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Novel polycyclic conjugated compounds containing eight-membered ring: on the aromaticity of [4n] annuleno[4n] annulenes

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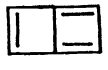
Abstract - Bicyclo[6.2.0]decapentaenes and related new members of [4n]annuleno[4n]annulenes were synthesised and their properties examined. It was shown that these compounds are diatropic in nature though not typical. Based on the experimental and recently reported theoretical studies, the following general conclusion is reached: [4n]annuleno[4n]annulenes can be, in principle, weakly aromatic, if strain in the planar or near planar geometry is not so large.

INTRODUCTION

An eight-membered ring conjugated system has a variable face depending on its electronic structure. For instance, cyclooctatetraene takes a deep tub form and accordingly is a polyolefin, whereas its dianion and dication are aromatic with planar geometry by virtue of a good deal of resonance stabilisation which exceeds strain energy associated with the planar eight-membered ring (ref. 1). In this regard, polycyclic conjugated compounds containing an eight-membered ring(s), especially planar or near planar one, are of interest as novel, potentially full conjugated systems. They are, however, still rather scarce.
In connection with our interest in the aromaticity of [4n]annuleno[4n]annulenes, we were interested in the properties of bicyclo[6.2.0]decapentaene 2 where the eight-membered ring is potentially planar due to aromatic stabilisation as a 10 π-electron system and/or fusion of a small ring and commenced the studies on 2 and related compounds. We here describe those results in relation to the question on the aromaticity of [4n]annuleno[4n]annulenes.

As well-known, the Huckel rule states that planar, monocyclic conjugated systems with 4n+2 π-electrons will be aromatic (ref. 2). This theoretical prediction has been proved experimentally (ref. 3). However, the applicability of this rule to polycyclic conjugated systems has been a matter of question. As a closely related problem, there has been a question about the properties of fused bicyclic conjugated systems composed of two 4n π-electron rings, namely [4n]annuleno[4n]annulenes. Important memberes are butalene 1, bicyclo[6,2,0]decapentaene 2, octalene 3, and related ionic compounds such as 4~8. These compounds have total 4n+2 π-electrons, and the question is whether they show aromaticity owing to total 4n+2 π-electrons or reflect strongly anti-aromaticity of the component 4n π-electron rings.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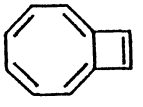
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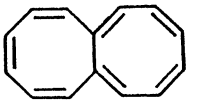
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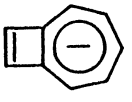
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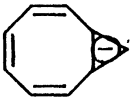
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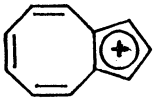
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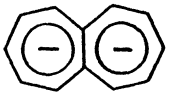
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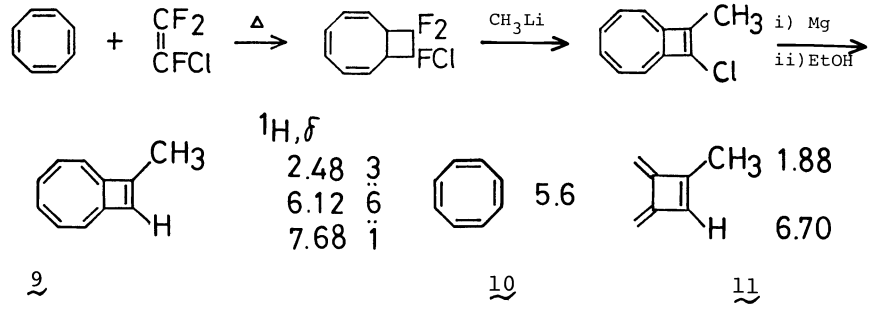
Until recently this problem has remained a matter of experimental and theoretical controversy.
Breslow et al. first worked on this problem experimentally, synthesising

benzooctalene (ref. 4) and more recently butalene 1 (ref. 5). Benzooctalene was a polyolefinic compound and 1 was a transient species. Schröder et al. synthesised a few derivatives of 2 as shown in Scheme 1 for 9-methylbicyclo-[6.2.0]decapentaene 9, the simplest derivative prepared, and described them to be polyolefinic substances (ref. 6). Dürr et al. prepared some derivatives of cation 7 briefly described as aromatic (ref. 7). Vogel et al. concluded dianion 8 to be rather aromatic based on the NMR studies (ref. 8). They also synthesised the parent octalene 3 but found this molecule to be nonaromatic with nonplanar geometry (ref. 9).
These results hardly point to any general conclusion on the problem, and further studies seemed necessary.

Scheme 1

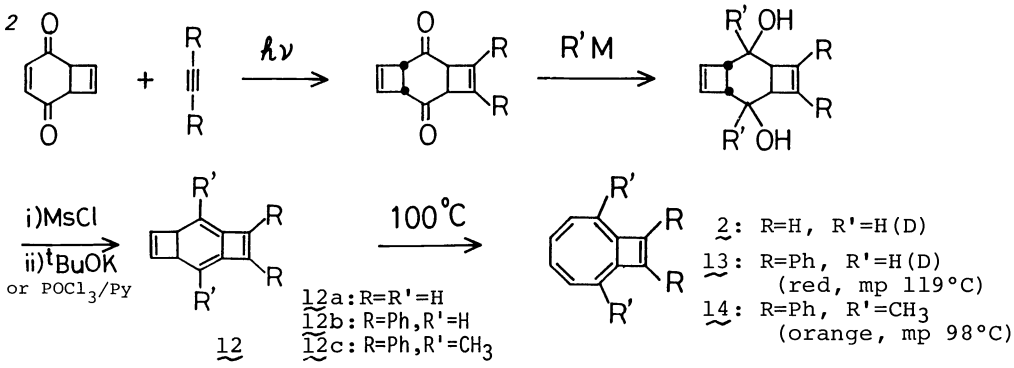


Though 9 was simply described as polyolefinic, its ^{1}H NMR data (Scheme 1) suggest diatropic nature because all the protons are observed at appreciably lower field than those of cyclooctatetraene 10 and 1-methyl-3,4-dimethylene-cyclobutene 11. Therefore, we started the synthesis of the parent hydrocarbon 2, which had remained unknown, and its crystalline derivatives in order to make the magnetic property clearer and in addition to elucidate the molecular geometry by X-ray crystallographic analysis.

BICYCLO[6.2.0]DECAPENTAENES

In view of fair thermal stability of the reported derivatives, we approached 2 through thermal electrocyclic ring opening of the tricyclic valence isomer 12, and this approach turned out good for not only phenyl derivatives 13 and 14 (ref. 10) but also 2 itself (ref. 11) (Scheme 2).

Scheme 2



The precursors 12b and 12c were obtained in moderate yields and their thermal isomerisation at 100°C was quantitative; however, the yield of 12a was poor despite efforts to improve and in addition its thermal reaction gave competitively 2 and its dimer in varied ratio depending on reaction time (ref. 11). Considerably large activation energies for the isomerisations (30 kcal mol^{-1}) should reflect the anti-aromatic destabilisation of cyclobutadiene at the transition state.
Recently Vogel et al. developed a new synthesis of 2 via tricarbonyl iron complex (ref. 12).
The parent hydrocarbon 2 is a red-orange, air-sensitive but thermally fairly stable (much more stable than benzocyclobutadiene) liquid and slowly dimerises at 100°C in benzene to give cyclooct[c]octalene. Deep red crystals of 13 are definitely stable at room temperature in a sealed glass tube and allowed X-ray crystallographic analysis, whereas 14 shows hypsochromic shift to orange and appears less stable.

Table 1 ^{1}H NMR data of bicyclo[6.2.0]decapentaenes and related compounds (* in C_6D_6, ** in CCl_4 or $CDCl_3$, δ ppm)

Compds	4-ring	8-ring	others
2	7.43 s	6.30 s*	—
Me 9	7.66	6.12**	2.48 (CH_3)
Ph Ph 13	—	6.32 2, 6.72 1 (6.24, 6.71)**	7.15 3, 7.55 2 (C_6H_5)
Me Ph Ph Me 14	—	5.98*	2.03 (CH_3)
15	—	5.97 1*, 5.52 2	7.52 (C_6H_4)
	2.38	5.3~5.6**	—
3	—	5.65**, 6.30	—

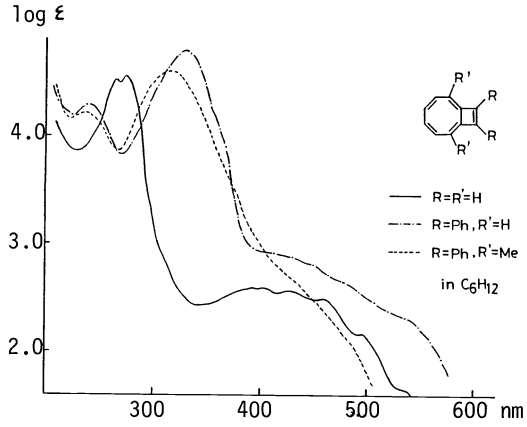


Fig. 1 UV-VIS spectra of 2, 13 and 14

Table 2 ^{13}C Chemical shifts of 2 and 13

	δ ppm ($CDCl_3$)
2	109.67 (C-2,7), 122.36, 122.61 (C-3,4,5,6) 140.50 (C-1,8), 143.43 (C-9,10)
13	108.57 (C-2,7), 122.61, 123.14 (C-3,4,5,6) 128.79 (C-2',3',5',6'), 129.13 (C-4') 132.25 (C-1'), 137.90 (C-1,8), 149.26 (C-9,10)

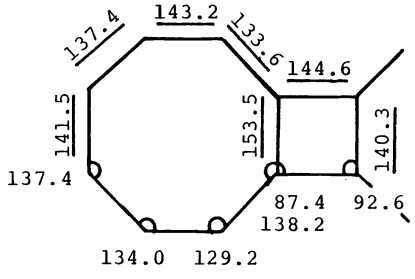
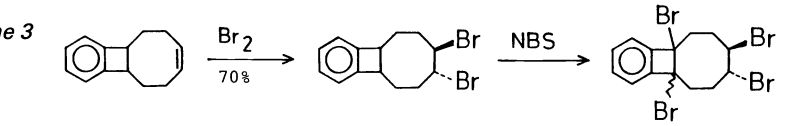


Fig. 2 Bond lengths (pm) and angles (°) of 13 by X-ray analysis

The physical peroperties are summarised in Table 1 and 2, and Fig. 1 and 2. Following features are notable. i) The chemical shifts of eight-membered ring protons of 2 and 13 are definitely lower than those of cyclobutacyclooctatetraene and 3 (Table 1). ii) Hypsochromic shift of 14 in the UV-Vis absorptions and up-field shift (less diatropicity) of the eight-membered ring protons relative to 13 suggest greater deviation of the decapentaene nucleus from coplanarity, and accordingly high sensitivity of the molecular geometry toward intramolecular steric interactions. iii) There are two kind of molecules of 13 with slightly different geometry in the crystal: while one decapentaene nucleus is essentially planar, the other one takes a shallow tub form with folding angle of 10°. This suggests again a delicate energy balance in the molecule. iv) Although bond alternation around the decapentaene periphery is obvious (Fig. 2, ref. 13), the degree is appreciably smaller than that of 10 (ref. 14) and dimethylenecyclobutene (ref. 15). v) Very importantly, the bond length between C-1 and C-8, which determines relative contribution of the 10 π and local 4n π-electron peripheries, is very long (153.5 pm) for a sp^2-sp^2 C-C single bond.

It is well known that fusion of a benzene ring to an aromatic system decreases delocalisation of π-electrons around the original periphery due to strong aromaticity of benzene. If bicyclo[6.2.0]decapentaene system is truly diatropic, fusion of benzene to 2 should decrease its diatropicity. 9,10-Benzobicyclo[6.2.0]decapentaene 15 was therefore synthesised according to Scheme 3 as a highly air-sensitive crystalline substance (ref. 16). Qualitatively it is even less stable than 2. The eight-membered ring protons are observed at about 0.6 ppm higher field than those of 2, while the benzo protons do at similar chemical shifts to naphthalene in contrast with weakly paratropic biphenylene (Table 1). These observations suggest that although some diamagnetic ring current is induced around the 14 π-electron periphery of 15, contribution of the local 8 π-electron periphery substantially increased relative to that in 2 in agreement with above expectation.

Scheme 3



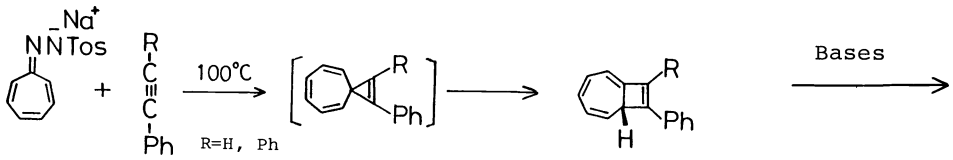
15

δ_{max} (C_6H_{12}) 261 (log ε 4.23)
287 (4.49)
297 (4.50)
382 (3.31)
402 (3.30)
426 (3.13)
454 (2.77) nm

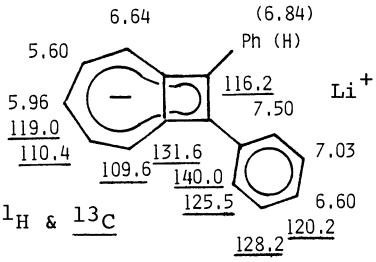
BICYCLO[5.2.0]- AND BICYCLO[6.1.0]NONATETRAENYL ANIONS

Next, we turned our attention to bicyclo[5.2.0]nonatetraenyl anion 5 and bicyclo[6.1.0]nonatetraenyl anion 6 which are isoelectronic to 2 and members of [4n]annuleno[4n]annulene.
8-Phenyl- and 8,9-diphenyl derivative of 5, 18 and 19, were readily obtained in thermally fairly stable solutions by deprotonation of respective precursors 16 and 17 with a variety of bases such as BuLi, $(i\text{-}Pr)_2NLi$ and CH_3SOCH_2Na (Scheme 4, ref. 17). Clean formation of 18 and 19 in DMSO (pK_a=35) indicates considerably higher acidity of 16 and 17 than cycloheptatriene (pK_a 36).
9-Phenylbicyclo[6.1.0]nonatetraenyl anion 22 was directly generated from chloride 20 by treatment with excess $(i\text{-}Pr)_2NLi$ (Scheme 5, ref. 18). The intermediate tetraene 21 is too strained to be isolated by usual procedures. but could be trapped as a Diels-Alder adduct with diphenylisobenzofuran.

Scheme 4



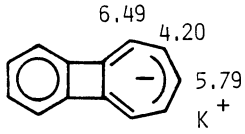
16:R=H; 17:R=Ph



δ^1H & ^{13}C

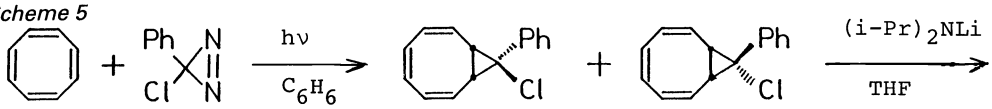
18:R=H; 19:R=Ph
$J_{2,3}$=8.3; $J_{3,4}$=9.3 Hz

23
δ_{av}=6.11



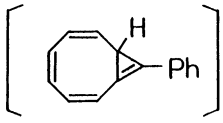
24
$J_{2,3}$=9.9 Hz
$J_{3,4}$=7.6 Hz

Scheme 5



m.p. 81°C 1 : 1 m.p. 75°C

20a 20b



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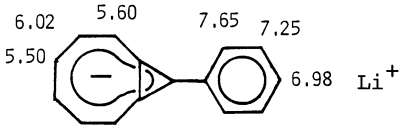
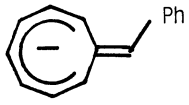


22
δ_{av}=5.70



25
δ_{av}=4.48

Anions 18 and 19 show little ion-pairing effects in the ^1H NMR spectra.

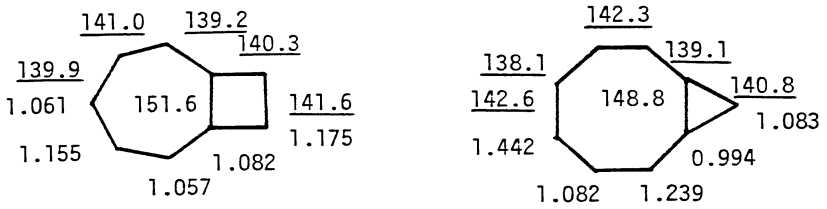
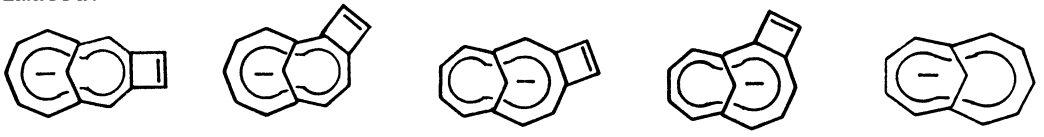


Fig. 3 Calculated bond lengths (pm) and π-electron densities of 5 and 6 by a variable β SCF-CI method (ref. 21)

The averaged chemical shift of the seven-membered ring protons of 19 (δ_{av}= 6.08) is comparable to that of aromatic 1,5-methano[9]annulenyl anion 23 (δ_{av}=6.11, ref. 19) and 0.6 ppm lower than that of 8,9-benzobicyclo[5.2.0]-nonatetraenyl anion 24 (δ_{av}=5.43, ref. 20). The small difference between $J_{2,3}$ (8.3 Hz) and $J_{3,4}$ (9.3 Hz) of 19 suggests good planarity of the bicyclic skeleton as well as rather small bond alternation if any. These observations are in agreement with the results of a variable β SCF-CI MO calculation which shows only a small bond alternation around the 10 π-electron periphery and a long juncture bond (Fig. 3, ref. 21). The same calculation predicts a greater bond alternation for 6. A good reference compound for 22 is benzylidenecyclo-octatrienyl anion 25 reported by Staley et al. (ref. 22). The latter anion is atropic and was suggested to have a locally delocalised structure as shown. The averaged chemical shift of the eight-membered ring protons of 22 (δ_{av}= 5.70) is, however, considerably lower than that of 25 (δ_{av}=4.48), demonstrating the diatropic contribution of the cyclic conjugation enabled by C-1,9 bonding.
Thus, anions 18, 19 and 22 are concluded to be rather diatropic. Since the phenyl group(s) would not perturb the electronic properties of the parent system severely, unsubstituted anion 5 and 6 would be also diatropic.

METHANO BRIDGED [4n]ANNULENO[4n] ANNULENYL ANIONS

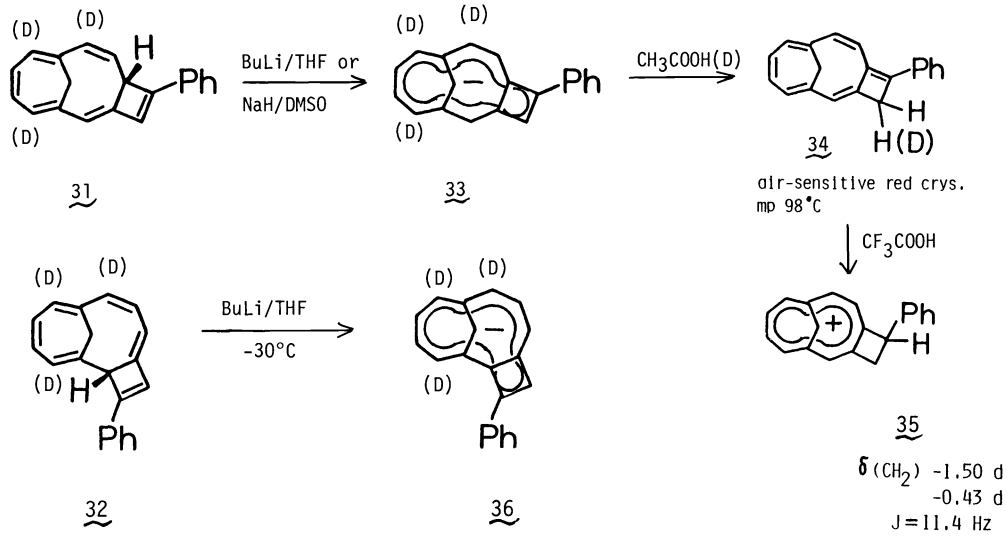
Although the three 10 π-electron [4n]annuleno[4n]annulene systems, 2, 5 and 6, have shown diatropic properties, their diatropicity is far from typical. This is a natural consequence, because they inevitably stand on a counter-balance between the total 4n+2 π-electron periphery and the local 4n π-electron peripheries. In order to obtain further support for the diatropic nature of planar or near planar [4n]annuleno[4n]annulenes, we chose cyclobutadiene-fused methano[11]annulenyl anions 26~29 for three reasons. i) There have been reported a good number of methano bridged annulenes suitable for NMR comparisons. ii) The bridge methylene protons of these annulenes are more sensitive towards ring current than the peripheral ring protons, thus providing a better measure for judgement of tropicity. iii) Staley et al. has prepared and revealed that 1,6-methano[11]annulenyl anion 30 shows a distinct paratropicity (ref. 23), and therefore, the effects of cyclobutadiene fusion can be directly estimated.



26 27 28 29 30

Jones et al. have reported the formation of 31 and 32, which could be suitable precursors for derivatives of 28 and 29, in their studies on 1,6-methano[10]-annulenyl carbene (ref. 24). The reaction also allows the preparation of trideuterated compounds starting from 2,5,7,10-tetradeuterio-1,6-methano[10]-annulene (ref. 25), which contributed to simplification of the complex ^{1}H NMR spectra.
Treatment of 31 with BuLi or CH_3SOCH_2Na cleanly gave expected anion 33 in deep green, thermally moderately solutions. When quenched with acetic acid, 33 gave undecafulvene derivative 34 which was further protonated to 10π aromatic methano[11]annulenyl cation derivative 35 in trifluoroacetic acid (Scheme 6). On the other hand, anion 36 generated from 32 by treatment with BuLi at low temperature was unstable and decomposed at -10°C. The difficulty of clean generation and instability has prevented full characterisation of 36.
The δ_{av} of annulene protons of 33 and 36, 6.52 and 5.07 respectively, are definitely higher than that (2.89, ref. 23) of paratropic 30. While 33 appears appreciably diatropic, 36 is rather atropic. This view is further supported by the chemical shifts of the bridge methylene protons (Table 3).

Scheme 6



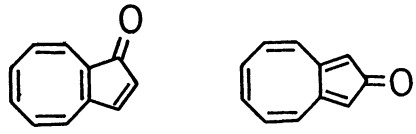
The averaged chemical shift of methylene protons of 33 (δ_{av}=0.61) is higher by as large as 11.6 ppm than that of 30 (δ_{av}=12.30) and close to those of typically aromatic methano bridged annulenes. Thus, the fusion of a cyclobutadiene to 30 forming 28 causes a striking change of tropicity from clear paratropicity to moderate diatropicity. One of the methylene protons of 36 has not been observed due to experimental problem associated with its instability. The signal is believed to be hidden in the signals of butane from BuLi, and δ_{av}=3.0±0.5 is estimated. The decrease of diatropicity in 36 may be ascribed to increase of strain in the near planar conformation due to fusion of the four-membered ring next to the bridge-head carbon. Accordingly, 33 must better stand for near planar [4n]annuleno[11]-annulenyl anion. In this regard symmetric anion 26 is of interest, because it would also show a substantial diatropicity.

Table 3 The chemical shifts of the methylene protons of 1,6-methano[11]annulenes

	Ha	Hs	$\frac{Ha+Hs}{2}$
	−0.25	−1.74	−1.00
	−0.81	−0.49	−0.65
33	−0.05	1.26	0.61
	0.04	1.68	0.86
	0.3	2.2	1.25
	0.21	3.72	1.97
36	—	4.77	2.5~3.5
	1.24	6.28	3.76
30	10.4	14.19	12.30

BICYCLO [6.3.0] UNDECA-2,4,6,8,11-PENTAENE-10-ONE

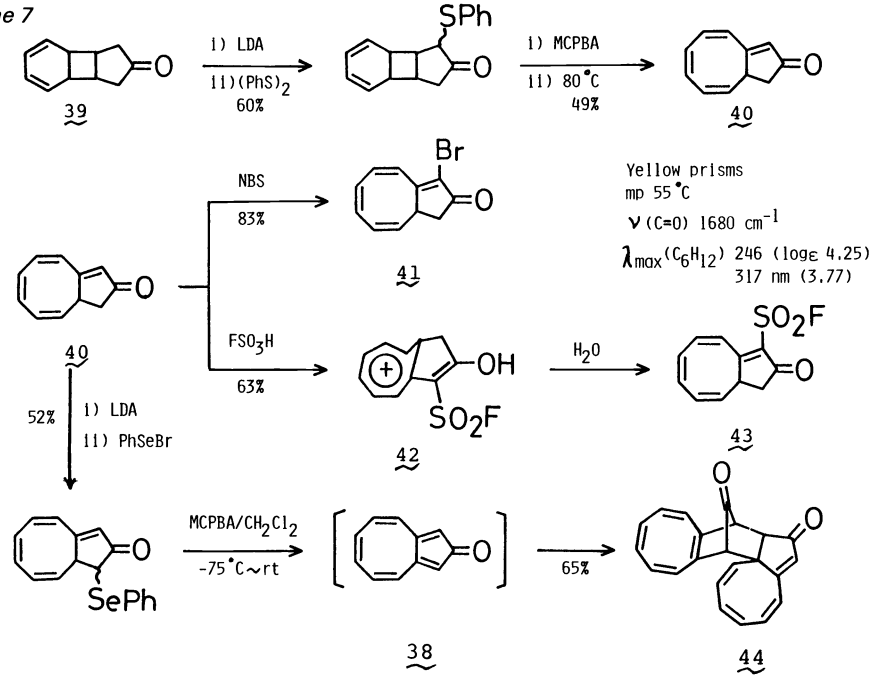
Although some derivatives were prepared and isolated (ref. 7), the parent cation 7 remains unknown. In connection to the qestion on the aromaticity of 7, the properties of its ketonic congeners such as 37 and 38 are of interest. Breslow et al. synthesised a monomethyl derivative of 37 as an unstable but very basic substance (ref. 26). We have attempted the synthesis of 38 (Scheme 7, ref. 27). Phenylsulfenylation of tricyclic ketone 39 followed by oxidative elimination gave bicyclic tetraenone 40. This ketone is appreciably basic probably owing to the contribution of homotropylium ion structure, and gave bromo substituted ketone 41 on attempts to brominate the methylene carbon with N-bromosuccinimide. Dissolution of 40 in fluorosulfonic acid appears to generate protonated cation 42 (^{1}H NMR) which gave again substituted ketone 43 on dilution with water. Generation of 38 was achieved through phenylselenylation of 40 and subsequent oxidative elimination. But 38 dimerised to 44 under the reaction conditions. Thus, 38 is not sufficiently stabilised as a 10 π-electron system but rather



37 38

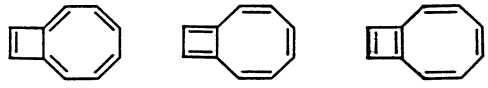
behaves as a derivative of cyclopentadienone. However, we expect some resonance stabilisation of 38 relative to other disubstituted cyclopentadienones, and attempts to isolate are under way.

Scheme 7



THEORETICAL HISTORY ON BICYCLO[6.2.0]DECAPENTAENE

Simple HMO or graphtheoretical considerations have predicted non-aromatic or anti-aromatic character of bicyclo[6.2.0]decapentaene (ref. 28-32). Among these, Randic's "Conjugated Circuits" leads to a strong anti-aromaticity (ref. 30). This theory, however, treats the three canonical forms 2a, 2b and 2c in equal weights, and hence overestimates anti-aromatic contribution of 2b and 2c. Aihara reported based on his graph theory that 2 is diatropic but anti-aromatic in nature (ref. 32). An MMP2 force field calculation by Allinger et al. also resulted in anti-aromatic character with a resonance energy of -4 kcal mol^{-1} (ref. 33). A MNDO study suggested, however, that 2 behaves as a peripheral 10 π-electron system (ref. 34). A CNDO/S method was used for assignments of the absorption spectra (ref. 35). Recently Cremer et al. performed ab initio HF/STO-3G and MNDOC calculations and reached a conclusion that 2 is weakly aromatic with a resonance energy of 4 kcal mol^{-1} (ref. 36). Nakajima et al. investigated octalene 3 by MNDO and ab initio methods, and found that the peripherally delocalised structure is the most stable among the planar structures of 3 (ref. 37).



2a 2b 2c

CONCLUSIONS

Thus, both experimental and theoretical results point to aromatic character of bicyclo[6.2.0]decapentaene 2. This is further supported by the recent results from heat of hydrogenation of 2 (ref. 38). The diatropic anions 5, 6 and 28 described in the text would be also weakly aromatic. Therefore, we conclude that [4n]annuleno[4n]annulenes can be in principle aromatic. Butalene 1 is too strained to be characterised well. Planar octalene 3 is substantially strained, and accordingly a non-planar conformation is more stable.

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