

**23** ( $R^1 = C_6H_5$ ,  $R^2 = CO_2CH_3$ ): yield 80%, bp 120 °C (0.2 torr),  $[\alpha]_D^{20} +150.5^\circ$  ( $c$  0.5,  $C_6H_6$ ); optical yield 84% ( $S$ ) ( $[\alpha]_D^{20}$  174.8° ( $C_6H_6$ ) for the pure  $S$  enantiomer<sup>67</sup>);  $^1H$  NMR ( $CDCl_3$ )  $\delta$  3.3 (br s, 1 H), 3.75 (s, 3 H), 7.3 (s, 5 H);  $^{19}F$  NMR ( $CDCl_3$ )  $\delta$  -72.07 ( $R,R$ ), -72.21 ( $R,S$ ), in relative proportion of 10:90, ee 80% ( $S$ ).

**23** ( $R^1 = C_6H_5$ ,  $R^2 = CO_2(CH_2)_2OCH_3$ ): yield 61%;  $^1H$  NMR ( $CDCl_3$ )  $\delta$  3.15 (s, 3 H), 3.4 (m, 3 H), 4.1 (m, 2 H), 5.0 (s, 1 H), 7.2 (s, 5 H);  $^{19}F$  NMR ( $CDCl_3$ )  $\delta$  -71.97 ( $R,R$ ), -72.70 ( $R,S$ ), in relative proportion of 25:75, ee 50% ( $S$ ).

**23** ( $R^1 = 4-C_2H_5C_6H_4$ ,  $R^2 = CO_2CH(CH_3)_2$ ): yield 55%, bp 110 °C (0.2 torr);  $^1H$  NMR ( $CDCl_3$ )  $\delta$  1.4 (d, 6 H), 1.6 (q, 2 H), 3.4 (br s, 1 H), 5.1 (s, 1 H), 5.1 (h, 1 H), 7.2-7.5 (m, 4 H);  $^{19}F$  NMR ( $CDCl_3$ )  $\delta$  -71.81 ( $R,R$ ), -72.17 ( $S,R$ ), in relative proportion of 26:74, ee 48% ( $S$ ).

**Reductions of Activated Ketones 22 by 7a, R = CH(CH<sub>3</sub>)<sub>2</sub>, to the Corresponding Alcohols.** **23** ( $R^1 = C_6H_5$ ,  $R^2 = CF_3$ ): yield 58%;  $[\alpha]_D^{22} +9.7^\circ$  ( $c$  0.2, EtOH); optical yield 68% ( $S$ ) ( $[\alpha]_D^{24} +14.2^\circ$  ( $C_6H_6$ ) for pure  $S$  enantiomer<sup>68</sup>).

**23** ( $R^1 = C_6H_5$ ,  $R^2 = CONHC_2H_5$ ): yield 37%;  $[\alpha]_D^{20} +26.5^\circ$  ( $c$  0.58, EtOH); optical yield 78% ( $S$ ) ( $[\alpha]_D^{16} -34.4$  (EtOH) for the pure  $R$  enantiomer<sup>69,70</sup>).

**23** ( $R^1 = C_6H_5$ ,  $R^2 = CONH_2$ ): yield 69%;  $[\alpha]_D^9 +47.8^\circ$  ( $c$  0.55,  $CH_3COCH_3$ ); optical yield 64% ( $S$ ) ( $[\alpha]_D^9 +74.4^\circ$  ( $CH_3COCH_3$ ) for the pure  $S$  enantiomer<sup>70,71</sup>).

**Reductions of Activated Ketones 22 by 7a, R = CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>, to the Corresponding Alcohols.** **23** ( $R^1 = C_6H_5$ ,  $R^2 = CONHC_2H_5$ ): yield 30%;  $[\alpha]_D^{16} +29.1^\circ$  ( $c$  0.43, EtOH); optical yield 85% ( $S$ ).

**23** ( $R^1 = 3-C_6H_5OC_6H_4$ ,  $R^2 = CO_2CH_3$ ): yield 55%;  $[\alpha]_D^{20} +45.8^\circ$  ( $c$  0.36, EtOH); optical yield 60% ( $S$ ) ( $[\alpha]_D^{25} +75.9^\circ$  (MeOH) for the pure  $S$  enantiomer<sup>72</sup>).

**23** ( $R^1 = 3-C_6H_5OC_6H_4$ ,  $R^2 = CONH_2$ ): yield 58%;  $[\alpha]_D^{20} +6.3^\circ$  ( $c$  1.2,  $CH_3OH$ ); optical yield 21% ( $S$ ) ( $[\alpha]_D^{25} +30.3^\circ$  for the pure  $S$  enantiomer<sup>73</sup>).

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**Supplementary Material Available:** Details of synthesis, melting points, NMR spectra, mass spectra, and optical rotations of the compounds not listed belonging to the series **10**, **11**, **12**, **14**, **17**, **19**, **20**, **21**, **26**, **27**, and **31** together with other necessary synthetic information and references (43 pages). Ordering information is given on any current masthead page.

## Substituent and Conformational Effects on the Ring Current in 9-Arylmethylenecyclooctatrienyl Anions

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**Abstract:** Treatment of *anti*-9-[1-(4-X-phenyl)]-*cis*-bicyclo[6.1.0]nona-2,4,6-trienes (**4a-e**) ( $X = OCH_3$ ,  $CH_3$ ,  $H$ ,  $Cl$ , and  $Br$ ) with lithium amide in liquid ammonia causes formation of the corresponding 9-[1-(4-X-phenyl)]methylenecyclooctatrienyl anions (**1a-e**). A conformational analysis based on their  $^1H$  NMR spectra led to the conclusion that electron acceptors cause an increase in the angle ( $\theta$ ) formed by the planes of the two rings in **1a-e** and that  $\theta$  is smaller than in the corresponding 9-[1-(4-X-naphthyl)]methylenecyclooctatrienyl lithiums (**2a-d**) ( $X = OCH_3$ ,  $CH_3$ ,  $H$ , and  $Cl$ ). The chemical shifts of the eight-membered ring protons in **1a-e** and **2a-d** in liquid ammonia (as well as in hexamethylphosphoramide for **2a-d**) exhibit an inverse substituent effect when plotted against Hammett  $\sigma$  parameters. This effect arises from a decreased paramagnetic contribution to the ring current in the eight-membered ring as  $\pi$ -electron donors cause an increase in the energy gap between occupied and unoccupied orbitals, particularly the HOMO and LUMO. This conclusion is supported by ring current calculations based on the London-McWeeny formalism. Comparison of the  $^1H$  NMR spectra of **1c**, **2c**, and 9-(2-naphthyl)methylenecyclooctatrienyl anion (**3**) demonstrates a dependence of the ring current in the eight-membered ring on  $\theta$ . The relationship between Hückel molecular orbital parameters and the paramagnetic component of the ring current is also discussed.

The existence of a "ring current" in planar, cyclic, delocalized molecules perturbed by an external magnetic field has been inferred from the enhanced diamagnetic susceptibility (diamagnetic susceptibility exaltation)<sup>2,3</sup> exhibited by these compounds as well as from their unique shielding and deshielding effects on nearby magnetic nuclei (most commonly protons) as determined by NMR spectrometry. The ring current model has been the target of some criticism<sup>4,5</sup> (which has in each case been answered<sup>6,7</sup>) and is now generally accepted.<sup>8</sup>

Ring currents can, in principal, be understood on the basis of the Ramsey screening tensor,<sup>9</sup> which is the sum of a diamagnetic ( $\sigma_d$ ) and a paramagnetic term ( $\sigma_p$ ), the average values of which are given by

$$\sigma_d = \frac{e^2}{3mc^2} \langle \psi_0 | \sum_i r_i^{-1} | \psi_0 \rangle \quad (1)$$

and

$$\sigma_p = -\frac{e^2}{3mc^2} \sum_n (\epsilon_n - \epsilon_0)^{-1} \langle \psi_0 | \sum_i L_i r_i^{-3} | \psi_n \rangle \langle \psi_n | \sum_i L_i | \psi_0 \rangle + c.c. \quad (2)$$

In these equations, the wave functions for the ground state ( $\psi_0$ ) and excited states ( $\psi_n$ ) have eigenvalues  $\epsilon_0$  and  $\epsilon_n$ , respectively,

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**Table 1.** Chemical Shift Data<sup>a</sup> for **1a–e** in Liquid Ammonia at  $-60\text{ }^{\circ}\text{C}$ 

anion	X	$\delta(\text{H}_1)$	$\delta(\text{H}_2)$	$\delta(\text{H}_3)$	$\delta(\text{H}_4)$	$\delta(\text{H}_5)$	$\delta(\text{H}_6)$	$\delta(\text{H}_7)$	$\delta(\text{H}_9)$
<b>1a</b>	OCH <sub>3</sub>	4.67	5.37	3.78	5.12	3.70	5.30	4.30	6.22
<b>1b</b>	CH <sub>3</sub>	4.61	5.28	3.73	5.07	3.63	5.24	4.22	6.18
<b>1c</b>	H	4.53	5.24	3.66	5.00	3.56	5.20	4.18	6.17
<b>1d</b>	Cl	4.30	5.12	3.55	4.86	3.44	5.06	4.03	5.95
<b>1e</b>	Br <sup>b</sup>	4.27	5.10	3.54	4.86	3.42	5.05	4.02	5.95
$\Delta\delta(\text{H}_r)^c$		0.37	0.25	0.23	0.26	0.26	0.24	0.27	0.27

<sup>a</sup>All shifts were measured relative to trimethylamine (TMA) as an internal standard and are reported relative to TMS ( $\delta_{\text{TMS}} = \delta_{\text{TMA}} + 2.135$ ).  
<sup>b</sup>This spectrum was weak and displayed poor resolution. <sup>c</sup> $\Delta\delta(\text{H}_r) = \delta(\text{H}_r) (\text{X} = \text{OCH}_3) - \delta(\text{H}_r) (\text{X} = \text{Cl})$ .

**L** and **r** are the angular momentum and position vectors, respectively, of the *i*th electron relative to the origin, c.c. is the complex conjugate, other terms have their usual values, and the sums are taken over all excited states *n* and all electrons *i*. Van Vleck had derived a similar equation for the molar magnetic susceptibility nearly 2 decades previously.<sup>10</sup>

The difficulty of solving eq 2 for large systems has led to the development of expressions for the shielding due to a ring current derived from simple molecular orbital theory. Of particular interest is the London–McWeeny ring current model based on simple Hückel molecular orbital (HMO) theory.<sup>8,11–14</sup> This method allows the calculation of a reduced bond current  $J_{rs}$  which is proportional to the total ring current and, for monocyclic systems, is determined by eq 3–5 where  $p_{rs}$  is the  $\sigma$  bond order of bond *rs*,

$$J_{rs} = P_{rs} + \beta \bar{\pi}_{(rs)(rs)} \quad (3)$$

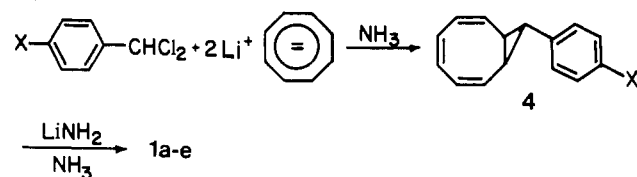
$$P_{rs} = \sum_i^{\text{occ}} c_{ir} c_{is} \quad (4)$$

$$\bar{\pi}_{(rs)(rs)} = 2 \sum_i^{\text{occ}} \sum_j^{\text{unocc}} \frac{(c_{ir} c_{js} - c_{is} c_{jr})^2}{\Delta\epsilon_{ij}} \quad (5)$$

$\bar{\pi}_{(rs)(rs)}$  is the complex bond–bond polarizability, and the HMO coefficient of orbital *i* at carbon *r* is given by  $c_{ir}$ . The diamagnetic contribution is related to the bond order, while the paramagnetic component is related to the complex bond–bond polarizability.

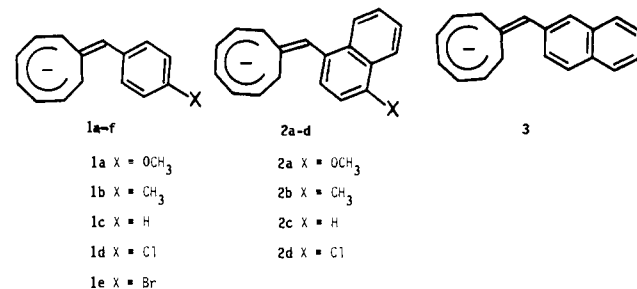
Inspection of eq 5 shows  $\bar{\pi}_{(rs)(rs)}$  to be inversely proportional to the energy gap between pairs of occupied and unoccupied orbitals. Attention has been focused on the HOMO–LUMO mixing which, having the smallest energy gap ( $\Delta\epsilon_{\text{HL}}$ ), is assumed to make the dominant contribution to the paramagnetic term in monocyclic systems.<sup>15</sup> This relationship has been successfully used to estimate the relative importance of paramagnetic ring currents in a variety of compounds.<sup>16</sup> Although the correlation of  $\Delta\epsilon_{\text{HL}}$  with the magnitude of paramagnetic ring currents has been generally successful, no systematic experimental investigation of this relationship has yet appeared. In addition, the influence of the distribution of the coefficients of the frontier orbitals (which contribute to the numerator of eq 5) has been relatively unexamined. This study (an expansion of a previous communication)<sup>17</sup> addresses these points and successfully relates changes in <sup>1</sup>H chemical shifts which result from enhanced paramagnetic components of the ring current to HMO parameters.

To probe the influence of substituent-dependent changes in frontier orbital parameters on the paramagnetic ring current term, various 9-[1-(*p*-X-phenyl)]methylene cyclooctatrienyl anions (**1a–e**), 9-[1-(4-X-naphthyl)]methylene cyclooctatrienyl anions

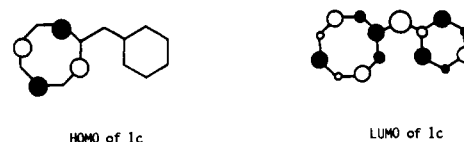
**Scheme 1**

a X = OCH<sub>3</sub>                      d X = Cl  
 b X = CH<sub>3</sub>                      e X = Br  
 c X = H                          f X = CF<sub>3</sub>

(**2a–d**), and the 9-(2-naphthyl)methylene cyclooctatrienyl anion (**3**) have been studied by <sup>1</sup>H NMR spectrometry. These anions



were chosen both because they possess small  $\Delta\epsilon_{\text{HL}}$  values and because magnetic dipole transitions between the HOMO and LUMO are symmetry-allowed. In addition, owing to a node in the HOMO passing through C<sub>4</sub>, C<sub>8</sub>, and C<sub>9</sub>, a substituent at C<sub>9</sub> has (to a first approximation) no effect on the energy of the HOMO. Since no such node exists in the LUMO, the energy of the latter orbital (and hence  $\Delta\epsilon_{\text{HL}}$ ) is expected to be a sensitive function of the substituent. The presence of the node also ensures that the coefficients of the HOMO will be essentially unaffected by a change of substituent. Thus changes in the frontier orbital contribution to the numerator of eq 5 will arise primarily from the LUMO. The magnitudes of the coefficients of the frontier



orbitals within the eight-membered ring (largest at C<sub>1</sub>, C<sub>3</sub>, C<sub>5</sub>, and C<sub>7</sub> of the HOMO and at C<sub>2</sub>, C<sub>4</sub>, C<sub>6</sub>, and C<sub>8</sub> of the LUMO)<sup>17</sup> is such that their contribution to eq 5 will be maximized. Finally, X is spatially remote from the eight-membered ring, thereby minimizing the effect of its magnetic anisotropy on the chemical shifts of H<sub>1</sub>–H<sub>7</sub>.

## Results and Discussion

**Synthesis of Anions, <sup>1</sup>H NMR Spectra, and Ion Pairing.** Anions **1a–e** were generated by bridgehead proton abstraction from the corresponding *anti*-9-[1-(*p*-X-phenyl)]bicyclo[6.1.0]nona-2,4,6-trienes (**4a–e**) with lithium amide in liquid ammonia (Scheme I). The *anti* configurations of **4a–f** were assigned on the basis of their small cyclopropyl coupling constants ( $J_{19} = J_{89} = 5.9\text{ Hz}$  in **4a–f**).<sup>18</sup>

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**Table II.** Chemical Shift Data for **2a-d** in Liquid Ammonia at  $-60\text{ }^{\circ}\text{C}^a$  and in HMPA at  $33\text{ }^{\circ}\text{C}^{b,c}$ 

anion	X	solvent	$\delta(\text{H}_1)$	$\delta(\text{H}_2)$	$\delta(\text{H}_3)$	$\delta(\text{H}_4)$	$\delta(\text{H}_5)$	$\delta(\text{H}_6)$	$\delta(\text{H}_7)$	$\delta(\text{H}_9)$
<b>2a</b>	OCH <sub>3</sub>	NH <sub>3</sub>	4.53	5.41	3.82	5.14	3.70	5.26	4.53	6.67
<b>2b</b>	CH <sub>3</sub>	NH <sub>3</sub>	4.47	5.37	3.79	5.11	3.66	5.24	4.52	6.67
<b>2c</b>	H	NH <sub>3</sub>	4.40	5.33	3.76	5.09	3.62	5.23	4.49	6.66
<b>2d</b>	Cl	NH <sub>3</sub>	4.30	5.33	3.76	5.06	3.62	5.19	4.45	6.58
$\Delta\delta(\text{H}_r)^d$			0.23	0.08	0.06	0.08	0.08	0.07	0.08	0.09
<b>3</b>		NH <sub>3</sub>	4.56	5.18	3.62	4.92	3.51	5.14	4.14	6.18
<b>2a</b>	OCH <sub>3</sub>	HMPA	<i>e</i>	4.97	<i>f</i>	4.71	<i>f</i>	4.89	<i>e</i>	6.08
<b>2b</b>	CH <sub>3</sub>	HMPA <sup>g</sup>	4.00	4.86	<i>f</i>	4.62	<i>f</i>	4.86	4.00	6.08
<b>2c</b>	H	HMPA <sup>g</sup>	3.97	4.82	<i>f</i>	4.62	<i>f</i>	4.82	3.97	6.07
<b>2d</b>	Cl	HMPA <sup>g</sup>	3.92	4.80	<i>f</i>	4.56	<i>f</i>	4.80	3.92	5.85

<sup>a</sup>Chemical shifts were measured relative to trimethylamine (TMA) as an internal standard and are reported relative to TMS ( $\delta_{\text{TMS}} = \delta_{\text{TMA}} + 2.135$ ). <sup>b</sup>Chemical shifts were measured relative to TMS. <sup>c</sup>Chemical shifts for NH<sub>3</sub> solutions and for **2b** in HMPA are taken from ref 20 and 21. <sup>d</sup> $\Delta\delta(\text{H}_r) = \delta(\text{H}_r)(\text{X} = \text{OCH}_3) - \delta(\text{H}_r)(\text{X} = \text{Cl})$ . <sup>e</sup>The signals due to H<sub>1</sub> and H<sub>7</sub> of **2a** were obscured by other signals. <sup>f</sup>The signals due to H<sub>3</sub> and H<sub>5</sub> were obscured by a solvent peak centered at  $\delta$  2.60. <sup>g</sup>Exchange averaged at 90 MHz.

All but **4f** underwent smooth deprotonation to the corresponding anion. The latter gave a green solution, but no interpretable <sup>1</sup>H NMR signals were observed. The syntheses of **1c** and **4c**,<sup>19</sup> of **2c** and **3**,<sup>20</sup> and of **2a**, **2b**, and **2d**<sup>21</sup> have been described elsewhere.

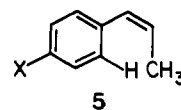
The <sup>1</sup>H NMR chemical shift data for H<sub>1</sub>–H<sub>9</sub> of **1a–e** in liquid ammonia are presented in Table I, whereas those for **2a–d** and **3** are given in Table II. The rationale for the assignments will be discussed in the next section. The spectra of all the anions are similar in appearance, H<sub>1</sub> and H<sub>7</sub> appearing as doublets and H<sub>2</sub>–H<sub>6</sub> as apparent triplets. The charge localization at C<sub>1</sub>, C<sub>3</sub>, C<sub>5</sub>, and C<sub>7</sub> causes protons bonded to these carbons to be shifted upfield from the remaining eight-membered ring protons.<sup>22</sup> The coupling constants between vicinal eight-membered ring protons (Tables I and II) indicate that this ring is essentially planar.

Generation of **2a–d** in hexamethylphosphoramide–lithium dimethylamide was accompanied by the formation of considerable amounts of side products. The method given in the Experimental Section was found (by <sup>1</sup>H NMR spectrometry) to give the highest yields of several procedures tried. The spectral data are of lower quality than those obtained in liquid ammonia because of (a) an uncertainty in the concentrations of the anions and the probable presence of intermolecular shielding effects due to the side products and (b) the loss of the chemical shift data for H<sub>3</sub> and H<sub>5</sub> due to overlap with the solvent signals. Nevertheless, the spectra exhibit patterns similar to those observed for the same anions in liquid ammonia.

Small upfield shifts of H<sub>1</sub>–H<sub>9</sub> and also, in **1d** and **2b–c**, coalescence phenomena associated with rapid rotation about the C<sub>8</sub>–C<sub>9</sub> bond are observed on warming samples of **1a–e** and **2a–d** in liquid ammonia.<sup>20,21</sup> Small upfield shifts of the eight-membered ring protons with increasing temperature, together with their upfield shifts in HMPA relative to ammonia, lead us to conclude that all the anions exist as contact ion pairs in liquid ammonia over the temperature range investigated and as solvent-separated ion pairs or free ions in HMPA.<sup>23,24</sup>

**Conformation of the Anions and Assignment of Their <sup>1</sup>H NMR Spectra.** Whereas styrene is thought to be planar,<sup>25</sup> theoretical analysis of the UV–visible spectrum of (*Z*)-1-phenylpropene (**5**, X = H) suggests that the double bond is twisted out of the plane of the phenyl ring by ca. 30°,<sup>26</sup> presumably due to unfavorable

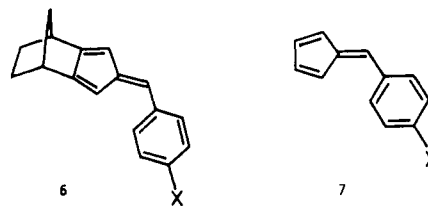
steric interactions between the methyl group and an ortho-hydrogen. Since H<sub>1</sub> and the C<sub>9</sub>-aryl group in **1–3** have a similar



geometric relationship, it is expected that there will be twisting about the C<sub>9</sub>-aryl bonds of the anions. A previously published comparison of the chemical shifts of H<sub>1</sub> and H<sub>9</sub> in **1c**, **2c**, and **3** with those of protons in similar positions in styrene and 1- and 2-vinylnaphthalene confirmed the presence of this twisting and established that the degree of twist increases in the order **1c**  $\approx$  **3** < **2c**.<sup>20</sup> The presence of this twist, as well as its substituent dependence, provides a key to assigning the <sup>1</sup>H NMR spectra of these anions.

Inspection of the  $\Delta\delta(\text{H}_r)$  values in Table I (where  $\Delta\delta(\text{H}_r) = \delta(\text{H}_r)(\text{X} = \text{OCH}_3) - \delta(\text{H}_r)(\text{X} = \text{Cl})$  and  $\delta(\text{H}_r)$  is the chemical shift of the *r*th proton) shows that the eight-membered ring protons of **1a–e** undergo a near-uniform upfield shift. This shift is due to substituent-induced changes in the paramagnetic component of the ring current in the eight-membered ring (vide infra). Exceptions to this general uniform shift are provided by one of the doublets due to either H<sub>1</sub> or H<sub>7</sub> and by the singlet due to H<sub>9</sub>. This doublet has a larger  $\Delta\delta(\text{H}_r)$  value than the other ring protons whereas  $\Delta\delta(\text{H}_9)$ , while similar to that of the other ring protons, cannot be explained solely on the basis of changes in a ring current because the response of H<sub>9</sub> to such a change will be less owing to its greater distance from the eight-membered ring.

The chemical shift data for the [1-(*p*-X-phenyl)]fulvenes **6** and **7** (where X represents substituents identical with those utilized in the present study) provide additional insight into this problem.



Substitution of progressively more powerful electron acceptors for X in **6** causes a deshielding of H<sub>4</sub> due to charge withdrawal from C<sub>4</sub>, yet H<sub>1</sub> simultaneously experiences shielding.<sup>27</sup> This is the result of an increased fulvene–phenyl dihedral angle resulting from reduced  $\pi$  delocalization with electron acceptors, thereby causing H<sub>1</sub> to move into a less deshielding (or more shielding) region of the phenyl rings. This effect dominates the deshielding caused by charge withdrawal at H<sub>1</sub>. Similar behavior is observed for H<sub>1</sub> in **7** which shifts upfield by 0.11 ppm upon changing X from OCH<sub>3</sub> to Cl for the same reason as in **6**, while the chemical shifts of the remaining ring protons are virtually unchanged.<sup>28</sup> By

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**Table III.** Self-Consistent HMO ( $\omega$  Technique)  $\pi$ -Electron Densities for 9-Arylmethylenecyclooctatrienyl Anions<sup>a</sup>

anion	X	C <sub>1</sub>	C <sub>2</sub>	C <sub>3</sub>	C <sub>4</sub>	C <sub>9</sub>
1a	OCH <sub>3</sub>	1.198	1.056	1.201	1.062	1.013
1b	CH <sub>3</sub>	1.198	1.056	1.201	1.063	1.012
1c	H	1.197	1.057	1.200	1.058	1.013
1d	Cl	1.197	1.053	1.201	1.059	1.013
1e	Br	1.197	1.052	1.201	1.059	1.013
2a	OCH <sub>3</sub>	1.198	1.056	1.201	1.062	1.012
2b	CH <sub>3</sub>	1.198	1.057	1.201	1.063	1.012
2c	H	1.196	1.049	1.200	1.056	1.012
2d	Cl	1.197	1.052	1.200	1.058	1.012
3		1.197	1.051	1.200	1.057	1.013

<sup>a</sup>The following heteroatom parameters were used in HMO  $\omega$ -technique calculations:  $h_0 = 2.7$ ;  $h_{\text{CH}_3} = 3.0$ ;  $h_{\text{Cl}} = 2.8$ ;  $h_{\text{Br}} = 2.2$ ;  $k_{\text{C-O}} = 0.6$ ;  $k_{\text{C-CH}_3} = 0.7$ ;  $k_{\text{C-Cl}} = 0.37$ ;  $k_{\text{C-Br}} = 0.3$ .<sup>27b,c</sup>

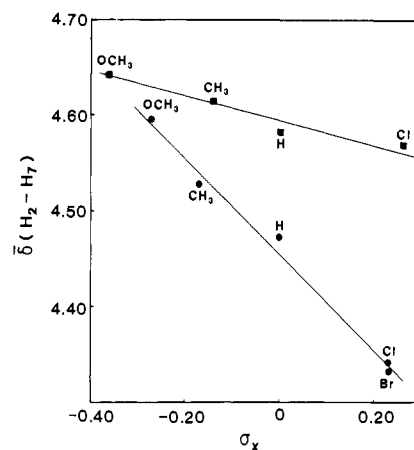
analogy, the doublet exhibiting the largest  $\Delta\delta(\text{H}_7)$  value in **1a-e** is assigned to  $\text{H}_1$ . The dihedral angle between the two ring systems ( $\theta$ ) increases as X becomes a poorer electron donor due to a decreasing LUMO(methylenecyclooctatrienyl)-HOMO(phenyl) interaction (the dominant frontier orbital interaction). This twisting also accounts for the large upfield shift of  $\text{H}_9$ , which will also be moved into less deshielding regions of the aryl ring as  $\theta$  increases.

While other effects arising from the substituted phenyl groups could contribute to the chemical shift of  $\text{H}_1$ , there is precedent for excluding them. The chemical shift of the methyl group of **5** (X = OCH<sub>3</sub>, CH<sub>3</sub>, H, and Cl) is virtually unaffected by para substitution, indicating that substituent field effects on the chemical shift of protons near  $\text{H}_1$  in **1a-e** are insignificant.<sup>29</sup> Changes in the ring current of the phenyl group as a function of the substituent may also be ruled out as a cause of the enhanced upfield shifts of  $\text{H}_1$  and  $\text{H}_9$ , because such changes were found to have statistically insignificant effects on the vinyl proton chemical shifts of para-substituted styrenes.<sup>30</sup>

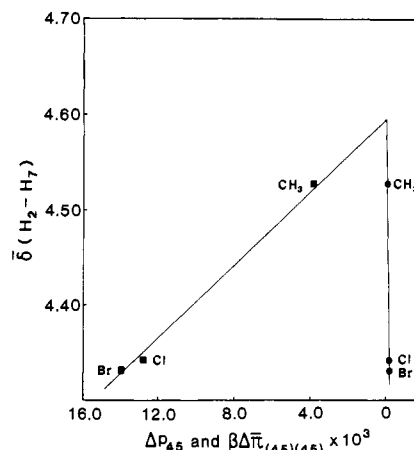
The remaining resonances are assigned on the basis of charge densities calculated by a self-consistent HMO ( $\omega$  technique) method<sup>31</sup> (see Table III), with the apparent triplets due to  $\text{H}_3$  and  $\text{H}_5$  appearing upfield of those of  $\text{H}_2$ ,  $\text{H}_4$ , and  $\text{H}_6$  because of the negative charge localized on  $\text{C}_3$  and  $\text{C}_5$ , and also by analogy to the five-membered ring protons of **7**, where protons syn to the phenyl group are deshielded relative to protons in otherwise equivalent positions anti to the phenyl group.<sup>28</sup>

The chemical shift data of **2a-d** in liquid ammonia (Table II) demonstrate behavior similar to those of **1a-e**. A consequence of the increased degree of twist in the 1-naphthyl series relative to the phenyl series<sup>20</sup> is that  $\text{H}_1$  is more shielded relative to  $\text{H}_7$  in the former than in the latter. Whereas  $\text{H}_1$  is always *downfield* of  $\text{H}_7$  in **1a-e**,  $\text{H}_1$  and  $\text{H}_7$  have identical chemical shifts in **2a**, while in **2b-d**  $\text{H}_1$  moves progressively *upfield* of  $\text{H}_7$  as the degree of twist increases. This reversal (relative to the phenyl series) is limited to  $\text{H}_1$  and  $\text{H}_7$ , and the remaining protons are assigned on the basis of charge densities (Table III) and also by analogy to **7**, so that those protons syn to the naphthyl group appear downfield of otherwise equivalent protons anti to it. The latter reasoning is supported by the fact that interchanging the assignments of  $\text{H}_2$  and  $\text{H}_6$  ( $\text{H}_3$  and  $\text{H}_5$ ) would cause  $\text{H}_2$  ( $\text{H}_3$ ) to be upfield of  $\text{H}_6$  ( $\text{H}_5$ ) by an amount larger than  $\text{H}_1$  is upfield of  $\text{H}_7$ , an unreasonable result given the greater distance of  $\text{H}_2$ - $\text{H}_6$  from the naphthyl group. The resonances for **2a-d** in HMPA were assigned on the same basis as those for **2a-d** in liquid ammonia.

**Substituent Effects on Chemical Shifts.** The most striking feature of the chemical shifts of  $\text{H}_1$ - $\text{H}_7$  in **1a-e** and **2a-d** is the increased shielding caused by electron acceptors. The average



**Figure 1.** Plot of the average chemical shift for  $\text{H}_2$ - $\text{H}_7$  ( $\delta(\text{H}_2-\text{H}_7)$ ) in **1a-e** in liquid ammonia (circles) and **2a-d** in liquid ammonia (squares) vs. the  $\sigma$  value of the *p*-phenyl substituent ( $\sigma_X$ ).



**Figure 2.** Plot of the average chemical shift for  $\text{H}_2$ - $\text{H}_7$  ( $\delta(\text{H}_2-\text{H}_7)$ ) in **1a**, **1b**, **1d**, and **1e** in liquid ammonia vs. the difference between  $p_{45}$  or  $\beta\pi_{(45)(45)}$  for **1a** and the corresponding values for **1b**, **1d**, and **1e** ( $\Delta p_{45}$  (circles) or  $\Delta\beta\pi_{(45)(45)}$  (squares), respectively).

chemical shift value of  $\text{H}_2$ - $\text{H}_7$  ( $\delta(\text{H}_2-\text{H}_7)$ ) of these anions correlate very well with Hammett  $\sigma$  constants (Figure 1).<sup>32,33</sup> The shielding caused by acceptors is a remarkable result, for all previous studies of the chemical shift dependence of protons attached to alkyl, alkenyl, and alkynyl side chains of substituted phenyl moieties showed acceptors to cause *deshielding*, presumably through a resonance effect.<sup>34</sup> Self-consistent HMO calculations indicate that there is essentially no substituent effect on the charge densities of  $\text{C}_1$ - $\text{C}_9$  (Table III). This result is supported by the substituent independence of the chemical shift differences between *adjacent* eight-membered ring protons (except between  $\text{H}_1$  and  $\text{H}_2$  because of the dependence of the chemical shift of  $\text{H}_1$  on  $\theta$ ) which are due primarily to charge density differences between adjacent carbon atoms. Furthermore, field effects do not explain the observed shifts since these are expected to be attenuated by distance, and yet  $\text{H}_2$ - $\text{H}_7$  exhibit nearly uniform substituent-dependent shifts despite their varied distances from the substituent. Hence, the usual

(32) For **1a-e** in liquid ammonia,  $r = 0.994$ ; for **2a-d** in liquid ammonia,  $r = 0.971$ .

(33) Values of  $\sigma$  for the *p*-phenyl substituents were taken from: March, J. "Advanced Organic Chemistry: Reactions, Mechanisms, and Structure", 2nd ed.; McGraw-Hill: New York, 1977; p 253. Values of  $\sigma$  for the 4-substituted naphthyl compounds were taken from: Dewar, M. J. S.; Grisdale, P. J. *J. Am. Chem. Soc.* **1962**, *84*, 3546.

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Table IV. Hückel Molecular Orbital Parameters for **1a-e**, **2a-d**, and **3**<sup>a</sup>

anion	X	$\sum_{r=1}^8 (c_r^{\text{LUMO}})^2$ <sup>b</sup>	$\Delta\epsilon_{\text{HL}}(\beta)$ <sup>b</sup>	LUMO coefficients				
				C <sub>1</sub>	C <sub>2</sub>	C <sub>3</sub>	C <sub>4</sub>	C <sub>8</sub>
<b>1a</b>	OCH <sub>3</sub>	0.541	0.359	0.192	-0.348	-0.067	0.372	0.279
<b>1b</b>	CH <sub>3</sub>	0.544	0.355	0.190	-0.349	-0.066	0.373	0.282
<b>1d</b>	Cl	0.551	0.345	0.186	-0.353	-0.065	0.375	0.289
<b>1e</b>	Br	0.551	0.343	0.186	-0.353	-0.064	0.375	0.299
<b>2a</b>	OCH <sub>3</sub>	0.474	0.328	0.165	-0.329	-0.057	0.348	0.275
<b>2b</b>	CH <sub>3</sub>	0.478	0.320	0.162	-0.331	-0.056	0.349	0.279
<b>2d</b>	Cl	0.488	0.304	0.156	-0.336	-0.054	0.353	0.288
<b>1c</b>	H	0.544	0.340	0.184	-0.354	-0.064	0.376	0.292
<b>2c</b>	H	0.493	0.297	0.153	-0.339	-0.053	0.354	0.293
<b>2c</b> (twisted) <sup>c</sup>	H	0.385	0.311	0.161	-0.339	-0.055	0.356	0.289
<b>3</b>		0.520	0.323	0.170	-0.345	-0.059	0.364	0.290

<sup>a</sup>The following heteroatom parameters were used in simple HMO calculations:  $h_{\text{O}} = 2.0$ ;  $h_{\text{CH}_3} = 2.0$ ;  $h_{\text{Cl}} = 2.0$ ;  $h_{\text{Br}} = 1.5$ ;  $k_{\text{C-O}} = 0.8$ ;  $k_{\text{C-CH}_3} = 0.7$ ;  $k_{\text{C-Cl}} = 0.4$ ;  $k_{\text{C-Br}} = 0.3$ .<sup>27b</sup> <sup>b</sup>See text. <sup>c</sup> $\beta_{9,10} = 0.9 \beta_0$ .

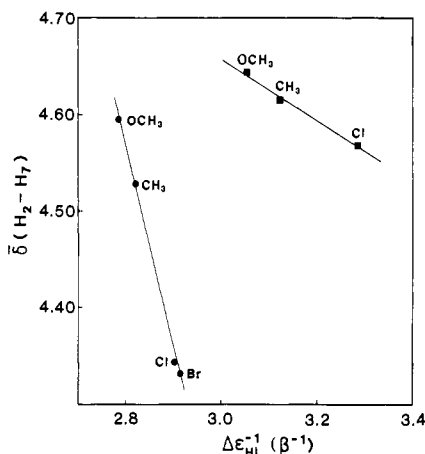


Figure 3. Plot of the reciprocal of the Hückel HOMO-LUMO energy gap ( $\Delta\epsilon_{\text{HL}}^{-1}$ ) vs. the average chemical shift of H<sub>2</sub>-H<sub>7</sub> ( $\delta(\text{H}_2\text{-H}_7)$ ) for **1a**, **1b**, **1d**, and **1e** in liquid ammonia (circles) and **2a**, **2b**, and **2d** in liquid ammonia (squares). See footnote a, Table IV for the parameters employed.

interpretations of substituent-induced chemical shift changes in terms of inductive, resonance, and field effects<sup>30,34</sup> do not apply to these anions. The *uniform* shift of all protons as a function of substituent (X) is clearly consistent with a ring current effect in the eight-membered ring.

In Figure 2 are plotted the differences between the  $p_{45}$  value of **1a** (X = OCH<sub>3</sub>) and those of the other *p*-X-phenyl-substituted anions (**1b**, **1d**, and **1e**) against the average chemical shift ( $\delta(\text{H}_2\text{-H}_7)$ ) of H<sub>2</sub>-H<sub>7</sub>.<sup>35,36</sup> A similar treatment of  $\bar{\pi}_{(45)(45)}$  (in units of  $\beta^{-1}$ ) is also plotted.<sup>36</sup> The latter term correlates with  $\delta(\text{H}_2\text{-H}_7)$  at a confidence level ( $r$ ) of 0.999, whereas  $\Delta p_{45}$  and  $\delta(\text{H}_2\text{-H}_7)$  are independent of each other. Thus, in agreement with experiment, substituent-induced changes in the ring current are calculated to arise almost exclusively from changes in  $\bar{\pi}_{(rs)(rs)}$  (which is related to the  $\sigma_p$  term (eq 2) in the Ramsey equation). Similarly, the correlation of  $\bar{\pi}_{(rs)(rs)}$  with  $\delta(\text{H}_2\text{-H}_7)$  is very good ( $r = 0.996$ ) for the ammonia data for **2a**, **2b**, and **2d**, and the changes in this term overwhelmingly dominate those in  $p_{45}$ .

Having determined that the chemical shift changes in our anions are controlled by the paramagnetic term, it now becomes meaningful to investigate the relative importance of the contribution of the frontier orbitals to  $\bar{\pi}_{(rs)(rs)}$  (eq 5). An explanation based on  $\Delta\epsilon_{\text{HL}}$  would proceed as follows. Electron acceptors lower the energy of the LUMO, whereas, owing to its nodal properties, the energy of the HOMO is unaffected. Hence  $\Delta\epsilon_{\text{HL}}$  decreases (Table IV) and the paramagnetic ring current increases as X becomes a better electron acceptor. This reasoning is supported by the

(35) Compound **1c** was not included in this correlation because it is not isolectronic with **1a**, **1b**, **1d**, and **1e** as defined by the parameters in footnote a of Table IV.

(36) Values of  $p_{rs}$  and  $\bar{\pi}_{(rs)(rs)}$  for any bond in the eight-membered ring give equivalent results; the C<sub>4</sub>-C<sub>5</sub> bond was chosen arbitrarily.

Table V. Calculated Ring Current Parameters for **1c**, **2c**, and **3**<sup>a</sup>

anion	$p_{45}$	$\beta\bar{\pi}_{(45)(45)}$ <sup>b</sup>	$J_{45}$ <sup>c</sup>
<b>1c</b>	0.634	-0.738	-0.104
<b>3</b>	0.633	-0.742	-0.109
<b>2c</b>	0.632	-0.753	-0.121
<b>2c</b> (twisted) <sup>d</sup>	0.633	-0.745	-0.112

<sup>a</sup>The C<sub>4</sub>C<sub>5</sub> bond was arbitrarily chosen for the calculation of the ring current parameters. <sup>b</sup> $\bar{\pi}$  has the units of  $\beta^{-1}$ . <sup>c</sup>Negative  $J_{45}$  corresponds to a paramagnetic ring current (upfield shift for H<sub>1</sub>-H<sub>7</sub>). <sup>d</sup> $\beta_{9,10} = 0.9 \beta_0$ .

excellent linear correlation<sup>37</sup> between  $\Delta\epsilon_{\text{HL}}^{-1}$  values determined by self-consistent HMO theory and  $\delta(\text{H}_2\text{-H}_7)$  for both the phenyl and naphthyl anion series (Figure 3). The calculated  $\Delta\epsilon_{\text{HL}}^{-1}$  values also parallel the  $\lambda_{\text{max}}$  values determined for **1a-d** in HMPA, with electron-withdrawing groups causing bathochromic shifts in the long-wavelength band.<sup>17</sup>

As noted previously, it is the coefficients of the LUMO at even-numbered carbons which make nonzero contributions to the numerator of eq 5. Inspection of Table IV shows that it is just these sites which experience the largest increase in absolute values of the coefficients in **1a-e** and **2a-d** as X becomes a better electron acceptor. A convenient measure of the change in the LUMO due to substituents is to evaluate  $\sum_r (c_r^{\text{LUMO}})^2$ , where the index  $r$  encompasses the eight-membered ring carbons. This value is the fraction of the LUMO in the eight-membered ring and should, by the above discussion, increase in concert with increased paramagnetic ring currents. The tabulation in Table IV shows that, within each series of substituted anions, the fraction of the LUMO in the eight-membered ring indeed increases as X becomes a better electron acceptor. Hence arguments based on frontier orbital coefficient changes as well as on  $\Delta\epsilon_{\text{HL}}^{-1}$  are in agreement in predicting enhanced paramagnetic ring currents on going from **1a** to **1e** and from **2a** to **2d**. This topic is dealt with further in the section on HMO parameters which follows.

**Conformational Effects on Ring Currents.** On the basis of the values of  $J_{rs}$  in Table V,  $\delta(\text{H}_2\text{-H}_7)$  is expected to decrease in the order **1c** > **3** > **2c**. In contrast, the experimentally determined order is **2c** > **1c** > **3**; i.e., **2c** is *less shielded* than predicted. The same result is found on comparing **1a**, **1b**, and **1d** with **2a**, **2b**, and **2d**, respectively. In order to resolve these discrepancies, the effect on the ring current of a change in  $\theta$  was investigated.

The effect of twisting about the C<sub>9</sub>-aryl bond on the ring current parameters can be determined by varying the resonance integral  $\beta_{9,\text{aryl}}$  according to eq 6.<sup>38</sup> Both  $p_{rs}$  and  $\Delta\epsilon_{\text{HL}}$  increase on twisting,

$$\beta_{9,\text{aryl}} = \beta_0 \cos \theta \quad (6)$$

as does  $J_{45}$  (Tables IV and V). It is clear that an increase in  $\theta$  causes a quenching of the paramagnetic component of the ring current in the eight-membered ring. Having already demonstrated

(37) We calculate  $r = 0.999$  for the phenyl and 0.997 for the naphthyl anions in liquid ammonia and 0.982 for the naphthyl anions in HMPA.

(38) Reference 31a, p 105.

that **2a-d** are more twisted than **1a-e** (note the significantly greater slopes for the latter anions in Figures 1 and 3) and 3, we conclude that the apparent discrepancy between theory and experiment noted above is due to the larger degree of twist in the 1-naphthyl series relative to the phenyl and 2-naphthyl anions. To our knowledge, this is the first demonstration of such conformational changes influencing paratropic character.

It is interesting to note that the increase in  $\theta$  which we have shown to occur on going from **1a** to **1e** and from **2a** to **2d** tends to increase  $\Delta\epsilon_{\text{HL}}$  and therefore serves to attenuate the overall decrease in  $\Delta\epsilon_{\text{HL}}$  caused by HOMO(substituent)-LUMO(anion) mixing. If only the latter effect were operating, the slopes in Figures 1 and 3 would be somewhat steeper.

**Ring Currents and HMO Parameters.** Although changes in the LUMO coefficients and  $\sum_r (c_r^{\text{LUMO}})^2$  parallel changes in the paramagnetic ring currents (as determined by either the calculated  $\bar{\pi}_{(rs)(rs)}$  or experimental  $\Delta\delta(\text{H}_r)$  values) within the series **1a-e** and **2a-d**, they fail to give proper predictions when the  $\delta(\text{H}_2-\text{H}_7)$  values of **1c** and **3** (which are known to have similar degrees of twist about the  $\text{C}_5$ -aryl bond<sup>20</sup>) are compared. Whereas the  $\sum_r (c_r^{\text{LUMO}})^2$  values predict the paramagnetic component of the ring current to be greater in **1c**, the  $\delta(\text{H}_2-\text{H}_7)$  values show it to be greater in **3**, in agreement with  $\Delta\epsilon_{\text{HL}}$ <sup>39</sup> and  $J_{ij}$  values. These results show that the coefficients of the frontier orbitals alone do not make the dominant contribution to the value (or even indicate the proper relative values) of  $\bar{\pi}_{(rs)(rs)}$  in these systems.

The excellent correlation between  $\delta(\text{H}_2-\text{H}_7)$  and  $\Delta\epsilon_{\text{HL}}^{-1}$  is intriguing, particularly since we calculate that the HOMO-LUMO mixing contributes only 20-30% of the total value of  $\bar{\pi}_{(rs)(rs)}$  in these anions. Nevertheless, plots of  $\bar{\pi}_{(rs)(rs)}$  vs.  $\Delta\epsilon_{\text{HL}}^{-1}$  for **1a,b,d,e** and **2a,b,d** are linear, with correlation coefficients > 0.999. This suggests that changes in  $\Delta\epsilon_{ij}$  for all pairs of occupied and unoccupied orbitals ( $i$  and  $j$ ) are proportional to changes in  $\Delta\epsilon_{\text{HL}}$ . This can be the case for HMO calculations of systems which differ only in the value of  $\beta_{\text{Xr}}$ , the resonance integral between heteroatom X and the carbon atom ( $r$ ) to which it is bonded.<sup>40</sup> The change in energy  $\delta\epsilon_i$  of the  $i$ th orbital due to a variation in  $\beta_{\text{Xr}}$  is given by eq 7<sup>41</sup> where  $c_{ir}$  and  $c_{iX}$  are the coefficients of atom

$$\delta\epsilon_i = 2c_{ir}c_{iX}\delta\beta_{\text{Xr}} \quad (7)$$

$r$  or X in orbital  $i$ . For a pair of orbitals  $i$  and  $j$ , the change in their energy gap  $\delta\Delta\epsilon_{ij}$  will be given by eq 8.

$$\delta\Delta\epsilon_{ij} = (\delta\epsilon_i - \delta\epsilon_j) = 2\delta\beta_{\text{Xr}}(c_{ir}c_{iX} - c_{jr}c_{jX}) \quad (8)$$

To a first approximation, the term in parentheses on the right-hand side of eq 8 will be unaffected by a change in X,<sup>42</sup> and to the extent that this approximation is valid, all the  $\delta\Delta\epsilon_{ij}$  values will be proportional to  $\delta\beta_{\text{Xr}}$  and hence to each other. It is this relationship that accounts for the excellent correlations of  $\Delta\epsilon_{\text{HL}}^{-1}$  with both the calculated ring current values and the experimental chemical shifts of **1a-e** and **2a-d**.

## Experimental Section

**General.** IR spectra were obtained on a Perkin-Elmer 337 or 283 spectrophotometer. The <sup>1</sup>H NMR spectra were obtained on a Varian A60-D, XL-100, or EM-390 NMR spectrometer equipped with a variable temperature probe. The chemical shifts of all neutral compounds are relative to tetramethylsilane (TMS). Elemental analyses were performed by Dr. Franz Kasler of the University of Maryland or by Gal-

braith Laboratories. All melting points are uncorrected.

**General Method for the Synthesis of Para-Substituted 9-Phenyl-*cis*-bicyclo[6.1.0]nona-2,4,6-trienes.** A 500-mL three-necked flask equipped with a dry ice-acetone condenser, a mechanical stirrer, and a 125-mL pressure-equalizing addition funnel was flame-dried under a stream of ammonia, and ca. 125 mL of ammonia was condensed. Lithium wire was dissolved in the ammonia and freshly distilled cyclooctatetraene, dissolved in 10 mL of anhydrous ether, was added dropwise at a slow enough rate to avoid foaming, resulting in a deep-red solution containing a tan precipitate.  $\alpha,\alpha$ -Dichlorotoluene in 10 mL of anhydrous ether was then added dropwise over a 15-30-min period. After stirring for 1 h at ca. -33 °C, 5 mL of a saturated aqueous ammonium chloride solution was slowly added, followed by 50 mL of ether and 200 mL of water. The resulting layers were separated, the aqueous layer was saturated with sodium bromide and extracted with several 50-mL portions of ether, and the organic material was dried over anhydrous magnesium sulfate. The ether was removed by rotary evaporation, and the unchanged cyclooctatetraene was distilled off in vacuo.

**anti-9-(*p*-Anisyl)-*cis*-bicyclo[6.1.0]nona-2,4,6-triene (4a).** The general procedure was followed by utilizing 0.65 g (0.94 mol) of lithium, 4.90 g (0.047 mol) of cyclooctatetraene, and 6.0 g (31.0 mmol) of *p*-methoxy- $\alpha,\alpha$ -dichlorotoluene. The residue from the vacuum distillation was chromatographed on neutral alumina with pentane. The crude product was recrystallized from pentane to yield 1.5 g (22%) of **4a**: mp 54.5-55.5 °C; IR (CCl<sub>4</sub>) 3010, 2840, 1605, 1515, 1455, 1350, 1248, 1178, 1112, 1056, 1042, 690 cm<sup>-1</sup>; NMR (CCl<sub>4</sub>)  $\delta$  6.98 (2 H, d, H<sub>3</sub> and H<sub>6</sub>,  $J$  = 9.0 Hz), 6.70 (2 H, d, H<sub>3</sub> and H<sub>5</sub>,  $J$  = 9.0 Hz), 5.7-6.1 (6 H, m, olefinic), 3.72 (3 H, s, methyl), 1.73 (2 H, B of AB<sub>2</sub>, H<sub>1</sub> and H<sub>8</sub>), 1.43 (1 H, A of AB<sub>2</sub>,  $J_{19} = J_{89} = 5.8$  Hz). Anal. Calcd for C<sub>16</sub>H<sub>16</sub>O: C, 85.68; H, 7.19. Found: C, 85.44; H, 7.42.

**anti-9-(*p*-Tolyl)-*cis*-bicyclo[6.1.0]nona-2,4,6-triene (4b).** The general procedure was followed by using 1.67 g (0.24 mol) of lithium, 12.35 g (0.12 mol) of cyclooctatetraene, and 14.0 g (0.04 mol) of  $\alpha,\alpha$ -dichloro-*p*-xylene. The residue from the vacuum distillation was chromatographed on neutral alumina with pentane and the crude product recrystallized from pentane to yield 3.4 g (21%) of **4b**: mp 30-30.5 °C; IR (CCl<sub>4</sub>) 3010, 2930, 2875, 1610, 1515, 1450, 1218, 1125, 1056, 1021, 688 cm<sup>-1</sup>; NMR (CCl<sub>4</sub>)  $\delta$  6.94 (4 H, s, phenyl), 5.7-6.1 (6 H, m, olefinic), 2.27 (3 H, s, methyl), 1.75 (2 H, B of AB<sub>2</sub>, H<sub>1</sub> and H<sub>8</sub>), 1.47 (1 H, A of AB<sub>2</sub>, H<sub>9</sub>,  $J_{19} = J_{89} = 5.9$  Hz). Anal. Calcd for C<sub>16</sub>H<sub>16</sub>: C, 92.31; H, 7.59. Found: C, 92.02; H, 7.77.

**anti-9-Phenyl-*cis*-bicyclo[6.1.0]nona-2,4,6-triene (4c).** The general procedure was followed by using 1.35 g (0.195 mol) of lithium, 10.0 g (0.096 mol) of cyclooctatetraene, and 10.5 g (0.065 mol) of  $\alpha,\alpha$ -dichlorotoluene. The residue from the vacuum distillation was chromatographed with pentane on neutral alumina. The crude product thus obtained was recrystallized from pentane to yield 2.96 g (25%) of **4c**: mp 61.5-62.0 °C; IR (CCl<sub>4</sub>) 3015, 1600, 1500, 1216, 1081, 1048, 732, 695 cm<sup>-1</sup>; NMR (CCl<sub>4</sub>)  $\delta$  6.9-7.2 (5 H, m, phenyl), 5.7-6.1 (6 H, m, olefinic), 1.80 (2 H, B of AB<sub>2</sub>, H<sub>1</sub> and H<sub>8</sub>), 1.47 (1 H, A of AB<sub>2</sub>, H<sub>9</sub>,  $J_{19} = J_{89} = 5.8$  Hz). Anal. Calcd for C<sub>19</sub>H<sub>16</sub>: C, 93.40; H, 6.60. Found: C, 93.51; H, 6.67.

**anti-9-[1-(*p*-Chlorophenyl)]-*cis*-bicyclo[6.1.0]nona-2,4,6-triene (4d).** The general procedure was followed utilizing 1.01 g (0.147 mol) of lithium, 7.66 g (0.074 mol) of cyclooctatetraene, and 9.6 g (0.05 mm) of *p*-chloro- $\alpha,\alpha$ -dichlorotoluene. The residue from the vacuum distillation of cyclooctatetraene was chromatographed on neutral alumina with pentane. The crude product was recrystallized from pentane-methanol (6:1) to yield 2.24 g (20%) of **4d**: mp 57.5-58.5 °C; IR (CCl<sub>4</sub>) 3015, 1610, 1495, 1215, 1092, 1052, 1014, 690 cm<sup>-1</sup>; NMR (CCl<sub>4</sub>)  $\delta$  7.15 (2 H, d, H<sub>3</sub> and H<sub>5</sub>,  $J$  = 8.5 Hz), 6.92 (2 H, d, H<sub>2</sub> and H<sub>6</sub>,  $J$  = 8.5 Hz), 5.7-6.1 (6 H, m, olefinic), 1.76 (2 H, B of AB<sub>2</sub>, H<sub>1</sub> and H<sub>8</sub>), 1.47 (1 H, A of AB<sub>2</sub>, H<sub>9</sub>,  $J_{19} = J_{89} = 5.9$  Hz). Anal. Calcd for C<sub>15</sub>H<sub>13</sub>Cl: C, 78.77; H, 5.73. Found: C, 78.50; H, 5.94.

**anti-9-[1-(*p*-Bromophenyl)]-*cis*-bicyclo[6.1.0]nona-2,4,6-triene (4e).** The general procedure was followed by using 0.87 g (0.125 mol) of lithium, 6.5 g (0.062 mol) of cyclooctatetraene, and 10.0 g (0.042 mol) of *p*-bromo- $\alpha,\alpha$ -dichlorotoluene. The residue from the vacuum distillation was chromatographed on neutral alumina with pentane. The crude product was recrystallized from pentane to yield 2.83 g (25%) of **4e**: mp 55.5-56.5 °C; IR (CCl<sub>4</sub>) 3015, 1610, 1490, 1435, 1213, 1075, 1052, 1010, 692 cm<sup>-1</sup>; NMR (CCl<sub>4</sub>)  $\delta$  7.37 (2 H, d, H<sub>3</sub> and H<sub>5</sub>,  $J$  = 8.5 Hz), 6.94 (2 H, d, H<sub>2</sub> and H<sub>6</sub>,  $J$  = 8.5 Hz), 5.9-6.1 (6 H, m, olefinic), 1.80 (2 H, B of AB<sub>2</sub>, H<sub>1</sub> and H<sub>8</sub>), 1.49 (1 H, A of AB<sub>2</sub>, H<sub>9</sub>,  $J_{18} = J_{89} = 5.9$  Hz). Anal. Calcd for C<sub>15</sub>H<sub>13</sub>Br: C, 65.95; H, 4.80. Found: C, 66.00; H, 4.72.

**anti-9-[1-(*p*-Trifluoromethyl)phenyl]-*cis*-bicyclo[6.1.0]nona-2,4,6-triene (4f).** The general procedure was followed except that the cyclooctatetraenedilithium (from 3.19 g (0.46 mol) of lithium and 2.4 g (0.23 mol) of cyclooctatetraene) was added to 3.3 g (0.14 mol) of *p*-(trifluoromethyl)- $\alpha,\alpha$ -dichlorotoluene in 25 mL of anhydrous ether over

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(40) See Table IV, footnote a for resonance integral values. For a discussion of the validity of considering methyl to be a two-electron donor, see: Pärkányi, C.; Herndon, W. C.; Shawali, A. S. *J. Org. Chem.* **1980**, *45*, 3529.

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15–20 min and allowed to stir at ca.  $-33\text{ }^{\circ}\text{C}$  for 45 min. After workup, the residue was chromatographed on neutral alumina with pentane and recrystallized from pentane to afford 0.48 g (13%) of **4f**: mp  $76\text{--}76.5\text{ }^{\circ}\text{C}$ ; IR ( $\text{CCl}_4$ ) 3050, 1615, 1420, 1215, 1070, 1052, 1020, 820 and  $694\text{ cm}^{-1}$ ; NMR ( $\text{CCl}_4$ )  $\delta$  7.47 and 7.13 (4 H, two d, phenyl protons ortho and meta to trifluoromethyl,  $J = 8.6\text{ Hz}$ ), 5.80–6.13 (6 H, m, olefinic), 1.85 (2 H, B of  $\text{AB}_2$ ,  $\text{H}_1$  and  $\text{H}_8$ ,  $J_{19} = J_{89} = 5.9\text{ Hz}$ ), and 1.46 (1 H, A of  $\text{AB}_2$ ,  $\text{H}_9$ ). Anal. Calcd for  $\text{C}_{16}\text{H}_{13}\text{F}_3$ : C, 73.27; H, 5.00. Found: C, 72.99; H, 4.94.

**Generation of the Lithium Salts of 1a–e.** These anions were obtained from 50–60 mg (ca. 0.25 mmol) of **4a–e** and lithium amide (from 8–12 mg of lithium) in 0.5 mL of liquid ammonia at ca.  $-60\text{ }^{\circ}\text{C}$  by our previously published general method.<sup>43</sup> The NMR chemical shifts are reported in Table I.

**Generation of the Lithium Salts of 2a–d and 3 in Liquid Ammonia.** The procedure for generating these anions has been previously reported.<sup>20,21,43</sup>

**General Procedure for the Generation of the Lithium Salts 2a–d in HMPA.** To a clean, dry 5-mm NMR tube was added ca. 45 mg (0.16

mmol) of **2a–d**, 0.5 mL of HMPA, and 40  $\mu\text{L}$  of TMS, followed by 20- $\mu\text{L}$  aliquots of a solution of 5 M  $\text{LiN}(\text{CH}_3)_2$  in HMPA. The contents of the tube were vigorously shaken after addition of each aliquot and examined by NMR to determine if the desired anion was present. Generally addition of 60–100  $\mu\text{L}$  of base solution was required to generate a satisfactory sample of dark-green anion solution. Chemical shift data are given in Table II.

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**Registry No.** **1a**, 96394-98-8; **1a<sup>-</sup>**, 96395-06-1; **1b**, 96394-99-9; **1b<sup>-</sup>**, 96395-07-2; **1c**, 76944-73-5; **1c<sup>-</sup>**, 96395-08-3; **1d**, 78585-74-7; **1d<sup>-</sup>**, 96395-09-4; **1e**, 96395-00-5; **1e<sup>-</sup>**, 96395-10-7; **2a**, 78585-69-0; **2a<sup>-</sup>**, 96395-11-8; **2b**, 78585-70-3; **2b<sup>-</sup>**, 96395-12-9; **2c**, 76944-71-3; **2c<sup>-</sup>**, 96395-13-0; **2d**, 78585-71-4; **2d<sup>-</sup>**, 96395-14-1; **3**, 76944-70-2; **3<sup>-</sup>**, 96395-15-2; **4a**, 96395-01-6; **4b**, 96395-02-7; **4c**, 53678-15-2; **4d**, 96395-03-8; **4e**, 96395-04-9; **4f**, 96395-05-0; *p*- $\text{MeOC}_6\text{H}_4\text{CHCl}_2$ , 21185-25-1; *p*- $\text{MeC}_6\text{H}_4\text{CHCl}_2$ , 23063-36-7;  $\text{PhCHCl}_2$ , 98-87-3; *p*- $\text{ClC}_6\text{H}_4\text{CHCl}_2$ , 13940-94-8; *p*- $\text{BrC}_6\text{H}_4\text{CHCl}_2$ , 67627-98-9; *p*- $\text{CF}_3\text{C}_6\text{H}_4\text{CHCl}_2$ , 82510-98-3; cyclooctatetraene, 629-20-9.

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## Electron-Transfer Valence Tautomerism. The Bicyclooctatetraenyl and 1,2-Dicyclooctatetraenylethylene Dianions

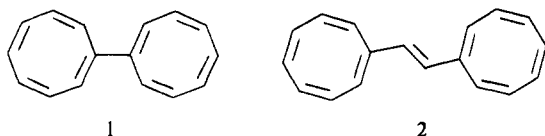
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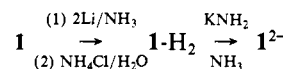
**Abstract:** Reduction of bicyclooctatetraenyl (**1**) with 2 or 4 equiv of potassium in liquid ammonia affords **1<sup>2-</sup>** and **1<sup>4-</sup>**, respectively. Treatment of a mixture of cyclooctatrienylcyclooctatetraenes or **3** with potassium amide in liquid ammonia affords **1<sup>2-</sup>** and **2<sup>2-</sup>**, respectively. The anions were characterized by <sup>1</sup>H NMR spectrometry as well as by proofs of structure of the products of quenching in the case of **1<sup>4-</sup>** and **2<sup>2-</sup>**. The charge in the ground states of **1<sup>2-</sup>** and **2<sup>2-</sup>** is localized in one planar eight-membered ring, while the other ring adopts a distorted tub conformation. However, electron exchange between the two eight-membered rings occurs at a rapid rate on the NMR time scale with each ring simultaneously changing from a planar to a folded (or vice versa) conformation. The activation barrier for this process in **2<sup>2-</sup>** can be estimated to be  $\leq 10.2\text{ kcal mol}^{-1}$ . The possible causes of this phenomenon, for which we propose the name "electron-transfer valence tautomerism", are discussed.

The structures of many carbanions are in part determined by a balance between stabilization by charge delocalization and/or by ion pairing and concomitant destabilization caused by increases in angle strain. Anions incorporating a cyclooctatetraene ring are of particular interest in this regard because of the large increase in CCC bond angles (from ca.  $126^{\circ 2}$  to ca.  $135^{\circ 3}$ ) caused by ring flattening as the eight-membered ring attains a  $10\pi$ -electron "aromatic" perimeter. A recent review has clearly demonstrated that the conformations adopted by the eight-membered rings in such anions are not fully understood.<sup>4</sup> To study this point, dianions **1<sup>2-</sup>** and **2<sup>2-</sup>** and tetraanion **1<sup>4-</sup>** have been synthesized and the conformations of the eight-membered rings investigated by <sup>1</sup>H NMR spectrometry.

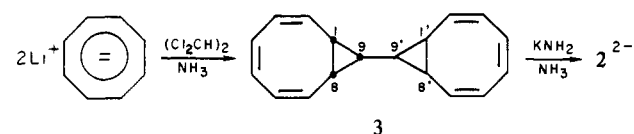


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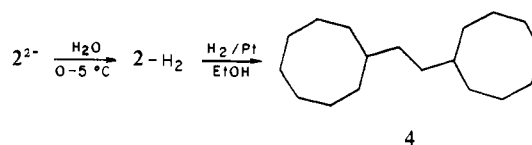
### Scheme I



### Scheme II



### Scheme III



### Results

Treatment of **1<sup>5</sup>** with 2 equiv of potassium in liquid ammonia at ca.  $-60\text{ }^{\circ}\text{C}$  gave a deep purple solution of **1<sup>2-</sup>** which was directly observed by <sup>1</sup>H NMR spectrometry (Table I). Alternatively, **1<sup>2-</sup>** could be formed by the route given in Scheme I. Treatment

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