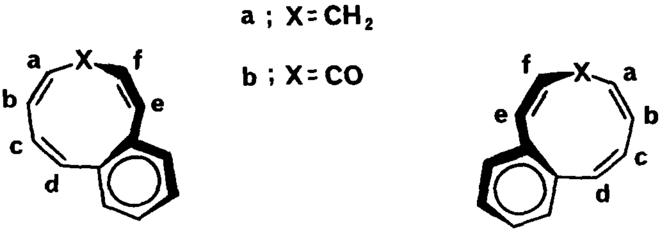
Tetrahedron Letters,Vol.24,No.40,pp 4279-4282,1983 0040-4039/83 $3.00 + .00
Printed in Great Britain

EVIDENCE FOR SKELETAL ENANTIOMERISM IN BENZO[9]ANNULENONE

A. G. Anastassiou[1] and M. Hasan
Department of Chemistry
University of Petroleum and Minerals
Dhahran, Saudi Arabia

The X-ray crystallographic molecular dimensions of the title substance 1b are reported and the molecule's tendency to adopt helically enantiomeric forms in solution is demonstrated with the use of a chiral NMR-shift reagent.

A particularly intriguing structural feature of the C_9 moiety of benzocyclononatetraene 1a[2] is its apparent inability to undergo molecular flattening without developing sterically congestive interaction between the two benzylic protons, H_d and H_e and their benzenoid "peri" neighbours, a revealing experimental observation in this connection being offered by the ready isomerization of the aromatically delocalized all-cis anion of 1a[3] to an equally diatropic mono-trans variant.[4] Translated into molecular dynamics this "peri" constraint[5] may reasonably be expected to give rise to a heightened inversion barrier relative to the parent molecule, 1,3,5,7-cyclononatetraene, and thus to the interesting possibility that 1 may exist as a racemate of two helically enantiomeric forms. We have tested this hypothesis experimentally and have, for obvious practical reasons, done so with the use of a highly crystalline, suitably functionalized relative of 1a, namely benzo[9]annulenone 1b.[6]



A 1 B

An X-ray crystallographic study of **1b**[7] yielded the molecular dimensions summarized in Figure 1 wich clearly establish the presence of a heavily buckled molecular frame possessing (i) uniformly compressed ethylene units and (ii) consistently wider-than-normal bond angles.

Torsion Angle	
Unit	Angle (τ)
C4-C5-C6-C7	-80.0°
C5-C6-C7-C8	0.0°
C6-C7-C8-C9	+59.3°
C7-C8-C9-C1	+10.7°
C8-C9-C1-C2	- 8.1°
C9-C1-C2-C3	-63.2°
C1-C2-C3-C4	+ 4.7°
C2-C3-C4-C5	+79.5°
C3-C4-C5-C6	+ 1.2°

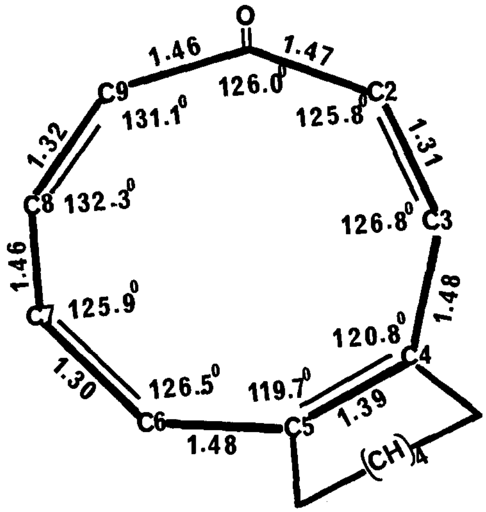


Figure 1. X-ray Molecular Dimensions[a] and Torsion Angles for Benzo[9] annulenone **1b**[7]

[a] Bond lengths given in angstroms (Å)

The interesting question as to whether the solid's pronounced skeletal helicity persists in solution as well, was examined by ^{1}H-NMR spectroscopy with the use of the *chiral* "shift" reagent tris(d,d-dicampholymethanato) europium (III) **2** or $Eu(dcm)_3$,[8] the reasoning being, of course, that if **1b** does indeed exist in solution as a skeletally-induced two component racemate, *e.g.*, A and B, complexation of its oxygen function with **2** ought to produce two diastereomeric environments incorporating chirally-related but magnetically distinct protons.

Brief examination of the well-resolved ^{1}H-NMR spectra recorded on mixtures consisting of various proportions of **1b** and **2**, summarized in Figure 2 immediately reveals the occurence of shifts and emergence of patterns which are entirely consistent with the development of a diastereomeric environment, the most pronounced shifts being, not unexpectedly, those associated with the protons closest to the site of complexation, *i.e.,* H_a($\Delta\delta$ = 15.2 Hz) and H_f($\Delta\delta$ = 12.7 Hz).[9] Further convincing evidence that the shifts seen in Figure **2** are due to helicity-induced diastereomerism rather than regioselective complexation by **2**, derives from the fact that use of the *non*chiral "shift" reagent $Eu(dpm)_3$ in place of **2** leads to the expected downfield NMR shifts relative to uncomplexed **1b** with full retention of the original patterns.

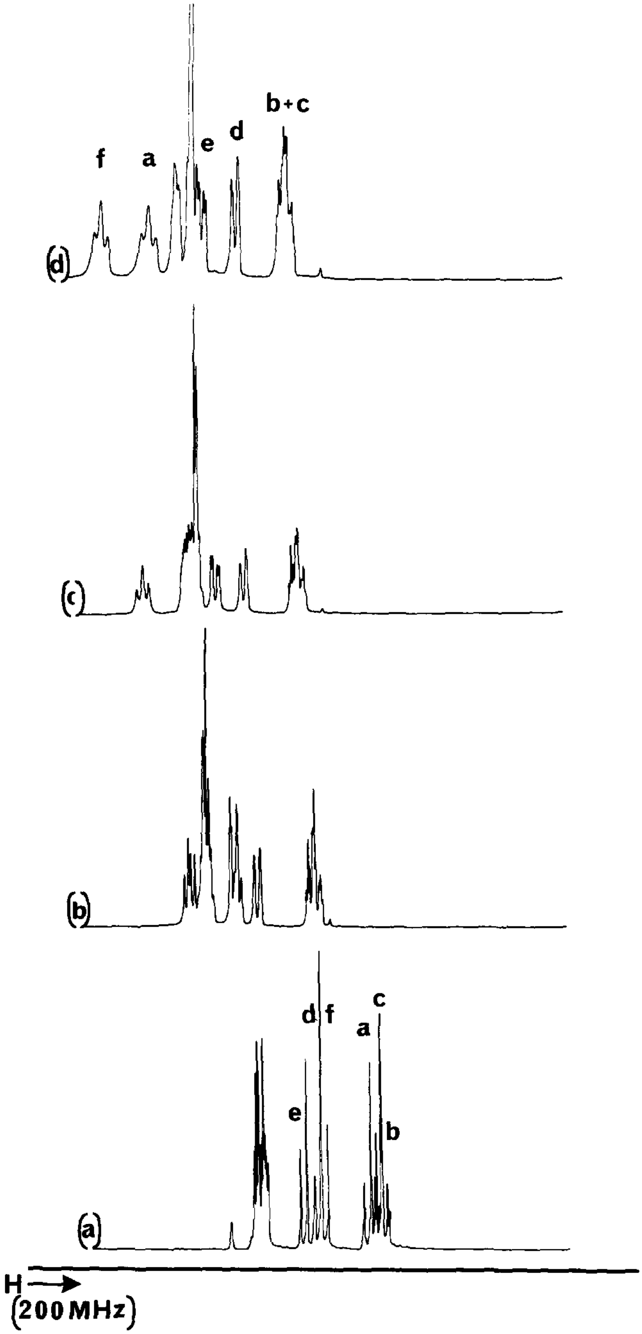


Figure 2. ^{1}H-NMR Spectra (benzene-d_6) of a. 1b, b. 1b + 2 (2/1b ~ 0.09)^a, c. 1b + 2 (2/1b ~ 0.11)^a, d. 1b + 2 (2/1b) ~ 0.18)^a.

^{a}Molar ratio

Acknowledgement: Financial support for this research (CY/NINERING/57) by the University of Petroleum and Minerals is gratefully acknowledged with special appreciation being expressed to Dr. F. D. Dakhil, Vice Rector for Research, whose strong support proved vital to the initiation of this project.

References and Notes

(1) On leave from the Department of Chemistry, Syracuse University, Syracuse, New York, 13210.
(2) A. G. Anastassiou, S. S. Libsch and R. C. Griffith, Tetrahedron Lett. 3103 (1973).
(3) A. G. Anastassiou and R. C. Griffith, J. Am. Chem. Soc., **96**, 611 (1974).
(4) A. G. Anastassiou and E. Reichmanis, Angew Chem., **86**, 784 (1974).
(5) A. G. Anastassiou, Acc. Chem. Res., **9**, 453 (1976).
(6) A. G. Anastassiou, M. S. Kasmai and M. R. Saadein, Helv. Chim. Acta, **64**, 617 (1981).
(7) Full details of this X-ray study conducted in this department by Prof. M. Haque and his group will be described elsewhere.
(8) This substance may be purchased in a good state of purity from the Ventron Division of "Alfa" Chemicals.
(9) Unequivocal distinction between these two key protons was offered by decoupling procedures.

(Received in USA 24 March 1983)