Ring B conformation in 9,10-dihydroanthracenes by nuclear magnetic resonance[1]

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The nuclear magnetic-resonance data of some 9,10-dihydroanthracenes with substituents on the aromatic rings allow the assignment of a pseudoboat conformation for the central ring. The dihedral angle formed by the two planes in the molecule changes according to the substituents.

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The conformation of the central ring in some 9,10-dihydroanthracenes has been studied by several workers. It appears that some of these compounds have a pseudoboat conformation, with the molecule folded about the axis through the methylenes of the central ring, and a dihedral angle of 145° as in 9,10-dihydroanthracene (1), while others have a planar structure (2). The present paper is a contribution to the study of this problem.

The 9,10-dihydroanthracenes studied (2,6-dimethoxy-2,3,6,7-tetramethoxy- and 1,2,3,5,6,7-hexamethoxy-9,10-dihydroanthracene) were obtained by the Robinson's method (3), with some minor modifications, starting with the corresponding substituted benzyl alcohol. No 9,10-dihydroanthracene was obtained applying the same method with 5-bromo- and 5-chloroveratryl alcohol.

The 2,6-dimethoxy-9,10-dihydroanthracene (m.p. 245°) has not been reported in the literature. The spectroscopic data are consistent with the assigned structure, which was also confirmed by converting the product into 2,6-dimethoxyanthracene (4).

Discussion

The preparation of 9,10-dihydroanthracenes by this method is strongly dependent both on the nature and the position of the aromatic substituents. The high degree of selectivity is remarkable since the attack always occurs at positions *para* to the methoxyl groups. The low yield (10%) obtained with 3,4,5-trimethoxy benzyl alcohol, and the negative results with 5-bromo- and 5-chloro-veratryl alcohol and particularly in cases where the substituents are in close proximity to the reactive sites in the molecule provide support for this explanation.

Nuclear Magnetic Resonance Data Analysis

In the 9,10-dihydroanthracenes the signals of the aliphatic protons at C_9 and C_{10} correspond to an A–B system with different coupling constants and variable chemical shifts depending on the substituents. The chemical shifts for axial and equatorial protons as well as the mean chemical shifts may be explained by a combination of electronic and stereoelectronic effects.

In 9,10-dihydroanthracene itself there is only one signal for the methylene protons at 3.87 p.p.m. (5). This has been explained by a rapid interconversion between two extreme boat conformations (6). In 2,6-dimethoxy-9,10-dihydroanthracene, the introduction of two methoxyl groups in positions 2 and 6 reduces the rate of interconversion and the differences between the axial and the equatorial protons are now evident. The axial protons absorb at 3.51 and 3.73 p.p.m. and the equatorial protons at 4.67 and 4.87 p.p.m. (Table I). This difference is due to the shielding of the axial hydrogens by the aromatic magnetic fields. Considering that positions 2 and 6 are relatively far away from the hydrogens in 9 and 10, the steric effect of the two methoxyl groups seems remarkable.

With two more methoxyl groups in positions 3 and 7 (in 2,3,6,7-tetramethoxy-9,10-dihydroanthracene), the electromagnetic effect increases

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TABLE I

Coupling constants and chemical shifts of some 9,10-dihydroanthracenes

Compound	J (c.p.s.)	Chemical shift (p.p.m.) A*	Chemical shift (p.p.m.) B*	ΔA–B	Mean chemical shift (p.p.m.)	Reference
9,10-Dihydroanthracene	0	3.87		0	3.87	5
2,6-Dimethoxy-9,10-dihydroanthracene	13.5	3.51, 3.73–4.67, 4.87 3.62	4.77	1.15	4.19	—
2,3,6,7-Tetramethoxy-9,10-dihydroanthracene	13.5	3.63, 3.37–4.60, 4.83 3.50	4.72	1.20	4.11	—
2,3,4,6,7,8-Hexamethoxy-9,10-dihydroanthracene	13.5	3.87, 4.09–4.32, 4.56 3.96	4.44	0.48	4.20	—
9-Terbutyl-9,10-dihydroanthracene	19	3.79	4.23	0.44	4.01	7
9,10-Diterbutyl-9,10-dihydroanthracene	0	3.94		0	3.94	7

*A = axial protons; B = equatorial protons.

the difference between the axial and the equatorial protons (3.63, 3.37, and 4.60, 4.83). In addition, there is an increased shielding both for axial and equatorial protons which results in a smaller mean chemical shift.

The introduction of two more methoxyl groups in positions 1 and 5 (in 1,2,3,5,6,7-hexamethoxy-9,10-dihydroanthracene) causes a different kind of effect which cannot be readily explained in terms of shielding due to substituents as in the above mentioned case. The interaction of the substituents with the equatorial protons in 9 and 10 forces the molecule to an even more planar conformation, thereby increasing the dihedral angle formed by the two halves of the molecule. The difference between the axial and the equatorial protons is thus diminished (3.87, 4.09 and 4.32, 4.56) together with the total electromagnetic shielding. This is also observed in 9-*tert*-butyl-9,10-dihydroanthracene (7).

The steric effect can be anticipated to become more critical with an increase in temperature and therefore the difference between the chemical shifts of the equatorial and the axial protons should therefore decrease. In agreement with this expectation we have found experimentally that the difference in the chemical shifts between axial and equatorial protons in 1,2,3,5,6,7-hexamethoxy-9,10-dihydroanthracene is diminished by 2 c.p.s. between −20 and 55°.

From the nuclear magnetic resonance (n.m.r.) spectra analysis it may be deduced that in the 9,10-dihydroanthracenes the chemical shifts of the axial and the equatorial protons is largely dependent on the dihedral angle formed by the two planes in the molecule. This angle is variable and dependent on the substituents, particularly in positions 1,4,5,8,9, and 10.

Experimental[3]

2,6-Dimethoxy-9,10-dihydroanthracene

m-Methoxy benzyl alcohol (5 g) was mixed with 20 ml of Lucas reagent (8), followed by 5 drops of acetic acid. The mixture was stirred for 12 h at room temperature. It was then diluted with water and extracted with ethyl acetate. Evaporation of the solvent left a dark yellow oil which was chromatographed on SiO_2, eluting with 80:20 ethyl acetate–hexane. The crystalline fraction yielded white crystals (495 mg) of m.p. 245° (sealed tube); λ_{max} 207, 230, 282, and 289 mμ (ε, 29 200, 15 900, 2740, and 2740); ν_{max} 2990, 2930, 2915, 2860, and 2830; 1610, 1575, 1495, 1472, and 1415; 1285, 1250, 1200, 1143, 1095, 1074, 1040; 930, 867, 820, 800, 785, 752, 730, 710, and 700 cm^{-1}; n.m.r. spectrum: 3.62 (2H, doublet, J = 13 c.p.s.) and 4.77 (2H, doublet, J = 13 c.p.s.); 3.75 (6H, singlet); ABX system, 6.64 (2H, multiplet, J = 8 and 2.5 c.p.s.), 6.9 (2H, doublet, J = 2.5 c.p.s.), 7.29 (2H doublet, J = 8 c.p.s.).

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[3] Melting points were determined in a Kofler block and are uncorrected. The infrared spectra were run in a Perkin–Elmer 521 spectrometer, in KBr. The ultraviolet spectra were determined in a Perkin–Elmer 450 spectrophotometer, in hexane solution. The n.m.r. spectra were run in a Varian A-60 spectrometer using TMS as internal standard. The elemental analysis was carried out by Dr. Franz Pascher, Bonn, Germany.

Anal. Calcd. for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71; O, 13.32. Found: C, 80.08; H, 6.30; O, 13.91.

2,6-Dimethoxyanthracene

To 100 mg of 2,6-dimethoxy-9,10-dihydroanthracene were added 500 mg of lead oxide (litharge) and the mixture heated at 200° for 5 h. The reaction product was sublimed *in vacuo*, yielding pale yellow crystals (40 mg) which, when recrystallized from ethyl acetate, afforded white crystals of m.p. 260° (lit. (4) 257°, from benzene); the ultraviolet spectrum is in agreement with that reported for the product (4).

2,3,6,7-Tetramethoxy-9,10-dihydroanthracene

Veratryl alcohol (2 g) was mixed with 10 ml of concentrated hydrochloric acid and stirred for a few minutes. The thick paste so formed was filtered and washed with water, resulting in 1.540 g of white crystals, m.p. 220–224°. These were recrystallized from ethyl acetate raising the m.p. to 227° (lit. (3) 227°, from benzene); ν_{max} 2995, 2950, 2934, and 2908; 1675, 1603, 1584, 1500, 1457, 1390, and 1340; 1180–1270, 1130, 1080, 1015; 990, 935, 865, and 838 cm^{-1}; n.m.r. spectrum: 3.5 (2H, doublet, J = 13 c.p.s.) and 4.72 (2H, doublet, J = 13 c.p.s.): 3.82 (12H, singlet): 6.84 (4H, singlet).

1,2,3,5,6,7-Hexamethoxy-9,10-dihydroanthracene

3,4,5-Trimethoxy benzyl alcohol (2 g) was mixed with 10 ml of concentrated hydrochloric acid and stirred for 1 h. The reaction mixture was diluted with water and extracted with ethyl acetate. After evaporation of the solvent an orange oil was obtained. This oil crystallized from ethanol–water yielding 200 mg of white crystals with m.p. 199–201° (lit. (9) 202–203°, from ethanol). No change in the m.p. was observed after recrystallization from ethyl acetate; ν_{max} 3000, 2960, 2937, and 2833; 1710, 1570, 1490, 1464, 1450, 1430, 1400, and 1332; 1287, 1192, 1160, 1115, 1057, and 1033; 990, 960, 910, and 850 cm^{-1}; n.m.r. spectrum: 3.96 (2H,doublet, J = 13 c.p.s.) and 4.44 (2H, doublet, J = 13 c.p.s.); 3.78 (6H, singlet); 3.82 (6H, singlet), and 3.99 (6H, singlet); 7.26 (2H, singlet).

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Concerning the problems involved with use of external references for variable temperature chemical shift measurements[1]

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The importance of making bulk susceptibility corrections to nuclear magnetic resonance chemical shifts measured versus an external reference is emphasized. The special significance of this correction for variable temperature studies is demonstrated by comparing data obtained with external and internal references for uridine-5′-phosphate. Opposite trends in chemical shift and inaccurate activation energies can result.

En utilisant une référence externe en résonance magnétique nucléaire pour déterminer et comparer des déplacements chimiques, il est très important de tenir compte de l'effet dû à la susceptibilité magnétique. Nous nous sommes servi de l'uridine-5′-phosphate et de références internes et externes pour bien démontrer l'importance de cette correction, spécialement lorsqu'on varie la température. Nous soulignons également la possibilité de variations de déplacements chimiques en sens opposés et la mise en garde contre le danger d'obtenir des énergies d'activation inexactes si de telles corrections ne sont pas appliquées.

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The use of external reference compounds for measurement of nuclear magnetic resonance (n.m.r.) chemical shifts is becoming increasingly widespread (1–4). This is principally to avoid

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