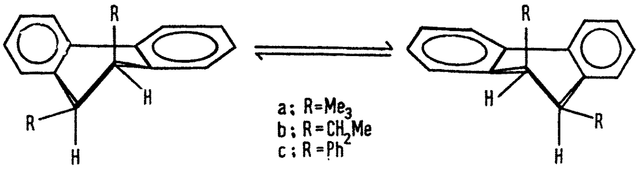
Ring Inversion in 9,10-Dihydrophenanthrene Derivatives

By Peter W. Rabideau and Ronald G. Harvey*
(*Ben May Laboratory, University of Chicago, Illinois,* 60637)
and J. B. Stothers
(*Department of Chemistry, University of Western Ontario, London, Canada*)

Summary The free-energy barrier for conformational interconversion of *cis*-9,10-disubstituted-9,10-dihydrophenanthrenes follows the unusual order: Ph $<$ Me $<$ Et.

Conformational interconversion of 9,10-dihydrophenanthrene is rapid at the lowest temperatures attained (−90°) in previous n.m.r. studies.[1,2] We report the synthesis and variable-temperature n.m.r. investigation of some *cis*- and *trans*-9,10-disubstituted-9,10-dihydrophenanthrenes.

Lithium–ammonia reduction[3] of 9,10-dimethylphenanthrene in the presence of colloidal iron led to stereospecific formation of *cis*-9,10-dimethyl-9,10-dihydrophenanthrene† (Ia). The n.m.r. spectrum‡ showed aromatic multiplets at τ 2·5 and 2·8 (8H), a symmetrical multiplet for the methine protons at τ 7·1 (2H), and a methyl doublet at τ 8·9 (8H, *J* 6·9 Hz.). The appearance of only one signal for both the axial and equatorial groups (methyl and methine) must



(I) (I′)

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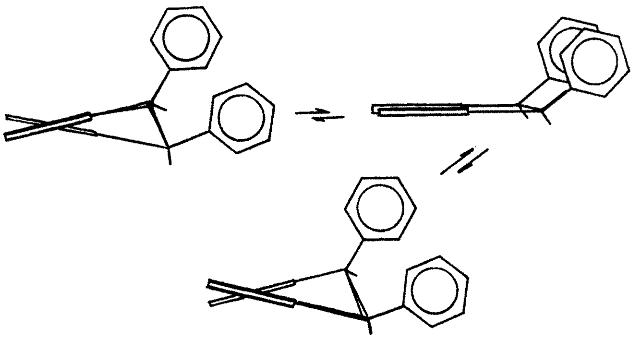
† All new compounds gave satisfactory microanalysis and spectral data consistent with their structures.

‡ N.m.r. spectra were taken at *ca.* 10% *w/v* concentration in CS_2 or CCl_4 on either a Varian A-60 or HA-100 spectrometer. Temperature measurements were made from the temperature-dependent n.m.r. spectrum of methanol. A methanol sample containing Me_4Si (as a lock signal) was calibrated against pure methanol at 60 MHz. Chemical shifts are relative to Me_4Si as internal standard.

represent an average spectrum indicative of the rapid (n.m.r. time scale) interconversion of (Ia) and (Ia′) (see Figure). Lowering of the temperature produced coalescence of the doublet§ and ultimately (−80°) the formation of two doublets of equal intensity separated by 65·2 Hz. Upon re-warming, the two doublets (representing the axial and equatorial methyls) coalesced at −47°. A value of $\Delta F^{\ddagger} = 10{\cdot}8$ kcal./mole was calculated[4] for the ring inversion process.



FIGURE

The *cis*-diethyl system (Ib)[3]† exhibited, as expected, a higher coalescence temperature (+27°) with a correspondingly higher inversion barrier ($\Delta F^{\ddagger} = 14{\cdot}9$ kcal./mole).

Contrary to expectation, the n.m.r. spectrum of *cis*-9,10-diphenyl-9,10-dihydrophenanthrene (Ic) displayed a single average signal for the benzylic protons τ 5·7 (2H) at ambient temperature, and coalescence required a temperature of −70°. Below −80°, an AB system (J 4·5 Hz, $\delta\nu = 54{\cdot}2$) developed, and a value of $\Delta F^{\ddagger} = 9{\cdot}7$ kcal./mole was calculated for inversion. The barrier to conformational interconversion is, therefore, in the unexpected order[5] Ph < Me < Et.

Molecular models suggest that the two phenyl rings of (Ic) are restricted in a parallel orientation, with no significant increase in steric interaction during conformational inversion. If, as this suggests, the two rings slide by each other "face-to-face," the *ortho*-protons may be expected to experience shielding due to diamagnetic anisotropy.[6] In agreement, the aromatic region of (Ic) showed a multiplet at τ 3·1 (14H) and a well separated multiplet at τ 3·5 (4H)¶ assigned to the four *ortho*-protons.

The *trans*-isomers of (Ia) and (Ib) (IIa, b), synthesized *via* alkylation of the corresponding 9-alkyl-9,10-dihydrophenanthrenes with n-butyl-lithium in *NNN′N′*-tetramethylenediamine, showed temperature-independent n.m.r. spectra** from −80 to +150°. Although this could be interpreted as inversion too rapid to measure by n.m.r. a preferred diaxial conformation appears more plausible from inspection of molecular models. Consistent with this tentative assignment are the relatively high-field positions of both the methyl and methylene signals of the *trans*-diethyl compound (τ 8·60 and 7·83, respectively) compared with the time-average values of the *cis*-isomer (τ 8·45 and 7·62, respectively).

Cis- and *trans*-Assignments are based on observation of equivalent numbers of axial and equatorial protons in the frozen conformations of only the former. Strong additional support was provided by detection of AB coupling between the benzylic protons of (Ic) at low temperature, thus excluding the possibility of equal populations of diaxial and diequatorial conformers.

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§ Kinetic data were obtained by observation of the methyl signal, the strongest and least complex absorption; the other non-aromatic protons exhibited expected temperature variation. In all cases the original spectra were reproduced.

¶ The n.m.r. spectrum of 9-phenyl-9,10-dihydrophenanthrene shows no aromatic signals higher than τ 3·0. This suggests a shielding effect in (Ic) of *ca.* 0·5 p.p.m.

** At 60 MHz., (IIa) exhibited signals at 465, 433 (m, 8H, Ar), 170 (m, 2H, CH), and 64 Hz. (d, 6H, CH_3, J 7 Hz.); (IIb) showed 460, 428 (m, 8H, Ar), 156 (t, 2H, CH, J 7 Hz.), 78 (m, 4H, CH_2), and 50 Hz. (t, 6H, CH_3, J 7 Hz.).

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[2] Substitution at the 4- and 5-positions inhibits this process sufficiently to permit optical resolution. K. Mislow and H. B. Hopps, *J. Amer. Chem. Soc.*, 1962, **84**, 3018.

[3] R. G. Harvey, L. Arzadon, J. Grant, and K. Urberg, *J. Amer. Chem. Soc.*, 1969, **91**, 4535; R. G. Harvey and K. Urberg, *J. Org. Chem.*, 1968, **33**, 2206, 2570.

[4] Values were calculated using the expression $k = \pi\delta\nu_e/\sqrt{2}$ at the coalescence temperature (H. S. Gutowsky and C. H. Holm, *J. Chem. Phys.*, 1956, **25**, 1228) and the Eyring relationship from transition-state theory.

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[6] L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon, New York, 1959, p. 19.