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STEREOCHEMISTRY AND CONFORMATION OF 9,10-DIISOPROPYL-9,10-DIHYDROANTHRACENES

Herman E. Zieger, David J. Schaeffer and Regina M. Padronaggio
Department of Chemistry, Brooklyn College of the City University of New York
Brooklyn, New York 11210

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The reaction of 9-lithio-10-ethyl-9,10-dihydroanthracene, 1, with methyl iodide or ethyl bromide has been reported to give high yields of *cis*-9,10 dialkyl-9,10-dihydroanthracenes [2, DHA = dihydroanthracene].[1,2] Only for reactions of 1 with carbon dioxide or deuterium oxide could traces of trans stereoisomers be detected.[1] The formation of *cis*-9,10 dialkyl-9,10-DHAs appears to be independent of whether the organolithium intermediate is formed by addition of ethyllithium to anthracene or by hydrogen metal exchange of 9-ethyl-9,10-DHA with *n*-butyllithium.[1] These observations could be interpreted as suggesting that 1 is an equilibrating mixture of cis and trans stereoisomers which react with methyl iodide [or ethyl bromide] at vastly different rates to give exclusively *cis*-9,10-dialkyl-9,10-DHAs. Alternately, it could be inferred that 1 possesses high stereochemical integrity and reacts with an alkyl halide with high stereospecificity to give cis dihydroanthracenes.

9-Isopropyl-9,10-DHA, 3, mp 28-29°; *Anal*., Calcd for $C_{17}H_{18}$: C 91.84; H 8.16. Found C 91.82, H 8.22,[3] was metalated in tetrahydrofuran [THF] with n-butyllithium [Foote Mineral in hexane] to give 9-lithio-10-isopropyl-9,10-DHA, 4. After treatment with isopropyl iodide, 4 gave a mixture of *cis*- and trans-9,10-diisopropyl-9,10-dihydroanthracenes in 80% yield. The 76-77° mp isomer predominated over that of mp 108-110° [2:1] as determined by integration of the benzylic hydrogen doublets in the pmr spectrum of the two isomers [see Table 1].

Table 1

Proton Chemical Shifts For 9,10-Diisopropyl-9,10-DHAs

Isomer	lit [4] mp	aromatic hydrogens	benzylic	J	$-CH(CH_3)_2$	J
76-77° [a]	73.5-74.0°	δ 7.25 [multiplet]	δ 3.78	5.0 Hz.	δ 0.97	6.8 Hz.
109-110° [b]	116.5-117.0°	δ 7.20 [singlet]	δ 3.27	9.5 Hz.	δ 1.00	6.2 Hz.

[a] % C 90.91, % H 8.93 Calcd C, 90.85; H 9.15

[b] % C 90.89, % H 9.09

The formation of both isomeric 9,10-dialkyl-9,10-DHAs strongly suggests that the organolithium intermediate is an equilibrating mixture of *cis*- and trans-9-lithio-10-isopropyl-9,10-DHAs.

In 9,10-dialkyl-9,10-DHAs [R=methyl or ethyl-] the less soluble, higher melting point stereoisomer has been regarded as possessing cis geometry. [2] The assignment of cis configuration to 9-methyl-10-ethyl-9,10-DHA of mp 103-104° has been confirmed through a stereospecific synthesis. [1]

In order to determine which isomer has the cis configuration among the 9,10-diisopropyl-9,10-DHAs, 9-isopropyl-10-deutero-9,10-DHA was metalated with *n*-butyllithium to give 9-lithio-9-deutero-10-isopropyl-9,10-DHA, **4d**$_1$, together with **4** which forms by removal of D rather than H during metalation. After reaction with isopropyl iodide, **4d**$_1$ and **4** gave 9-deutero-9,10-diisopropyl-9,10-DHA of m p 76-77° and its isomer of m p 109-110° in a 2:1 ratio in 90% yield. These hydrocarbons were separated by chromatography over alumina and carbon-deuterium infrared stretching vibrations were measured in KBr pellets and in CCl_4 solutions.

The isomer of m p 109-110° has a single sharp C-D stretching absorption at 2127 cm^{-1} [CCl_4] and 2128 cm^{-1} [KBr]., while the isomer of m p 76-77° has two C-D stretching signals at 2137 cm^{-1} [strong] and 2099 cm^{-1} [weak] in CCl_4; in KBr these absorptions were observed at 2137 cm^{-1} [strong] and 2114 cm^{-1} [weak].

9,10-Dialkyl-9,10-DHAs may have two different conformational isomers with the central ring in a boat-like form. [6] For a symmetrically disubstituted trans-9-deutero-9,10-DHA these two conformers will be of equal energy, and hence equally populated. The deuterium atom in the benzylic position will be quasiaxial in half of the molecules and quasiequatorial in the other half. Such a mixture of conformational isomers would be expected to have two C-D stretching signals in the ir.

In contrast, cis-9-deutero-9,10-diisopropyl-9,10-DHA is expected to favor the conformation having both of the alkyl groups quasiaxial. [2,5,6]. Consequently, the deuterium would have to occupy a quasiequatorial position in the more highly populated conformer. Thus the isomer of m p 109-110° having one C-D stretching vibration is assigned the cis configuration. This assignment also finds experimental support from the observed pmr coupling constants between the isopropyl methinyl hydrogens and the benzylic protons. The cis isomer must have the quasiaxial groups rotated such as to minimize non-bonding interactions between each other. This maximizes the dihedral angle [$\phi = 180°$] between the isopropyl methinyl- and benzylic hydrogens leading to the observed coupling constant of 9.5 Hz.

The trans isomer has no non-bonding interactions between the isopropyl groups, but rather between the isopropyl groups and the peri hydrogens at C_1, C_4, C_5 and C_8. To alleviate these interactions, the isopropyl groups are rotated such that their methinyl hydrogens are gauche [$\phi = 120°$] to the benzylic hydrogens as evidenced by the coupling constant of 5.0 Hz.

Interestingly, this assignment of configuration leads to the conclusion anticipated by Lansbury that in 9,10-dialkyl-9,10-DHAs as in some 7,12-dihydropleiadenes, the quasiequatorial hydrogen atoms in the benzylic postions are more shielded than quasiaxial hydrogen atoms. [7] This behavior is the antithesis of that often observed in cyclohexyl systems and is traceable to the shielding effects of the aromatic ring currents on the quasiequatorial proton. This conclusion is not in agreement with analyses of pmr spectra for 9-t-butyl-9,10-DHA and 9,10-di-t-butyl-9,10-DHA [8] or for 9-ethyl-9,10-DHA [9] which assumed that the quasiaxial hydrogens in the benzylic positions of 9,10-DHAs would absorb "...at higher fields than equatorial hydrogens in line with the general finding in cyclohexane derivatives." [8] The reason for this disagreement arises from the fact that the central ring in 9,10-DHAs is in a boat conformation. Comparison of the carbon-deuterium ir stretching vibrations of 9-deutero-9,10-dialkyl-9,10-DHAs with data for 9,10-dideutero-9,10-DHA-9,10-endo-α,β-succinic anhydride have provided further evidence that in cis 9,10-dialkyl-9,10-DHAs the alkyl groups prefer to be quasiaxial. Current work in progress will be reported shortly.

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3. *UV* λmax = 252.5 mu, ϵ = 27,000; *NMR* δ7.14 [s, 8 H], δ4.05 and 3.70 [AB quartet of C_{10} benzylic hydrogens J_{AB} = 18.2 Hz.], δ3.55 [d, H at C_9, J = 7.0 Hz.], a methinyl multiplet at δ1.87, and δ0.80 [d 6 H, J = 6.5 Hz.].

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