mechanism. To this end 2 mM solutions of **2** in $CHCl_3$/DMSO (9:1 v/v) were titrated with DNB both in the absence and in the presence of 8 mM KSCN. The absorbances of the solutions were monitored at 415 nm during the titrations. Fitting of the data gave association constants of 1.2 ± 0.3 M^{-1} and 7.2 ± 1 M^{-1} for the salt-free and the potassium-containing solutions, respectively. These results show that binding of DNB is stronger by a factor of 6 in the presence of potassium ions. This enhancement is caused by the conversion of **2** into the *aa* conformer and not by an ionic strength effect, as we verified in a control experiment with 2,7-dimethoxynaphthalene and DNB.

The magnitude of the allosteric effect depends on the solvent mixture used. We observed by UV-vis that in $CHCl_3$/DMSO (3:1 v/v) the increase in DNB binding by KSCN is only 1.7 (K_a without KSCN, 0.3 ± 0.15 M^{-1}; K_a in the presence of 4 equiv KSCN, 0.5 ± 0.12 M^{-1}). An approximately 2-fold increase was calculated from ^1H NMR experiments, measuring the induced shifts on DNB. Further experiments are in progress.

Synthesis of the First Large Annulene Fused to Cyclopentadienide. A Comparison of the Effective Aromaticity of Cyclopentadienide Anion with Benzene

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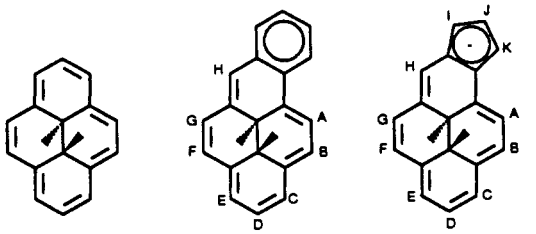
While the cyclopentadienide anion (Cp^-) is the prototype and best known of the charged aromatic species, very few experimental comparisons of its aromaticity with that of benzene are available. We here present evidence that the effective aromaticity of Cp^- is substantially less than that of benzene, contrary to most calculations.

When resonance energies of aromatic molecules are calculated, the reference compound used is a (hypothetical) polyene with the same number of atoms. Thus in a comparison of Cp^- with benzene, the two reference compounds are different. A comparison of resonance energies can therefore be somewhat misleading. For example, both Aihara[1] and Trinajstic[2] calculate that Cp^- has a greater resonance energy than benzene. Only Dewar,[3] using MINDO/3, has suggested that the aromatic stabilization energy (ASE) of Cp^- is about half that of benzene, although he points out that his estimate may be too low. Two more recent calculations of indices of aromaticity suggest that Cp^- might be somewhat less aromatic than benzene.[4,5] The only experimental evidence, so far, comes from Bordwell's[6] measurements of acidity of Cp in DMSO, from which he estimates the ASE of Cp^- to be about 24-27 kcal/mol, similar to that calculated for benzene. We have found that aromaticity can be probed by examination of the annelation effects from fusion of the aromatic molecule in question on to a [14]annulene, dimethyldihydropyrene (**1**).[7,8] Thus, Cp^- can be directly compared to benzene by comparison of the two



1 2 3

fused annulenes **2** and **3**. The more aromatic species will suppress the macrocyclic ring current to a greater extent and will result in a less shielded chemical shift for the internal methyl protons of **2** or **3**, resulting in less deshielded distant protons, H_D, in more alternating bond orders, and hence, in different vicinal coupling constants in the macrocyclic ring of **2** or **3**. No hypothetical reference molecules are required, and the measurements are simple, although in a charged species the effect of the charge will have to be considered. To date, however, no large-ring annulenes have ever had a Cp^- fused on to them; thus the stability of such a system was unknown.

Hopf's[9] route to the indenophane anions looked most promising and was adapted for the synthesis of **3** as shown in Scheme I. The green cyclopentadiene, **6**, mp 114-116 °C, showed its internal methyl protons at δ -4.15 and -4.16, indicating no disturbance of the ring current of **1**. Since **6** was not very stable, it was chromatographed immediately prior to its conversion to **3**, which was achieved by using KH in dry d_8-THF. The resulting red solution of **3** gave the ^1H NMR data given in Table I. The spectrum was also run in the presence of [2.2.2]cryptand to simulate a cation-free anion; however, changes in chemical shift were all small (see Table I). Immediately apparent is the large difference between the chemical shift of the methyl protons of **3** and the benzo derivative **2**. *If* the methyl protons are not much affected by the charge, this would clearly indicate Cp^- to have an aromaticity substantially less effective than that of benzene! As will be explained below, we believe that the effect of the charge on the methyl protons of free $\mathbf{3}^-$ is small, giving a shielding of about 0.4 ppm, and that the chemical shift of the methyl protons which should be used for comparison with **2** is thus about -2.8 ppm (-3.2 + 0.4). Two specific approaches and one more general approach yield this result. π-SCF calculations on free $\mathbf{3}^-$ indicate that about 40% of the charge is delocalized over the macrocyclic ring. From the atom charge densities, corrected chemical shifts for the external protons A-H can easily be calculated from known[10] relationships, and these are given as the corrected values in Table I. The value for H_D can then be used to predict the chemical shift for the internal methyl protons using the correlation[11] $\delta_{Me} = 16.94 - 2.60\delta_H$ and yields a value of $\delta_{Me} = -2.6$ *corrected for delocalized charge*. This correction of about 0.6 ppm is the same as would be calculated on the basis of the difference in chemical shift of H_a between $\mathbf{7}^{2-}$ and $\mathbf{7}^{2+}$, which is observed[12] to be 2.8 ppm, where there is on average a difference of 0.3 unit charge per atom between these species. In $\mathbf{3}^-$ there is only 0.07 unit charge (maximum) per atom. Similarly, the difference in chemical shift between H_a of the neutral [14]annulene[13] **8** and the [14]annulenyl anion[14] **9** (δ -1.13 and -0.84, respectively) is also small, as is the difference in chemical shift[15] of H_a (0.4 ppm) in **10** and **11**. On the basis of molecular mechanics calculations, both have H_a placed

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(12) Mullen, K.; Meul, T.; Vogel, E.; Kurschner, U.; Schmickler, H.; Wennerstrom, O. *Tetrahedron Lett.* **1985**, *26*, 3091-3094.
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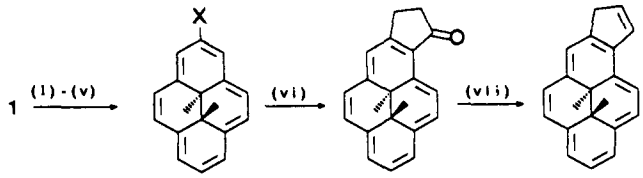
Scheme I[a]

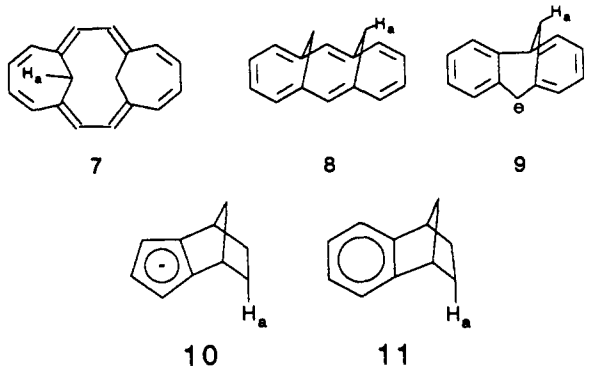


[a] **4a-e**: **a**, X = CHO; **b**, X = CH=CHCOOEt; **c**, X = CH_2CH_2COOEt; **d**, X = CH_2CH_2COOH; **e**, X = CH_2CH_2COCl. (i) $TiCl_4/Cl_2CHOMe$, 75%; (ii) $(EtO)_2P(O)CH_2COOEt/NaH$, >95%; (iii) Pd/H_2, >95%; (iv) aqueous NaOH, >90%; (v) $(COCl)_2$; (vi) $BF_3{\cdot}OEt_2$, 63% from **4e**; (vii) LAH, then 20% aqueous HCl, room temperature, 81%.

Table I. ^{1}H NMR Data (δ) for Anion **3** and Benzannulene **2**

proton	3^--K^+	3^--{K^+ cryptand}	3^- (corrected)[a]	**2**
Me	−2.85	−3.17	−2.6	−1.62
A	7.79	7.92	8.71	8.09
B	7.61	7.70	7.97	7.36
C	7.55	7.58	8.10	7.50
D	6.90	6.83	7.50	7.13
E	7.39	7.41	8.13	7.35
F	7.57	7.59	8.39	7.61
G	7.70	7.71	7.93	7.68
H	8.25	8.35	8.08	7.88
I	6.67	6.76		
J	6.97	7.10		
K	7.30	7.43		

in similar positions with respect to the center of the aromatic rings, *and in a similar position to the methyl protons of **2** and **3** with respect to the 6π rings.*



Finally, the coupling constants[16] of the macrocyclic rings in **2** and **3** give information on the bond orders[17] and hence on the delocalization.[18] The calculated chemical shift of the methyl protons of 3^-, based on the coupling constants, is −2.9 ppm. Thus, from the above estimates, δ_{Me} can be taken to be −2.8 ppm in comparison to the values of −1.6 ppm for **2** and −4.2 ppm for **1**. On this basis Cp^- has about 54% of the effective bond-fixing ability ("effective aromaticity") of benzene. That the effective aromaticity of Cp^- is less than that of benzene is certain when one combines this shift data together with the alternance parameters[17] (ratio of adjacent bond orders) for the macrocyclic rings of 1.20 (5) for 3^- and 1.47 for **2**, and the substantially more deshielded ring protons (corrected) for **3** than **2**. Even if none of the charge were delocalized over the large ring, the chemical shift change is not enough to reach the value for **2**. The fact that the charge is delocalized indicates that aromatic stabilization of the 6π anion is not large enough. According to the metalloaromaticity principle of Fenske,[19] complexation to give Cp–M derivatives should increase its aromaticity. We are currently investigating this.

Acknowledgment. We thank the University of Victoria and the Natural and Engineering Research Council of Canada for financial support.

(16) **3**: J_{CD} = 7.87 Hz; J_{DE} = 6.78 Hz; J_{FG} = 8.33 Hz; J_{AB} = 7.05 Hz. **2**: J_{CD} = 8.79 Hz; J_{DE} = 6.44 Hz; J_{FG} = 8.67 Hz; J_{AB} = 6.20 Hz.

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Entrainment by R•/R′MgBr Exchange

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Bromocyclopropane (CpBr) in pure diethyl ether (SH) reacts completely with magnesium metal, but the yield of the Grignard reagent (CpMgBr) is limited to about 50% by the formation of cyclopropane (CpH) and other byproducts.[2] The CpMgBr yield is enhanced by the presence of hexylmagnesium bromide (HxMgBr), by coreaction with 1-bromohexane (HxBr) or both (Table I).

The effect of HxBr is an example of "entrainment", a technique introduced in 1934 by Victor Grignard to induce RMgX formation in difficult cases.[3-5] In entrainment, the yield of RMgX is enhanced by allowing magnesium to react with a mixture of RX and an auxiliary halide R′X that readily forms a Grignard reagent R′MgX.[6] Explanations involving halogen–metal exchange (eq 1) have been ruled out in several cases, and no other chemical

$$RX + R'MgX \rightarrow RMgX + R'X \qquad (1)$$

basis has been found.[7] Instead, physical effects such as surface cleaning have been suggested.[3b,7] Since CpBr does not react with HxMgBr in SH (7 h at 34 °C) in the absence of magnesium, reaction 1 is also ruled out here, but the product distributions in Table I indicate another chemical basis for at least part of the entrainment effect.

The yield of CpMgBr is diminished by the attack of intermediate radicals Cp• on SH [giving CpH, CpS, SS, and S(−H) (ethyl vinyl ether)].[2] In contrast, 1-bromohexane (HxBr) gives HxMgBr without significant solvent attack.[2] When CpBr reacts in the presence of HxMgBr (preformed, formed during the reaction, or both), the increase in the yield of CpMgBr is accompanied by a decrease in that of SS, the appearance of CpHx and HxS, and the disappearance of some HxMgBr. These results are consistent with reaction 2 (R = Cp, R′ = Hx) (or its equivalent) and Scheme I.[8]

$$R^{\bullet} + R'MgBr \rightarrow RMgBr + R'^{\bullet} \qquad (2)$$

(1) Permanent address: Institute of Organic Chemistry, University of Veszprém, 8201 Veszprém, Hungary.

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(4) The general synthetic problem of reluctant RMgX formation has been successfully attacked with finely divided and especially reactive magnesium metal.[5]

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(6) Subsequently, "entrainment" has also been used to describe reactions with auxiliary halides, such as 1,2-dibromoethane, that do not form Grignard reagents.[5]

(7) Kharasch, M. S.; Reinmuth, O. *Grignard Reactions of Nonmetallic Substances*; Prentice-Hall: New York, 1954, pp 38–45. About two dozen examples of entrainment of reluctant aryl halides and one alkyl halide are cited: Tables II–VIII, pp 41–42.

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