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[8]Paratropyliophane[1,2]

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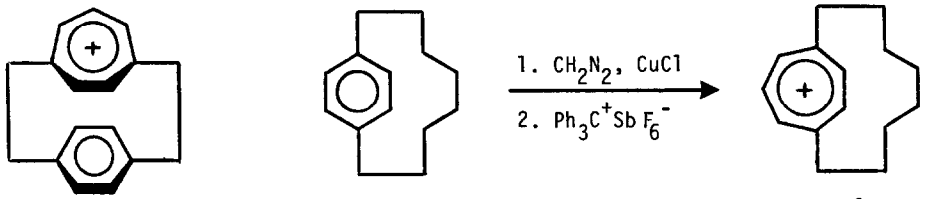
Abstract: The preparation of [8]paratropyliophane is described and its nmr spectral features are discussed with regard to ring strain and ring current shielding effects.

In examining a recent monograph on the subject of cyclophanes[3], we were surprised to find that the [n]paratropyliophanes were unknown. On the other hand, there have been two systems reported in the metatropyliophane series[4] and in 1976 cyclophane 1 was independently prepared by two different groups.[5] Herein we wish to report the synthesis and nmr spectral properties of the closely related [8]paratropyliophane (3).



1 2 3

Treatment of a mixture of [8]paracyclophane (2) and copper (I) chloride with diazomethane in dichloromethane resulted in 60% conversion (monitored by VPC) to a mixture of three isomers of an octamethylene bridged cycloheptatriene. According to a previously developed procedure[7], these trienes were not separated but rather the entire mixture was treated directly with tritylhexafluoroantimonate. Careful trituration with ethyl ether produced the tropylium salt 3 in an overall yield of 50% based on consumed [8]paracyclophane. The structure of 3 was confirmed by its nmr spectral features which are described below.

The aromatic protons of 3 appear as a broad singlet at 8.83 ppm which is exactly the value observed for the aromatic protons of the 1,4-dimethyltropylium ion. The 16 bridge protons of 2, resonating at 2.60, 1.42, 0.88, and 0.19 ppm, are a classic example of ring current shielding effects. The octamethylene bridge of 3 is less symmetrical, with 8 pairs of non-equivalent protons giving rise to three complex multiplets centered at 3.28(4H), 1.98(4H), and 1.05(8H) ppm. As has been observed for ortho-annelated tropylium salts, the four α-protons are deshielded by the cationic nucleus and absorb at lower field. This same deshielding effect appears to offset the ring current shielding effect, causing upfield shifts for the bridge protons to be less than observed for 2.

The aromatic carbon resonances of 3 are consistent with those observed earlier for annelated tropylium salts.[7] The α-methylene resonance occurs at 42.26 ppm which is about 5 ppm

downfield from the α-methylene carbons of the cyclohexenotropylium ion. The same difference is observed when comparing the α-methylene resonances of tetralin and 2. For the bridge carbons of 2, Misumi et al. claim that strain may obscure ring current effects, and they assign C_γ to higher field than C_δ.[8] The remaining three bridge carbons of 3 appear at values very close to those observed for 2. A tendency to assign these carbons in the same sequence as those of 2 is argued against by an examination of the bridge C-H coupling constants. All the bridge carbons of 2 show values of J_{CH} = 126 (±1) Hz which is similar to the coupling constant for cyclohexane[9] and implies that these carbons are hybridized alike. The situation for 3 is quite different with the coupling constant decreasing from 134 to 121 Hz as the associated resonance moves to higher field, suggesting that the α-methylene carbons are quite strained and hybridized similar to cyclobutane (J_{CH} = 136 Hz[9]). Ring strain appears to decrease along the chain, prompting us to assign C_γ and C_δ in the manner shown. The increased strain in the bridge may be understood when one considers that in expanding the aromatic ring from six carbons to seven the C_1-C_4 distance spanned by the octamethylene bridge is significantly increased.

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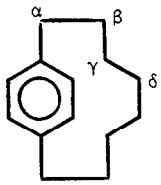
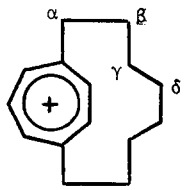
Table 1. ^{13}C NMR Data for Cyclophanes 2 ($CDCl_3$) and 3 (CD_3CN).



2

Carbon Resonance		J±1, Hz
140.42	(1,4)	
129.86	(2,3,5,6)	158
35.79	(α)	126
31.54	(β)	126
30.15	(δ)	126
26.07	(γ)	126



3

Carbon Resonance		J±1, Hz
177.96	(1,4)	
152.39	(6)	170
151.07 150.78	(2,3,5,7)	~166
42.26	(α)	134
31.61	(β)	128
28.07	(γ)	123
25.28	(δ)	121

References and Notes

1. Although the prefix "para" strictly refers only to benzene, it can also be unambiguously applied the tropylium nucleus.
2. Taken in part from the Ph.D. Dissertation of P. Chayangkoon, University of Houston, 1983.
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