectra from the C_7- and C_{12}- methylene groups[8]), was determined by variable temperature n.m.r. spectroscopy[5] at the coalescence temperature (T_c = +1 ± 1°C) from the expression[9] $k_r = \pi\sqrt{\Delta\nu_{AB}^2 + 6J_{AB}^2}/\sqrt{2}$ and the Eyring equation. In the absence of exchange, the C_7-methylene protons appeared as a quartet with $\Delta\nu_{AB}$ = 20.0 H_z and J_{AB} = 15.0 Hz from which

ΔF^{*}_{Tc} was calculated to be 13.5 kcal/mole, a value comparable to other 7,12-dihydropleiadenes.[1,5] The eight-membered rings in V and VI clearly invert much more slowly, since their benzylic methylene signals appeared as AB spectra up to 200°C, with no sign of impending coalescence. From $\Delta\nu_{AB}$ and J_{AB} for V and dideuterated VI, minimum values of ΔF^{*} inversion can be calculated[9] and these are tabulated below, along with data for the related dihydropleiadenes.

TABLE I

Compound	δ_{AB}	$\Delta\nu_{AB}$	J_{AB}	T_c(°C)	$\Delta F^{\ddagger}_{inv}$(kcal/mole)
1-methyl-7,12-dihydropleiadene-7,7-d_2	265	19	15	-10°	13.1[a]
1-methyl-7,12-dihydropleiadene-12,12-d_2	265	73	15	8°	13.5[a]
1-methyl-7(12H)-pleiadenone		--	--	<-60°	<10.4[b]
V	284	17	15	>200°	>23.8[c]
VI-d_2	306	80	15	>200	>23.2[c]

[a] F.D. Saeva, Ph.D. Dissertation, State University of New York at Buffalo,1967

[b] estimated, using $\Delta\nu$ = 19 Hz and J = 15 Hz, and Tc = -60°C.

[c] estimated, using T_c = 200°C.

Thus, like Agosta's diketone[3], V and VI should have high optical stability when resolved. The greater barrier height in V and VI compared with Agosta's compound[3] ($\Delta F^{*}_{rac} \simeq$ 21 kcal/mole at 200°C), may be a consequence of ground-state electrostatic repulsion of parallel carbonyl dipoles in the diketone, an influence not present in our compounds. It must also be remembered, however, that the buttressing methyl group in V and VI may raise the barrier to an extent not observed with methyl dihydropleiadenes.[11]

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1. P.T. Lansbury, Trans. N.Y. Academy Sci., 29, 357(1967) and references cited therein.

2. (a) W.B. Smith and B.A. Shoulders, J. Phys. Chem., 69, 2022(1965)
   (b) D.Y. Curtin, C.G. Carlson and C.G. McCarty, Can. J. Chem., 42, 565 (1964).

3. W.C. Agosta, J. Am. Chem. Soc., 89, 3926 (1967).

4. P.T. Lansbury and F.D. Saeva, Tetrahedron Letters, 599(1966).

5. For typical experimental procedures, see P.T. Lansbury, J.F. Bieron and M. Klein, J. Am. Chem. Soc., 88, 1477(1966) and ref. 7.

6. Satisfactory elemental analyses and consistent spectral data were obtained for this compound.

7. The synthesis of 7,12-dihydro-8,9-benzopleiadene(IV) was independently carried out by Houlton and Kemp (J. Chem. Soc. C, 591(1967)), whose results are entirely consistent with ours. These findings, of course, provide further substantion for the structures assigned to V and VI.

8. No observable steric deuterium isotope effect on the inversion rate is expected (cf. ref. 5).

9. R.J. Kurland, M.B. Rubin and W.B. Wise, J. Chem. Phys., 40, 2426(1964)

10. All n.m.r. spectra were measured at 60 mHz using A-60 or HA-60 spectrometers, in chloroform-d solutions. Temperature readings were calibrated by using methanol or ethylene glycol.

11. Methyl groups at C_1 and/or C_6 in DHPs produce no effect on ΔF^*_{inv}. whereas C_8 and C_{11}- methyl raise the barrier ca. 1 kcal/mole per methyl(ref. 5).