253. The Existence of Helical Chirality in a Sterically Congested Naphtho[9]annulenone

Preliminary Communication

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Summary

The existence of the naphtho[9]annulenone **1** in two skeletally enantiomeric forms is demonstrated with the use of ^{1}H-NMR. spectroscopy in conjunction with a chiral 'shift' reagent.

An interesting feature of cyclic frameworks which are sufficiently large to be nonplanar and to exist in a conformationally mobile state, is that restriction of such mobility should, in the absence of a center of symmetry, lead to the development of skeletal chirality. Work with the unsaturated nine-membered ring [1] has often raised the question as to whether congestive annulation might not sufficiently reduce the system's skeletal flexibility to the point of adopting a rigidly helical shape. The sterically congested naphtho[9]annulenone **1** [2] constitutes a suitable substance, and we examined this possibility by using ^{1}H-NMR. spectroscopy and a chiral 'shift'-reagent, namely tris(*d*, *d*-dicamphoylmethanato)europium(III) (Eu(dcm)$_3$, **2**)[2]). The reason for employing this composite system is that 'contact'

Table. *Chirally induced ^{1}H-NMR. shifts*[a]) *of* **1** *in the presence of Eu(dcm)$_3$* (**2**)

Run	Mol ratio	Signal separation (Δδ (Hz))						
	[**2**]/[**1**]	H_a[b])	H_b	H_c	H_d	H_g	H_h	H_o
1	0.21	16.0	5	4	2	[c])	[c])	7.7
2	0.25	[c])	6	5.8	3.5	[c])	[c])	9.0
3	0.38	[c])	13	11.3	6.0	5.5	[c])	18.1
4	0.52	72.9	18	16.4	9	[c])	10.6	27.0
5	0.71	96.2	23	21.5	11.9	[c])	10.8	35.2

[a]) 200 MHz in (D$_6$)benzene.

[b]) Unequivocal assignment relating to this proton by decoupling procedures in run 5.

[c]) Shift not available owing to signal overlap.

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[1]) On leave from Syracuse University.

[2]) This substance may be purchased in good purity from the *Ventron* Division of *Alfa* Chemicals.

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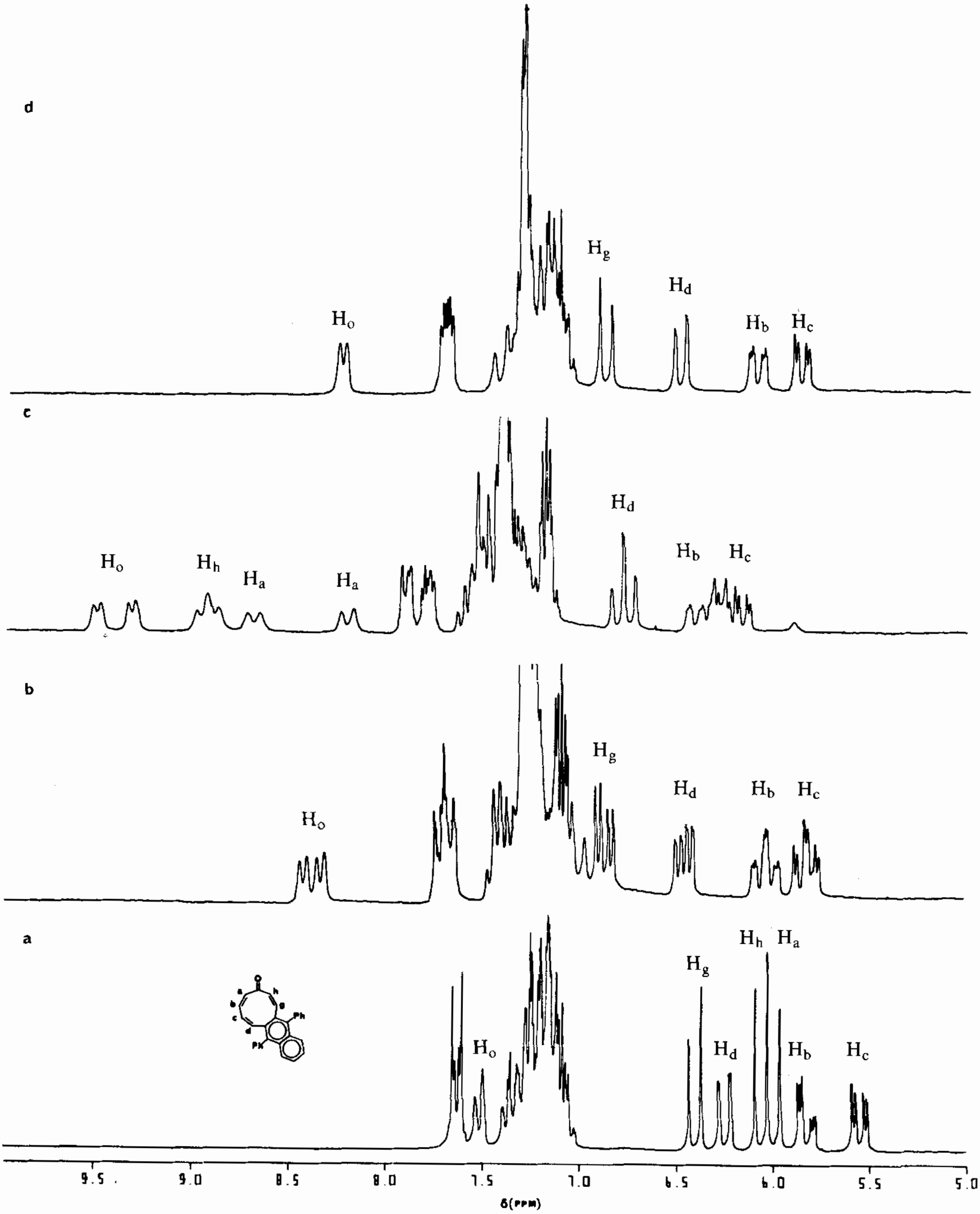

Figure. *^1H-NMR. spectra* (200 MHz, (D_6)benzene), *a:* **1**[a]); *b:* **1** + **2** (run 2 in the *Table*); *c:* **1** + **2** (run 5 in the *Table*); *d:* **1** + Eu(dpm)$_3$ (molar ratio: [Eu(dpm)$_3$]/[**1**] $\approx$ 0.27)

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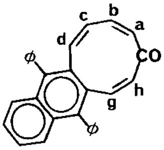
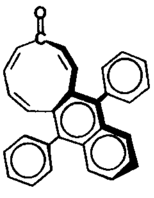
[a]) Measured coupling constants are as follows: J(a,b) = 12.9, J(b,c) = 3.6, J(c,d) = 11.9, J(b,d) = 1.6, J(g,h) = 12.6, J(o,m) = 7.3.

complexation between the carbonyl O-atom of helical enantiomers **A**, **B** and **2** would lead to two diastereoisomeric arrangements with pairs of chirally related but magnetically distinct protons H_a to H_h.

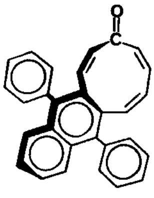
Our findings (*Table* and *Figure*) establish unequivocally that **1** indeed consists of two chirally related, conformationally rigid forms. The presence of **2** led to substantial separation between *all* enantiomerically related pairs of ring protons yielding the expected patterns (*Figure, b* and *c*) and enhancement in signal separation with increased amount of **2**. Particularly revealing in this connection is that the second most pronounced signal separation observed, *i.e.* between the lowest field doublets, measured at 35 Hz in run 5, relates *not* to a proton directly bound to the C_9-helix but rather to one whose general appearance in the spectrum (*d*, $J = 7.3$ Hz) requires it to be *ortho*-linked (H_o) to one of the phenyl appendages. The fact that such a proton experiences a helicity-induced shift in the ^{1}H-NMR. spectrum means that its phenyl host is subject to restricted rotation. Our interpretation is also strongly supported by the results of a suitable control experiment in which a mixture of **1** and the *nonchiral* shift reagent Eu(dpm)$_3$ displayed *(Figure, d)* the expected downfield ^{1}H-NMR. shifts relative to uncomplexed **1** but with *no change in overall pattern*[3]).



1



A



B

All attempts at this early stage to estimate key activation parameters for the skeletal inversion process required to interconvert helical enantiomers **A** and **B** were frustrated, not unexpectedly, by the fact that the degree of complexation between **1** and **2** decreases with increasing temperature as revealed by the observation of sharply reduced helicity-induced signal separation as well as overall downfield shifts. When recorded at 80° the ^{1}H-NMR. spectrum of the **1** + **2** mixture listed in (run 3, in the *Table*) displayed features distinctly similar to those of the uncomplexed host *(Figure, a)*.

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REFERENCES

[1] *A. G. Anastassiou*, Acc. Chem. Res. *5*, 281 (1972); ibid *9*, 453 (1976).
[2] *A. G. Anastassiou, H. S. Kasmai & M. Sabahi*, Chem. Commun. *1979*, 1031.

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[3]) Similar results were obtained upon using the *upfield* shift reagent (D_{27})Pr(fod)$_3$.