# Anodic Methoxylation of 9,10-Disubstituted Anthracenes. Comments on the Conformational Stability of 9,10-Dihydroanthracene Derivatives

VERNON D. PARKER, JOHN P. DIRLAM and LENNART EBERSON

Organic Chemistry 1, Chemical Center, P.O. Box 740, S-220 07 Lund 7, Sweden

Anodic oxidation of anthracene and 9,10-dimethylanthracene in methanol containing sodium methoxide results in the formation of II. In both cases, the *cis* isomer is preferred (3:1 with anthracene and 5:1 with 9,10-dimethylanthracene).[1,2] This reaction opens up a new route to both the *cis*- and *trans*-dimethoxy compounds, II, from a wide variety of 9,10-disubstituted anthracenes, I. In order to study
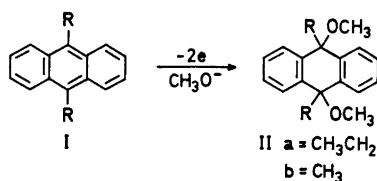

the conformational behaviour of II, the anodic methoxylation of I, with R being ethyl, propyl, and phenyl, was carried out, and the products were separated by fractional crystallisation. The reactions produced nearly quantitative yields of II, and in these three cases, nearly 1:1 mixtures of *cis* and *trans* isomers were obtained. The isomer distribution is easily determined from the methoxyl signals in the NMR spectra of the crude mixtures.

While this study was in progress, two reports appeared regarding conformations of the related *cis*- and *trans*-9,10-diethyl-9,10-dihydroxy-9,10-dihydroanthracenes.[3,4] The two groups [3,4] presented conflicting evidence and interpretations. Since the diethyl-dimethoxyl derivative (IIa) has the advantage that the chemical shifts of ethyl and methoxyl groups both serve as probes, we chose this system for conformational studies. The isomeric methoxy compounds (IIa) along with suitable model compounds (III – V) were prepared and

Table 1. Chemical shift (τ) for chloroform-d solutions, relative to TMS.

Compound		Chemical shift (τ)		
		CH₃	CH₂	CH₃O
IIa	*cis*	9.23	7.98	7.28
IIa	*cis*-diol [4]	9.18	8.28	—
IIa	*trans*	9.70	7.86	7.09
IIa	*trans*-diol [4]	9.78	7.85	—
IIb	*cis*	8.38	—	7.22
IIb	*trans*	8.29	—	7.22
III		9.77	7.78	—
IVa	locked e'-CH₃O	—	—	6.40
IVb	locked e'-Et	8.70	7.70	—
Va	locked a'-Et	9.25	—	—

the NMR spectra were examined. The pertinent spectral data are recorded in Table 1.
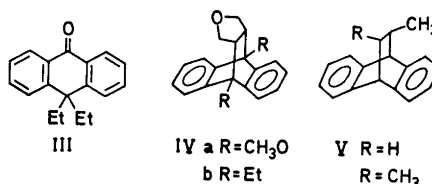
A striking feature of our data is that the shifts of the ethyl groups in *trans*-IIa are nearly identical to those observed for the corresponding *trans*-diol.[4] This indicates that the conformation of both derivatives is most likely the same. It has previously been noted that the methyl triplet (of the ethyl group) in the *trans*-diol is at unusually high field due to the shielding by the magnetic anisotropy of the aromatic rings.[3,4] This triplet in *trans*-IIa must represent an equal pseudo-axial-pseudo-equatorial contribution (planar on the NMR time-scale). A similar high-field value is observed for III.

In the case of the *cis*-IIa-diol where the triplet is shifted downfield *ca.* 0.6 ppm, Cohen *et al.*[3] postulated a boat conformer with the ethyl groups pseudo-equatorial. This assignment was supported by the presence of intramolecular hydrogen-bonding, which is only possible when the hydroxyl groups are *cis* and pseudo-axial. In contrast, MacMillan and Walker [4] observed no intramolecular hydrogen-bonding, and have proposed the other boat conformer with ethyl groups pseudo-

axial. This proposal was supported by comparison with model compounds in which the conformations is fixed (e.g. Vb and the photooxide of 9,10-diethyl-anthracene).

In the cis-dimethoxyl derivative (IIa) both boat conformers can clearly be ruled out by comparison with the model compounds IVa and IVb. The line of reasoning is as follows. If the ethyl groups were in the pseudo-equatorial positions, they would be predicted to be at ca. τ 8.7 as in IVb.[5] The value actually observed for the methyl triplet is τ 9.23, which is nearly identical to the axial ethyl group shift found in Va (as was the case in the cis-diol as well), but in such a conformation the methoxyl groups must be pseudoequatorial. The methoxyl signal at τ 7.28 is shifted slightly upfield relative to the trans isomer, instead of being shifted substantially downfield to ca. τ 6.4 as in IVa.

On the basis of our model compounds, neither boat conformer adequately explains the results for cis-IIa. Intuitively, we would expect that the conformational situation of cis- and trans-IIa not to differ appreciably; i.e. if one isomer is rapidly equilibrating, the other should also be. However, the NMR spectra show that the ethyl shifts are quite different, and one can argue that if both cis- and trans-IIa are nearly planar on the NMR time-scale, that almost identical ethyl shifts should be observed for the two isomers. We believe that the situation is more complex than the above argument indicates, and that chemical shift data do not constitute an entirely effective probe. This is illustrated by a comparable case; cis- and trans-IIb exhibit different shifts for the methyl groups, while the shift of the methoxyl groups are indistinguishable in the two spectra.[2] Using the chemical shift arguments, one would predict that since the methyl shifts of the two compounds differ, presumably due to differences in environments of the methyl groups in the two isomers, the shift of the methoxyl groups should also reflect this difference. We must emphasize that the model compounds do not rule out either shallow boat conformation for cis-IIa.

Experimental. NMR spectra (in CDCl₃) were recorded on a Varian A-60 spectrometer with internal TMS as reference. The anodic alkoxylations were carried out in the manner previously described.[2] Compound III was prepared by the method of Meyer and Schlös-

ser[6] and separated from the product mixture by column chromatography on neutral alumina. The ketone was eluted with ether, m.p. 134—135° (lit.[6] m.p. 135°). Compounds IVa and IVb were prepared by the Diels-Alder reactions of the corresponding anthracenes with maleic anhydride,[7] followed by lithium aluminum reduction[8] and acid catalyzed ring closure of the resulting diols. Compound IVa (m.p. 127—128°) gave the following NMR spectrum: τ 2.5—3.1 (m, 8, aromatics), 6.2—6.9 (m, 6), 6.40 (s, 6, methoxy groups). The mass spectrum (recorded at 70 eV on an LKB 9000 mass spectrometer) had the following peaks of interest: m/e 308 (M^+, 0.3 %), 238 (95 %), and 223 (100 %). Compound Va was obtained by lithium aluminum hydride reduction[9] (refluxing tetrahydrofuran as solvent) of the chloro compound prepared by Diels-Alder reaction of anthracene and allyl chloride.[10] The desired products (m.p. 91—92°) gave the following NMR spectrum: τ 2.7—3.2 (m, 8, aromatics), 5.84 (m, 1, bridgehead proton), 6.06 (m, 1, bridgehead proton), 8.0 (m, 2), 8.9 (m, 1), and 9.25 (d, $J = 6$ Hz, 3, methyl group). The mass spectrum was recorded at 70 eV: m/e 220 (M^+, 1.4 %) and 178 (100 %).

1. Parker, V. D. Doctoral Thesis, University of Lund, Lund 1970.
2. Parker, V. D. Acta Chem. Scand. In press.
3. Cohen, D., Hewitt, L. and Millar, I. T. J. Chem. Soc. C 1969 2266.
4. MacMillan, J. and Walker, E. R. H. Chem. Commun. 1969 1031.
5. A similar model compound, the photo-oxide of 9,10-diethylanthracene, shows a methyl triplet at τ 8.69.[4]
6. Meyer, K. H. and Schlösser, H. Ann. 420 (1919) 126.
7. Meek, J. S., Monroe, P. A. and Bouboulis, C. J. J. Org. Chem. 28 (1963) 2572.
8. Bussert, J. F., Greenlee, K. W., Derfer, J. M. and Boord, C. E. J. Am. Chem. Soc. 78 (1956) 6076.
9. Johnson, J. E., Blizzard, R. and Carhart, H. W. J. Am. Chem. Soc. 70 (1948) 3664.
10. Alder, K. and Windemuth, E. Ber. 71 (1938) 1939.

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