15–20 min and allowed to stir at ca. -33 °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 76–76.5 °C; IR (CCl$_4$) 3050, 1615, 1420, 1215, 1070, 1052, 1020, 820 and 694 cm^{-1}; NMR (CCl$_4$) δ 7.47 and 7.13 (4 H, two d, phenyl protons ortho and meta to trifluoromethyl, J = 8.6 Hz), 5.80–6.13 (6 H, m, olefinic), 1.85 (2 H, B of AB$_2$, H$_1$ and H$_8$, J_{19} = J_{89} = 5.9 Hz), and 1.46 (1 H, A of AB$_2$, H$_9$). Anal. Calcd for C$_{16}$H$_{13}$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 °C by our previously published general method.[43] 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.[20,21,43]

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 μL of TMS, followed by 20-μL aliquots of a solution of 5 M LiN(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 μL of base solution was required to generate a satisfactory sample of dark-green anion solution. Chemical shift data are give in Table II.

(43) Staley, S. W.; Cramer. G. M.; Orvedal, A. W. *J. Am. Chem. Soc.* **1974**, *96*, 7433.

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 **1²⁻** and **1⁴⁻**, respectively. Treatment of a mixture of cyclooctatrienylcyclooctatetraenes or **3** with potassium amide in liquid ammonia affords **1²⁻** and **2²⁻**, respectively. The anions were characterized by ¹H NMR spectrometry as well as by proofs of structure of the products of quenching in the case of **1⁴⁻** and **2²⁻**. The charge in the ground states of **1²⁻** and **2²⁻** 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 **2²⁻** can be estimated to be ≤10.2 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°[2] to ca. 135°[3]) caused by ring flattening as the eight-membered ring attains a 10π-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.[4] To study this point, dianions **1²⁻** and **2²⁻** and tetraanion **1⁴⁻** have been synthesized and the conformations of the eight-membered rings investigated by ¹H NMR spectrometry.

1   2
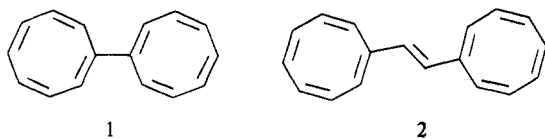
(1) Address correspondence to this author at the University of Nebraska.
(2) Traetteberg, M. *Acta Chem. Scand.* **1966**, *20*, 1724.
(3) Noordik, J. H.; van den Hark, T. E. M.; Mooij, J. J.; Klaassen, A. A. K. *Acta Crystallogr., Sect. B* **1974**, *30B*, 833.
(4) Staley, S. W.; Dustman, C. K. In "Reactive Intermediates"; Jones, M., Jr., Moss, R. A., Eds.; John Wiley and Sons, Inc.: New York, 1981; Vol. 2, pp 32–34.

Scheme I
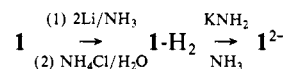
Scheme II
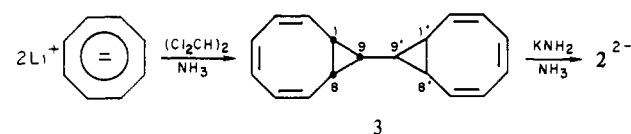
Scheme III
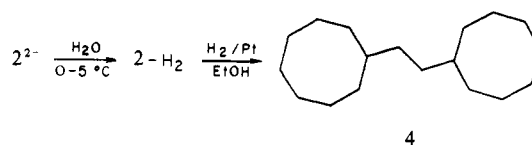
Results

Treatment of **1**[5] with 2 equiv of potassium in liquid ammonia at ca. -60 °C gave a deep purple solution of **1²⁻** which was directly observed by ¹H NMR spectrometry (Table I). Alternatively, **1²⁻** could be formed by the route given in Scheme I. Treatment

(5) Cope, A. C.; Marshall, D. J. *J. Am. Chem. Soc.* **1953**, *75*, 3208.

4004 *J. Am. Chem. Soc., Vol. 107, No. 13, 1985*

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Table I. ^{1}H NMR Chemical Shift Data of Various Potassium Salts in Liquid Ammonia at ca. $-40\,^\circ$C

| anion	chemical shift,^{a} δ				
	$H_{2(8)}$	$H_{3(7)}$	$H_{4(6)}$	H_5	H_9
$1^{2-\,b}$	6.01	5.86	5.66	5.77	
1^{4-}	6.32	{—5.3-6.1, multiplet—}			
$2^{2-\,c}$	{———5.4-6.1, multiplet———}				6.55
$7^{d,e}$	{———5.75, broad singlet———}				6.35
$7^{2-\,e}$	{———5.4-6.1, multiplet———}				6.91
$7^{2-\,b,e,f}$	5.84	5.72	5.50	5.69	6.86
5^g	4.42	5.38	3.80	5.20	5.00

^{a} Chemical shifts were measured relative to trimethylamine (TMA) ($\delta^{Me_4Si} = \delta^{TMA} + 2.135$) and were obtained at 60 MHz unless noted otherwise. ^{b} Spectrum obtained at 360 MHz and 20 °C; $J_{23} = 10.25$ Hz; $J_{34} = J_{45} = 8.8$ Hz. ^{c} 100 MHz. ^{d} Spectrum obtained in DCCl$_3$ at 37 °C. ^{e} Staley, S. W.; Cramer, G. M.; Dustman, C. K., unpublished data. ^{f} $J_{23} = 11.7$ Hz; ($J_{34} + J_{45}$)/2 = 10.7 Hz. ^{g} Reference 9. The numbering corresponds to that of the other compounds.
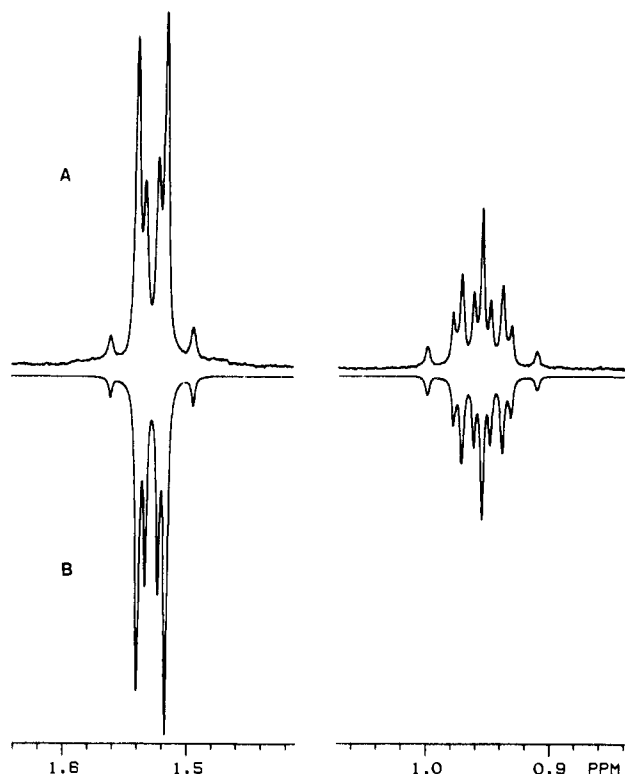

Figure 1. (A) 360-MHz NMR spectrum of the cyclopropyl protons of 3 (in CCl$_4$) with decoupling of the olefinic protons. (B) Computer synthesis of the spectrum in Figure 1A with $J_{19} = 8.90$ Hz, $J_{99'} = 10.22$ Hz, and $J_{19'} = -0.42$ Hz.

Figure 2. 360-MHz NMR spectra of bicyclooctatetraenyldipotassium ($2K^+1^{2-}$) in liquid ammonia at (A) $-80\,^\circ$C and (B) 20 °C. The line separation in the apparent triplet (doublet of doublets) at δ 5.86 in (B) in unsymmetrical due to second-order coupling as confirmed by computer synthesis. The multiplets in A display an area ratio of 1:1:12.

of 1 with 6 equiv of potassium in liquid ammonia at ca. $-60\,^\circ$C gave a deep purple solution of 1^{4-} which was also characterized by ^{1}H NMR spectrometry (Table I). Chemical proof was effected by quenching a solution of 1^{4-} in liquid ammonia into a solution of iodine in pentane. The major product (30% yield) was 1, determined by comparison of its infrared spectrum with that of an authentic sample.

The synthesis of 2^{2-} was accomplished by the route given in Scheme II. The A$_2$A$_2'$XX' bicyclopropyl portion of the 360-MHz ^{1}H NMR spectrum of 3 was solved by computer synthesis[6] (Figure 1). The cis configuration of the cyclopropyl rings of 3 was assigned on the basis of the magnitude of J_{19} ($=J_{1'9'}$) (9.0 Hz),[7] whereas the value of $J_{99'}$ (10.2 Hz) indicates that 3 adopts pre-

dominantly the anti conformation at the C$_9$–C$_9'$ bond.[8] Treatment of 3 with excess potassium amide in liquid ammonia at ca. -60 °C afforded a deep purple solution of 2^{2-} which was observed by ^{1}H NMR spectrometry (Table I). Chemical proof of the structure of 2^{2-} was obtained as shown in Scheme III. An attempt to obtain 2 by adding a sample of 2^{2-} in liquid ammonia to a solution of iodine in pentane produced intractable products. Addition of a similar sample of 2^{2-} to an ice water–ether slurry afforded (presumably) a mixture of C$_{18}$H$_{18}$ isomers, which was catalytically hydrogenated to a saturated hydrocarbon (4). The later compound was readily synthesized by the coupling of bromomethylcyclooctane with magnesium and was found to be identical by infrared spectroscopy and GLPC retention time with 4 obtained via the quench of 2^{2-}.

The 100-MHz ^{1}H NMR spectrum of $2K^+2^{2-}$ is unchanged by cooling from room temperature to ca. $-65\,^\circ$C although changes are observed in the 360-MHz spectrum. The former observation, together with the fact that the potassium salt of the methylenecyclooctatrienyl anion (5) exists predominantly as a contact ion

5

pair in liquid ammonia above $-60\,^\circ$C,[9] may be taken as evidence of the presence of contact ion pairs of 1^{2-} and 2^{2-} over the tem-

(6) ITRCAL (Nicolet Instrument Corp.), adapted from LAOCN3: Castellano, S.; Bothner-By, A. A. *J. Chem. Phys.* **1964**, *41*, 3863.

(7) Jackman, L. M.; Sternhell, S. "Applications of Nuclear Magnetic Resonance Spectroscpy in Organic Chemistry"; 2nd ed.; Pergamon Press: New York, 1969; p 286.
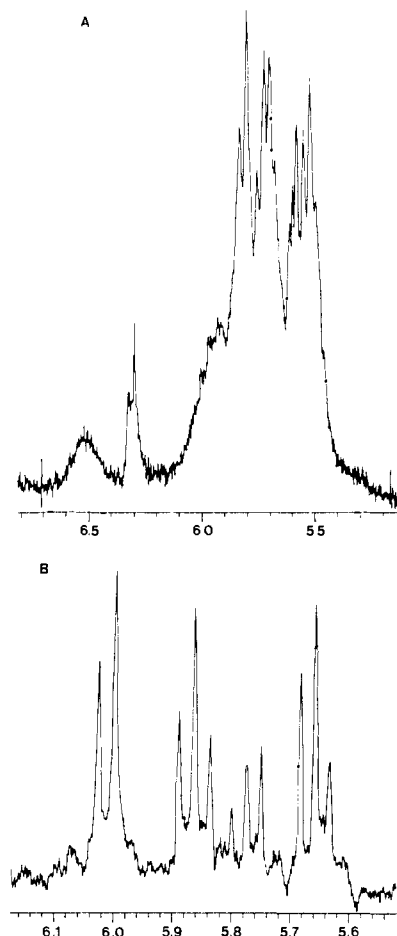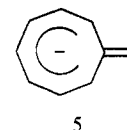
(8) de Meijere, A.; Lüttke, W.; Heinrich, F. *Justus Liebigs Ann. Chem.* **1974**, 306.

(9) Staley, S. W.; Cramer, G. M. *J. Am. Chem. Soc.* **1973**, *95*, 5051.

Table II. HMO $\beta\omega'\omega''$ [a] π-Electron Densities of Several Anions

| anion | π-electron density | | | | | |
	$C_{1(7)}$	$C_{2(6)}$	$C_{3(5)}$	C_4	C_9	C_{10}
5	1.195	1.038	1.230	1.031	1.074	
1^{2-} [b]	1.227	1.050	1.216	1.051	0.962	1.227
2^{2-} [b]	1.200	1.039	1.226	1.033	1.049	1.049
7^{2-}	1.243	1.186	1.241	1.178	0.985	1.350

[a] See ref 11. [b] The anions were assumed to be planar for the purposes of these calculations.

perature range investigated. The 360-MHz ^{1}H NMR spectrum of $2K^+1^{2-}$ in liquid ammonia, which appears as four nearly first-order multiplets at 20 °C, undergoes pronounced changes in appearance below ca. 0 °C which continue down to the freezing point of the solution at ca. -85 °C (Figure 2). This observation provides the key to understanding the structure of 1^{2-}.

Discussion

Charge Distributions and Conformations. Both 1^{2-} and 2^{2-} may, in principal, adopt several conformations, including a fully delocalized methylenecyclooctatrienyl anion form (A) and a more


1A   2A
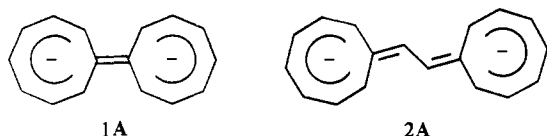
localized form (B) comprising one "aromatic" 10π-electron cyclooctatetraene dianion and one "neutral" tub-like cyclooctatetraene ring. An intriguing possibility is that of charge transfer between the two eight-membered rings (B $\rightleftarrows$ B' $\rightleftarrows$ B'' $\rightleftarrows$ B'''). An analogous process appears to occur in a related *fused*-ring system, viz., the octalene dianion (6).[10]

Scheme IV
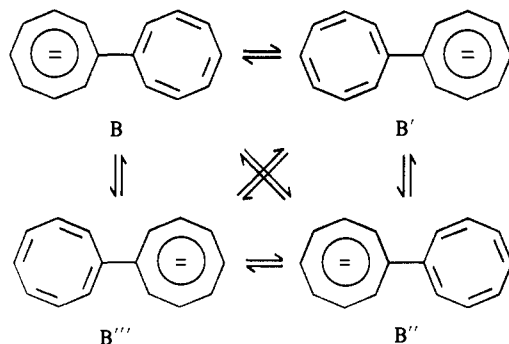
The π-electron densities calculated by a self-consistent ($\beta\omega'\omega''$) Hückel molecular orbital method[11] for 1^{2-} and 2^{2-} assuming conformation A (structures 1-A and 2-A) are given in Table II. The charge distributions are very similar to those calculated for 5. The effect of charge alternation in the eight-membered ring of 5 on its ^{1}H NMR spectrum is to shift protons bonded to the more highly charged carbon atoms upfield of those bonded to the less charged carbon atoms by as much as 1.6 ppm (Table I). In contrast, the ^{1}H NMR spectra of 1^{2-} and 2^{2-} encompass much smaller chemical shift ranges (0.42 ppm for 1^{2-} and 0.70 ppm for 2^{2-}). In addition, HMO ring current calculations based on the London–McWeeny method[12] predict the A type conformations of 1^{2-} and 2^{2-} to be more paramagnetic than 5, which would cause the center of gravity of the chemical shifts of the former anions to appear upfield of that of 5, instead of downfield as found

experimentally. For both of these reasons, the A type conformations must be rejected.

6   7
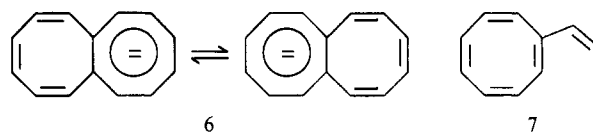
The spectral data are completely compatible with a B-type conformation. The proton chemical shift ranges of the model compounds vinylcyclooctatetraene (7) and its dipotassium salt ($2K^+7^{2-}$) coincide with those of 1^{2-} and 2^{2-} (Table I). This is expected because of the similar charge distributions and ring currents in 1^{2-}, 2^{2-}, and 7^{2-}.

There remains the important question of whether inter-ring electron exchange occurs at a detectable rate in 1^{2-} and 2^{2-}. That this is indeed the case for 1^{2-} is readily determined by inspection of its 360-MHz spectrum in Figure 2. A complex spectrum would be expected if charge were localized in one of the eight-membered rings. The simplicity of the spectrum at high temperatures as well as the exchange broadening evident at low temperatures can be rationalized only if the process in Scheme IV occurs at a rapid enough rate on the NMR time scale. In the case of 2^{2-}, this question is also answered by comparison of its ^{1}H NMR spectrum with those of 7 and 7^{2-}. The exocyclic protons (H_9) of the latter appear at δ 6.35 and 6.91, respectively, the difference being due primarily to charge and ring current effects. These results lead one to expect that the two exocyclic protons of 2^{2-} in a noninterconverting type B conformation will have different chemical shifts. However, the exocyclic protons of 2^{2-} appear as a sharp singlet at δ 6.55, close to the average value for H_9 in 7 and 7^{2-}. This result is consistent with the process in Scheme IV.

Tetraanion 1^{4-} has been previously synthesized but what was apparently a significantly broadened NMR spectrum was reported.[13] Our spectrum consists of a four-proton 11-Hz doublet at δ 6.36 arising from the "ortho" protons, and a twelve-proton multiplet at δ 6.2–5.3 representing the remaining protons.

It was previously concluded that there was no evidence that the two rings in 1^{4-} are mutually interactive and that they adopt a perpendicular or near-perpendicular conformation. It was also asserted that the "ortho" protons fall "well within" the deshielding region of the adjacent ring when in this conformation.[13] We believe that this conclusion is subject to serious doubt, since the two HOMOs of 1^{4-} will be either bonding or nonbonding at the inter-ring bond in any conformation other than the perpendicular. This would tend to cause a twisting away from the perpendicular and would also lead to a deshielding of the "ortho" protons, as is observed.

Detailed Conformations and Dynamic Behavior. From the doublet at δ 6.01, the triplet at 5.77, and the apparent triplet (doublet of doublets) at 5.66 in the 360-MHz spectrum of 1^{2-}, we can determine that $\bar{J}_{23} = 10.25$ Hz (where $\bar{J}_{23}$ is the average value for J_{23}, $J_{2'3'}$, J_{78}, and $J_{7'8'}$ in the two rings of 1^{2-}) and ($\bar{J}_{34}$ + $\bar{J}_{45}$)/2 = 8.8 Hz (Table I). If the coupling constants in 1^{2-} were the average of those for a cyclooctatetraene dianion ring and a cyclooctatetraene ring undergoing bond switching (Scheme IV) and if we use 7^{2-} ($\bar{J}_{23} = 11.7$ Hz; ($\bar{J}_{34}$ + $\bar{J}_{45}$)/2 = 10.7 Hz) (Table I) as a model for the former and cyclooctatetraene ($J_{12} = 11.4$ Hz, $J_{23} = 2.5$ Hz)[14] as a model for the latter, then we would predict $\bar{J}_{23} = 9.3$ Hz ((11.4 + 2.5 + 11.7 + 11.7)/4) and ($\bar{J}_{34}$ + $\bar{J}_{45}$)/2 = 8.8 Hz ((11.4 + 2.5 + 10.7 + 10.7)/4) for 1^{2-}. The latter value agrees perfectly with the experimental value but the experimental value for $\bar{J}_{23}$ is nearly 1 Hz higher than predicted. This discrepancy, which is well outside of our uncertainty (estimated to be ±0.2 Hz each for the experimental and predicted values), can be rationalized on the basis of the "neutral" ring in 1^{2-} being flattened somewhat at one end relative to cyclooctatetraene (see 8), presumably to permit a greater delocalization of negative

(10) Müllen, K.; Oth, J. F. M.; Engels, H.-W.; Vogel, E. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 229.

(11) Gayoso, J.; Andrieux, J.-C.; Herault, V. *J. Chim. Phys. Phys.-Chim. Biol.* **1969**, *66*, 1631.

(12) Review: Haigh, C. W.; Mallion, R. B. *Prog. Nucl. Magn. Reson. Spectrosc.* **1980**, *13*, 303.

(13) Paquette, L. A.; Ewing, G. D.; Traynor, S. G. *J. Am. Chem. Soc.* **1976**, *98*, 279.

(14) Oth, J. F. M. *Pure Appl. Chem.* **1971**, *25*, 573.
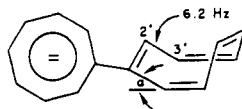
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charge. The experimental value of J_{23} can be reproduced with a value of $J_{2'3'}$ of 6.2 Hz in the "neutral" ring of **8**, which would correspond to a decrease of dihedral $\angle H_2C_2C_3H_3$ from 54° (α = 41°; see **8**) in cyclooctatetraene to 29° (α = 23°) in **1**$^{2-}$, on the basis of the Karplus relation ($^3J = 4.22 - 0.5 \cos \phi + 4.5 \cos 2\phi$).[15] The former dihedral angle compares closely with the value of 58° (α = 43°) in cyclooctatetraene as obtained by gas-phase electron diffraction.[2]

If it is assumed that the chemical shifts of H_9 and $H_{9'}$ of **2**$^{2-}$ in the absence of electron transfer are the same as those for H_9 in **7** and **7**$^{2-}$, then insertion of their frequency difference $\Delta\nu$ into eq 1[16] allows the minimum rate of electron transfer k required

$$k = \pi\Delta\nu/\sqrt{2} \qquad (1)$$

for coalescence of the exocyclic protons of **2**$^{2-}$ to be calculated as >74.6 s^{-1}. The *estimated* maximum free energy of activation for this process in **2**$^{2-}$ is then found from the Eyring equation[17] to be ≤10.2 kcal mol^{-1} at -65 °C, the lowest temperature at which **2**$^{2-}$ was observed.

The rate of electron transfer of >75 s^{-1} at -65 °C requires the eight-membered rings of **2**$^{2-}$ to complete a planar-to-tub (or vice versa) conformational change at that rate. However, the rate of inversion of a neutral cyclooctatetraene ring is only 26 s^{-1} at -10 °C,[18] implying that the ring goes from a planar-to-tub (or vice versa) conformation at a rate of 13 s^{-1}. There are several ways of reconciling the greater rate in **2**$^{2-}$ compared with that in cyclooctatetraene. First, the latter inversion forces the ring into a planar conformation having an 8π-electron "antiaromatic" perimeter. In the case of **2**$^{2-}$, the cyclooctatetraene ring undergoing flattening is simultaneously gaining charge density and eventually attaining a 10π-electron "aromatic" configuration. This change from a tub-like to an "aromatic" planar conformation could cause a lower activation barrier for the ring-flattening process. Second, the "neutral" ring in **2**$^{2-}$ may not fold up completely due to donation of charge from the planar ring which would also allow an increase in the rate of ring flattening. This is consistent with our conclusions regarding the conformation of **1**$^{2-}$ (vide supra).

If a type A conformation is considered to be the transition state or an intermediate for the electron-exchange process, it can lie no more than about 10 kcal mol^{-1} above the type B conformation. Solvents and counterions that promote solvent-separated ion pairs of free ions would favor a delocalized type A conformation at the expense of charge-localized type B conformations. In such a solvent, **2**$^{2-}$ might exist in a type A conformation.

In order to test this possibility, **3** was treated with lithium dimethylamide in hexamethylphosphoramide (HMPA) at ambient temperature to produce an emerald green solution whose 100-HMz ^{1}H NMR spectrum consisted of weak signals that were not interpretable. Treatment of **3** with potassium *tert*-butoxide in dimethyl sulfoxide at ambient temperature gave a blue solution whose 100-MHz ^{1}H NMR spectrum consisted of complex multiplets at δ 3.16–3.44 and 3.74–5.56. Hence attempts to observe a type A ground-state conformation are as yet inconclusive.

Although no estimate of the energy difference between the type A and type B conformations of **1**$^{2-}$ can be made, there are indications that the type A form of **1**$^{2-}$ may be the most stable form in HMPA.[19,20] On the basis of a positive enthalpy and entropy of addition of an electron from cyclooctatetraene radical anion

to **1**, Na$^+$**1**$^-$. is believed to adopt a type A conformation in HMPA.[21] ESR data for **1**$^-$. in 1:1 tetrahydrofuran/HMPA are consistent with either a type A conformation or a Scheme IV type process.[20]

In view of the repulsion energy between the π electrons in a cyclooctatetraene dianion, there must be present substantial energetic factors which cause the B forms of **1**$^{2-}$ and **2**$^{2-}$ to be preferred. One factor is the π-stabilization energy associated with the formation of a cyclooctatetraene dianion moiety. Another is the ca. 14 kcal mol^{-1} of strain energy released by the folding of one of the eight-membered rings[18] as was suggested to be important in the mechanism of bond rotation in 9-aryl derivatives of **5**.[22] An interesting possibility is that the second-order Jahn–Teller effect[23-25] plays a role in destabilizing type A relative to type B conformations. A relevant example is afforded by the radical cation and anion of heptafulvalene (**9**).[26] Whereas **9**$^+$.
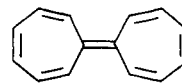
9

is found by ESR spectrometry to be a fully delocalized and symmetrical species, the two rings of **9**$^-$. are nonequivalent at -120 °C, although they become equivalent upon warming. The unpaired electron transfers from one ring to the other. Calculations have shown that the second-order Jahn–Teller effect destabilizes the symmetrical form of **9**$^-$. relative to the localized form and that the effect is negligible for **9**$^+$..[21] The relationship of this example to **1**$^{2-}$ and **2**$^{2-}$ is obvious, particularly when it is noted that one criterion for a large second-order Jahn–Teller effect is the presence of a small HOMO-LUMO energy gap. These values (determined by ω-technique HMO calculations)[27] are small and similar for **1**$^{2-}$ (0.233β), **2**$^{2-}$ (0.198β), and **6** (0.218β).

Summary. Compounds **1**$^{2-}$ and **2**$^{2-}$ undergo rapid electron exchange as represented by Scheme IV. This process is inherently different from that in traditional valence tautomers, such as bullvalene,[28] in that no σ bonds are formed or broken. We propose to name this class of compounds "electron-transfer valence tautomers" and the process "electron-transfer valence tautomerism".

Experimental Section

General. Infrared (IR) spectra were recorded on a Perkin-Elmer Model 337 or 283 infrared spectrophotometer in 1-mm NaCl cells or on KBr plates. NMR spectra were recorded on a Varian A-60D or XL-100 or on an NTC-360 wide bore spectrometer each of which was equipped with a variable-temperature probe. Gas–liquid phase chromatography (GLC) was performed on a Varian-Aerograph Model A90P-3 gas chromatograph. All melting points are uncorrected. Elemental analysis were performed by Galbraith Laboratories. Mass spectra were obtained by Dr. Martha Gay on a Bell and Howell 21-492 mass spectrometer.

Bi-9,9'-*cis*-bicyclo[6.1.0]nona-2,4,6-trienyl (3). Freshly distilled cyclooctatetraene (8.4 g, 0.08 mol) was added to a solution of lithium (1.5 g, 0.22 mol) in ca. 200 mL of refluxing anhydrous liquid ammonia. To the resulting solution was added a solution of 1,1,2,2-tetrachloroethane (5.5 g, 0.03 mol) in 25 mL of anhydrous ether over 15 min. The resulting green-black solution was stirred at -33 °C for 4.5 h. Anhydrous ether (100 mL), ethanol (25 mL), and water (50 mL) were added sequentially, and the ammonia was allowd to evaporate at room temperature. The aqueous layer was extracted with ether (5 × 25 mL) and the combined organic layers were dried over MgSO$_4$. Volatile materials were removed

(15) Karplus, M. *J. Am. Chem. Soc.* **1963**, *85*, 2870.
(16) Gutowsky, H. S.; Holm, C. H. *J. Chem. Phys.* **1956**, *25*, 1228.
(17) Glasstone, S.; Laidler, K. J.; Eyring, H. "Theory of Rate Processes"; McGraw-Hill: New York, 1941; p 195 ff.
(18) Anet, F. A. L. *J. Am. Chem. Soc.* **1962**, *84*, 671.
(19) Stevenson, G. R.; Concepción, J. G. *J. Am. Chem. Soc.* **1973**, *95*, 5692.
(20) Stevenson, G. R.; Ocasio, I. *J. Am. Chem. Soc.* **1976**, *98*, 890.

(21) Stevenson, G. R.; Forch, B. E. *J. Phys. Chem.* **1981**, *85*, 378.
(22) Staley, S. W.; Dustman, C. K. *J. Am. Chem. Soc.* **1981**, *103*, 4297.
(23) Nakajima, T. *Fortschr. Chem. Forsch.* **1972**, *32*, 1. Nakajima, T. *Pure Appl. Chem.* **1971**, *28*, 219.
(24) Binsch, G.; Tamir, I.; Hill, R. D. *J. Am. Chem. Soc.* **1969**, *91*, 2446. Binsch, G.; Tamir, I. *Ibid.* **1969**, *91*, 2450. Binsch, G.; Heilbronner, E. *Tetrahedron* **1968**, *24*, 1215.
(25) Salem, L. *Chem. Phys. Lett.* **1969**, *3*, 99. Salem, L.; Wright, J. S. *J. Am. Chem. Soc.* **1969**, *91*, 5947.
(26) Sevilla, M. D.; Flajser, S. H.; Vincow, G.; Dauben, H. J., Jr., *J. Am. Chem. Soc.* **1969**, *91*, 4139.
(27) Streitwieser, A., Jr. "Molecular Orbital Theory for Organic Chemists"; John Wiley and Sons, Inc.: New York, 1961; pp 115–116.
(28) Schröder, G. *Angew. Chem., Int. Ed. Engl.* **1963**, *2*, 481.

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at reduced pressure. This and all subsequent operations were carried out at temperatures below 30 °C. The orange-red residue was filtered through 20 g of silica gel by employing 0.5 L of hexane followed by 0.5 L of 1% methylene chloride/hexane as eluent. Solvent was removed by rotary evaporation and the residue was chromatographed with hexane on 80 g of silica gel (40-mL fractions). Fractions 15–24 were combined and concentrated to give fine white needles. These were washed with pentane at −70 °C to afford 65 mg (0.8% based on 1,1,2,2-tetrachloroethane) of **3**. An analytical sample was obtained by recrystallization from hexane: mp 174–175 °C; IR (CCl$_4$) 3001, 1640, 1615, 1081, 979 cm^{-1}; NMR (360 MHz; CCl$_4$) δ 5.77–6.02 (12 H, m, olefinic), 1.53 (4 H, X$_2$X$_2'$ of AA'X$_2$X$_2'$, H$_1$, H$_8$, H$_1'$, H$_8'$, J_{19} = 8.9 Hz), 0.96 (2 H, AA' of AA'X$_2$X$_2'$, H$_9$ and H$_{9'}$, $J_{99'}$ = 10.2 Hz). Anal. Calcd for C$_{18}$H$_{18}$: C, 92.26; H, 7.74. Found: C, 92.19; H, 7.79.

Dihydrobicyclooctatetraenyl (1-H$_2$). Bicyclooctatetraenyl (**1**)[5] (0.50 g, 2.4 mmol) in 10 mL of ether was added dropwise to a solution of 67 mg (9.7 mmol) of lithium in 250 mL of liquid ammonia in an inverse addition flask. After 2 h the reaction mixture was added dropwise to 150 mL of saturated aqueous NH$_4$Cl and 100 mL of ether. The layers were separated, and the aqueous layer was saturated with sodium bromide and extracted with 3 × 50 mL of ether. The combined organic material was washed with 2 × 50 mL of water, dried (MgSO$_4$), and concentrated. The residue was chromatogrphed as follows on 75 g of silica gel in 50-mL fractions: fractions 1–30 (100% hexane), 31–35 (0.25% chloroform), 36–40 (1% chloroform), 41–45 (2% chloroform), and 45–55 (3% chloroform). TLC (5% chloroform/95% hexane) of fractions 48 and 49 showed a mixture of two materials, while fraction 50 showed only the second component. An NMR spectrum of fractions 48–50 displayed a complex multiplet at δ 6.20–5.35 (ca. 12 H) and a broadened absorption at δ 2.18–2.83 (ca. 4 H), indicative of a mixture of trienes, and a mass spectrum of this material showed m/z 208 with minor peaks at m/z 210 and 206. The mixture was considered to be mostly cyclooctatrienylcyclooctatetraenes (**1-H$_2$**) with minor impurities due to starting material (**1**) and some tetrahydro product. The yield of the triene mixture was 170 mg.

Bicyclooctatetraenyldipotassium (2K$^+$1^{2-}). (a) From Dihydrobicyclooctatetraenyl. Treatment of 40 mg (0.19 mmol) of **1-H$_2$** with 0.76 mmol of potassium amide (from 29.7 mg of potassium) in 0.5 mL of liquid ammonia according to our general procedure[29] gave a deep purple solution of **1^{2-}** whose 60-MHz NMR spectrum showed at δ 5.57–6.21 with major peaks at δ 5.74, 5.92, and 6.04 at 37 °C.

(b) From Bicyclooctatetraenyl. Treatment of 40 mg (0.19 mmol) of **1**[5] with 15 mg (0.39 mmol) of potassium in 0.5 mL of liquid ammonia according to our general procedure[29] gave a 60-MHz NMR spectrum at 37 °C identical with that obtained for 2K$^+$1^{2-} from **1-H$_2$** and different from that of **1** in ammonia (a broadened singlet at δ 5.92). Data from a spectrum obtained at 360 MHz are given in Table I.

Bicyclooctatetraenyltetrapotassium (1^{4-}). Bicyclooctatetraenyl[5] (40 mg, 0.19 mmol) was treated with 45 mg (1.17 mmol) of potassium in 0.5 mL of liquid ammonia according to our general procedure[29] to afford a deep purple solution of **1^{4-}** whose NMR spectrum is given in Table I.

Oxidative Quench of Bicyclooctatetraenyltetrapotassium (1^{4-}). Bicyclooctatetraenyl[5] (100 mg, 0.485 mmol) in 5 mL of anhydrous ether was added to a solution of 114 mg (0.49 mmol) of potassium in 50 mL of refluxing liquid ammonia. After 20 min the deep purple solution was

cautiously added to a vigorously stirred suspension of 1.23 g (4.85 mmol) of iodine in 50 mL of pentane. The organic layer was washed with 3 × 20 mL of saturated aqueous sodium thiosulfate and dried over anhydrous Na$_2$SO$_4$. (**Caution** *should be observed due to the possible formation of nitrogen triiodide in this procedure.* However, we have never experienced any problems.) The organic layer was concentrated and the residue was chromatographed with hexane on neutral alumina to afford 30 mg (30%) of material whose NMR and infrared spectra were identical with those of authentic **1**.

1,2-Dicyclooctatetraenylethylenedipotassium (2^{2-}). Treatment of 20 mg (0.09 mmol) of **3** with potassium amide (from 8 mg (0.2 mmol) of potassium) in 0.5 mL of liquid ammonia according to our general procedure[29] gave a deep purple solution of **2^{2-}** whose NMR spectrum is given in Table I.

1,2-Dicyclooctylethane (4). (a) By Aqueous Quenching of 2^{2-}. 2K$^+$2^{2-} was formed as described above from 64 mg (0.27 mmol) of **3** and potassium amide (generated from 43 mg (1.1 mmol) of potassium) and characterized by ^{1}H NMR spectrometry. The sample was cooled in a dry ice–acetone bath, the sealed NMR tube was opened, and its contents were rapidly mixed into a stirred ice water/ether slurry. The organic layer was dried over MgSO$_4$ and concentrated to afford a yellow oil. This was dissolved in ethanol and hydrogenated at 1 atm over a 5% Pd/BaSO$_4$ catalyst. Removal of the solvent gave 33 mg of a colorless oil that was purified by GLC on a 2 m × 0.6 cm 10% Igepal CO-880 on 100/120 mesh Chromosorb P column at 180 °C. Due to severe aerosol formation, the actual yield of **4** could not be obtained, but it is estimated to be 35% on the basis of the 33 mg of crude material and the relative peak areas of the resulting chromatogram. The GLC retention time (determined by coinjection) and the IR spectrum of this material were identical with those of authentic **4** as synthesized below.

(b) From Bromomethylcyclooctane. To magnesium ribbon (60.6 mg, 2.49 mmol) in 5 mL of anhydrous ether under nitrogen was added a solution of 1.02 g (5.0 mmol) of bromomethylcyclooctane[30] in 5 mL of anhydrous ether. The solution was refluxed for 7 h. After cooling, 5 mL of water and a sufficient quantity of H$_2$SO$_4$ to dissolve the precipitate were added. The organic layer was washed with 10% NaHCO$_3$ and water and then dried over MgSO$_4$. Concentration by rotary evaporation gave a colorless oil which was purified by GLC on a 2 m × 0.6 cm 10% Igepal CO-880 on 100/120 mesh Chromosorb P column at 245 °C. The yield of **4** was 0.31 g (50%): IR 2931, 2859, 1463, 1451 cm^{-1}; NMR (DCCl$_3$) δ 0.76–1.94 (m). Anal. Calcd for C$_{18}$H$_{36}$: C, 86.32; H, 13.68. Found: C, 86.18; H, 13.72.

Registry No. 1, 6715-22-6; **1-H$_2$**, 85720-71-4; **1^{2-}**, 85735-21-3; **1^{2-}2K$^+$**, 59070-55-2; **1^{4-}**, 64317-43-7; **1^{4-}4K$^+$**, 59139-34-3; **2^{2-}**, 85735-22-4; **2^{2-}·2K$^+$**, 85720-73-6; **3**, 85720-69-0; **4**, 85720-70-3; (CH$_2$CH)$_2$, 79-34-5; I$_2$, 7553-56-2; cyclooctatetraene, 629-20-9; bromomethylcyclooctane, 3814-33-3.

(29) Staley, S. W.; Cramer, G. M.; Orvedal, A. W. *J. Am. Chem. Soc.* **1974**, *96*, 7433.

(30) Baggaley, K. H.; Evans, W. H.; Graham, S. H.; Jonas, D. A.; Jones, D. H. *Tetrahedron* **1968**, *24*, 3445.