J. Am. Chem. Soc. **1981**, *103*, 4297–4302

Mechanism of Bond Rotation in 9-(1-Naphthyl)methylenecyclooctatrienyl Anions

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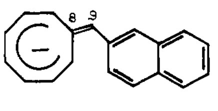
Abstract: The anti isomers of 9-(1-(4-X-naphthyl))-*cis*-bicyclo[6.1.0]nona-2,4,6-triene (**6a–d**) (X = OCH_3, CH_3, H, and Cl, respectively) as well as syn isomers **11b** and **11d** were synthesized by employing three different routes. Treatment of **6a–d** with lithium or potassium amide in liquid ammonia or with lithium dimethylamide in hexamethylphosphoramide (HMPA) affords the corresponding 9-naphthylmethylenecyclooctatrienyl anions (**2a–d**). The latter are considered to be contact ion pairs in liquid ammonia and solvent-separated ion pairs or free ions in HMPA on the basis of the effects of temperature and solvent on the ^{1}H NMR chemical shifts. The activation energies for rotation around the C_8–C_9 bond have been determined to be >17.0, 16.4, 14.4, and 12.2 kcal mol^{-1} for the lithium salts of **2a**, **2b**, **2c**, and **2d**, respectively, >17.0 and 15.1 kcal mol^{-1} for the potassium salts of **2a** and **2c**, respectively, and 16.4 kcal mol^{-1} for (9-(*p*-chlorophenyl)methylenecyclooctatrienyl)lithium (**2e**), all in liquid ammonia, and 16.2 kcal mol^{-1} for the lithium salt of **2b** in HMPA. These data, in conjunction with previous evidence that bond rotation in **2c** occurs by an unimolecular mechanism, lead to the conclusions that the negative charge is located in the region of C_9 and the naphthyl ring in the transition state (**5a–d**) and that folding of the eight-membered ring in **5a–d** provides a significant driving force for bond rotation by this mechanism.

We have recently reported the discovery of low-energy rotations around the C_8–C_9 π bonds in 9-(2-naphthyl)- and 9-(1-naphthyl)methylenecyclooctatrienyl anions (**1** and **2c**, respectively).[1] We have also described experiments which exclude bimolecular and higher kinetic order mechanisms for rotation in **2c**. However, the key problem concerning which of several conceivable unimolecular mechanisms, represented by transition states **3–5**, is operative has not been resolved. This question is of considerable interest because these low-energy rotations occur at bonds with high π-bond orders.



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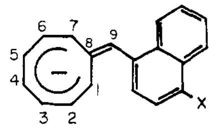
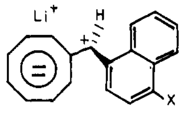


2a, X=OCH_3
b, X=CH_3
c, X=H
d, X=Cl



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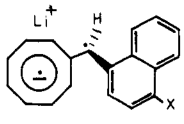

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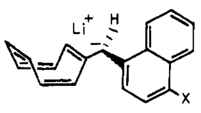


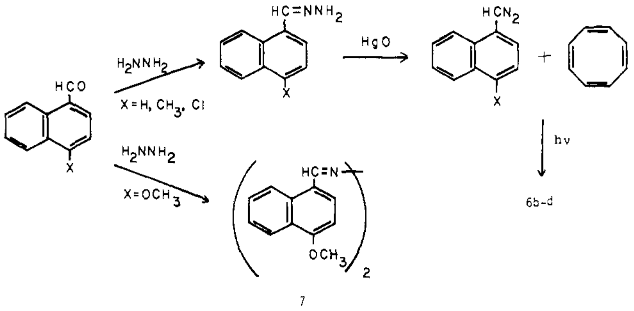
5

a, X=OCH_3
b, X=CH_3
c, X=H
d, X=Cl

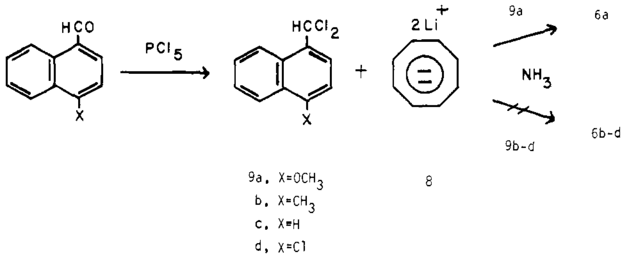
Since **3–5** differ in their charge distributions, it seemed probable that the nature of the transition state could be elucidated by determining the influence of substituents on the activation energy. This goal has been successfully accomplished, and our data lead to the unambiguous conclusion that bond rotation occurs by transition state **5**. A singular feature of this mechanism is the driving force provided by the conformational relaxation of the eight-membered ring in **5**.

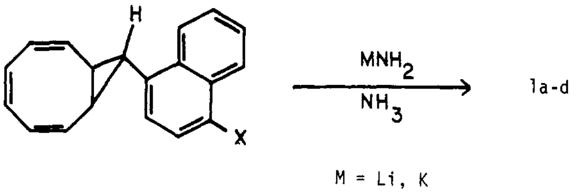
Synthesis of Anion Precursors. 9-Naphthylmethylenecyclooctatrienyl anions **2a–d** were obtained from the corresponding *anti*-9-(1-(4-X-naphthyl))-*cis*-bicyclo[6.1.0]nona-2,4,6-trienes (**6a–d**) by deprotonation with lithium or potassium amide in liquid ammonia. The synthesis of **6c** had previously been accomplished by the route given in Scheme I. This route was also utilized in attempts to synthesize **6a**, **6b**, and **6d** (and was ultimately productive in the case of **6d**), but the method suffers from low and variable percentage yields as well as from the formation of complex

Scheme I



Scheme II





6a, X=OCH_3
b, X=CH_3
c, X=H
d, X=Cl

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(1) S. W. Staley, C. K. Dustman, and G. E. Linkowski, *J. Am. Chem. Soc.*, **103**, 1069 (1981).

(2) This observation has precedent in the observation that anisaldehyde forms the corresponding azine exclusively when treated with hydrazine: R. L. Hinman, *J. Org. Chem.*, **25**, 1775 (1960).

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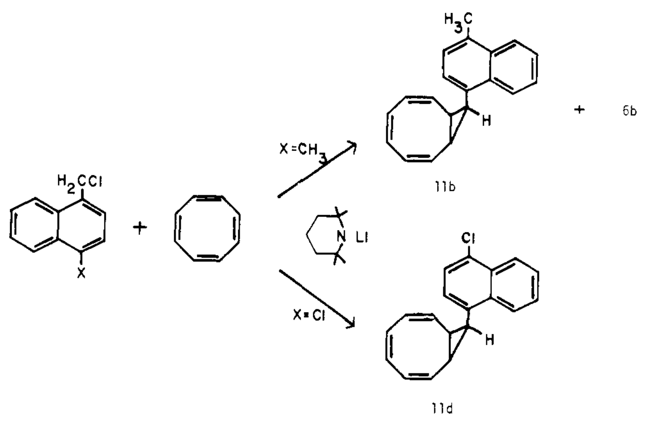
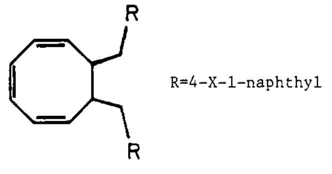
Scheme III



product mixtures in the photolysis step from which it is difficult to isolate the desired product(s). In addition, **6a** could not be synthesized by this route because of the preferential formation of azine **7** rather than the required hydrazone.[2] These difficulties prompted a search for alternate synthetic approaches.

A second route to 9-substituted bicyclo[6.1.0]nona-2,4,6-trienes involves the reaction of α,α-dichloromethylnaphthalenes with the cyclooctatetraene dianion (**8**) in liquid ammonia. As illustrated in Scheme II, this route led to the synthesis of **6a** (and also to a small quantity of **10a** in one run), but complex product mixtures which contained no **6b** or **6c** were obtained from the treatment of **9b** and **9c** with **8**, although **10c** was isolated from the product mixture resulting from the attempted synthesis of **6c**. Cyclooctatetraene was recovered in 95% yield when **9d** was added to a solution of **8** in liquid ammonia. This suggests that electron transfer from **8** to **9**, the ease of which would be expected to occur in the order **9d** > **9c** > **9b** > **9a**,[3] accounts for the lack of desired products.



10a X=OCH_3
c X=H

The syntheses of **6b** and **6d** were next attempted by the route given in Scheme III.[4] A ca. 5:1 mixture of the syn and anti isomers (**11b** and **6b**, respectively) was obtained in 25% overall yield and was separated by preparative HPLC. This procedure also gave the syn isomer **11d** exclusively. The assignment of configuration is based on the size of the cyclopropyl coupling constant which is larger for the syn than for the anti isomer.[5] Unfortunately, syn isomers **11b** and **11d** failed to form the desired anions in liquid ammonia in concentrations sufficient for detection by ^1H NMR spectrometry, although treatment of a solution of **11b** in hexamethylphosphoramide (HMPA) with a solution of lithium dimethylamide in HMPA afforded a dark green solution of **2b**. This seems to reflect a lower solubility of the syn relative to the anti isomers in liquid ammonia since the characteristic green color of **2b** or **2d** was formed very slowly on treatment of **11b** or **11d**, respectively, with lithium amide in liquid ammonia.

The synthesis of **6d** was finally accomplished in low yield by the route given in Scheme I; **6d** and **11d** were obtained in a ratio of 1.9:1. After partial purification by preparative HPLC, the isomers were separated from each other by dissolving the more soluble **6d** in hexane.

Table I. Approaches to the Synthesis of *syn*- and *anti*-9-(1-(4-X-Naphthyl))-*cis*-bicyclo[6.1.0]nona-2,4,6-trienes (11a–d and 6a–d, Respectively)

	% yield^a		
X	Scheme I^b	Scheme II^c	Scheme III^d
OCH_3	0 (azine only)	6 (anti only)	*e*
CH_3	*f*	0	25% (0.2)
H	2–10 (only anti isolated)	0	*e*
Cl	3 (1.9)	0^g	18% (syn only)

^{a} The anti/syn ratios are in parentheses. ^{b} Photolysis of 4-X-1-(diazomethyl)naphthalene in cyclooctatetraene. ^{c} Cyclooctatetraene dianion plus 4-X-1-(dichloromethyl)naphthalene. ^{d} Base-promoted addition of 4-X-1-(chloromethyl)naphthalene to cyclooctatetraene. ^{e} Not attempted but recommended for future investigation. ^{f} 6b and 11b could be detected in an NMR spectrum of the crude reaction mixture. ^{g} Electron transfer; 95% recovery of cyclooctatetraene.

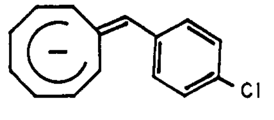
In Table I we summarize our various synthetic results. We recommend that the procedure given in Scheme III be employed initially in any attempts to prepare **6a** and **6c** due to the convenience of the procedure, the higher overall yields, and the ease of purification of the product mixtures.

NMR Studies of Anions. Treatment of **6a–d** with lithium amide in liquid ammonia led to the generation of the corresponding anions **2a–d**. The ^1H NMR spectral parameters of these compounds in the slow-exchange limit are presented in Table II.

A small upfield shift of all of the eight-membered ring protons occurs on warming the anion solutions. For **2b** the average shift is 0.11 ppm over an 85 °C temperature range (Table III). The other anions exhibit similar slight upfield shifts with increasing temperature.

The 90 MHz ^1H NMR spectrum of the lithium salt of **2a** is unchanged (except for the upfield shifts noted above) upon warming to 47 °C. In contrast, warming the lithium salts of **2b** and **2d** produces major changes similar to those which were taken as evidence for rotation about the C_8–C_9 π bond in **2c**.[1] The "coalescence" temperatures of the exchanging pairs of protons are given in Table V. The apparent triplets due to H_2 and H_6 in Li^+ **2b** as well as those due to H_3 and H_5 were exchange broadened at 39 °C, but their coalescence at a higher temperature was not observed due to the rapid decomposition of **2b** above 40 °C.

The facile rotation in **2d** prompted a reinvestigation of the 9-(*p*-chlorophenyl)methylenecyclooctatrienyl anion (**2e**).[6] The doublet of triplets due to H_2 and H_6 were separated by 2 Hz at −60 °C and at 24 °C were coalesced to a single triplet. Warming the sample to 38 °C caused the doublet of doublets due to H_1 and H_7 as well as the doublet of triplets due to H_3 and H_5 to exhibit exchange broadening. Further warming led to decomposition, so coalescence temperatures were not obtained.



2e

The potassium salts of **2a** and **2c** have also been generated in liquid ammonia. This requires considerable care since excess potassium amide will rapidly attack **2a** and **2c** at C_9 to form the corresponding aminomethylcyclooctatetraene dianions.[7] The chemical shifts of the lithium and potassium salts of **2a** and **2c** are compared at similar temperatures in Table IV. In both potassium salts ^1H NMR signals due to compounds other than

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(3) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists", Wiley, New York, 1961, pp 173–185.

(4) R. A. Olofson and C. M. Dougherty, *J. Am. Chem. Soc.*, **95**, 581 (1973).

(5) F. A. Bovey, "Nuclear Magnetic Resonance Spectroscopy", Academic Press, New York, 1969, p 360.

(6) S. W. Staley and G. E. Linkowski, *J. Am. Chem. Soc.*, **98**, 5010 (1976).

(7) S. W. Staley, G. E. Linkowski, and A. S. Heyn, *Tetrahedron*, **31**, 1131 (1975).

Table II. NMR Data for 9-Arylmethylenecyclooctatrienyl Anions (Lithium Salts)

				chemical shift,[a] δ				
anion[b]	X	*T*, °C	solvent	H_1, H_7	H_2, H_6	H_3, H_5	H_4	H_9
2a	OCH_3	−60	NH_3	4.53, 4.53 (d, $J = 13.5$ Hz)	5.41, 5.26 (two t, $J = 10.1$ Hz)	3.82, 3.70 (two t, $J = 11.3$ Hz)	5.14 (t, $J = 11.9$ Hz)	6.67 (s)
2b	CH_3	−60	NH_3	4.52, 4.47 (two d, $J_{12} = 12.9$ Hz, $J_{67} = 12.4$ Hz)	5.37, 5.24 (two t, $J = 10.5$ Hz	3.79, 3.66 (two t, $J = 11.4$ Hz, $J = 11.0$ Hz)	5.11 (t, $J = 11.0$ Hz)	6.67 (s)
2c	H	−60	NH_3	4.49, 4.40 (two d, $J = 13.0$ Hz)	5.33, 5.23 (two d of d, $J_{12} = 13.0$ Hz, $J_{23} = 10.8$ Hz)	3.76, 3.62 (two t, $J = 10.8$ Hz)	5.09 (t, $J = 11.0$ Hz)	6.66 (s)
2d	Cl	−60	NH_3	4.45, 4.30 (t, $J = 12.9$ Hz	5.33, 5.19 (two t, $J = 10.4$ Hz)	3.76, 3.62 (two t, $J = 10.5$ Hz)	5.06 (t, $J = 10.4$ Hz)	6.58 (s)
2b	CH_3	33	HMPA	4.00, 4.00 (d, $J = 13.1$ Hz)	4.86, 4.86 (two t, $J = 11.0$ Hz)	*c*	4.62 (t, $J = 10.7$ Hz)	6.08 (s)

[a] Trimethylamine ($\delta_{NH_3}{}^{Me_4Si}$ 2.135) was used as an internal standard in NH_3; Me_4Si was used in HMPA. [b] Ca. 0.33 M solutions. [c] Obscured by solvent signals centered at δ 2.6.

Table III. Chemical Shifts of H_1–H_9 of the Lithium Salt of 2b (X = CH_3) in Liquid Ammonia at Various Temperatures in the Slow-Exchange Limit

	chemical shift,[a] δ								
T, °C	H_1	H_2	H_3	H_4	H_5	H_6	H_7	H_9	CH_3
−54	4.47	5.37	3.79	5.11	3.66	5.24	4.52	6.67	2.70
−42	4.43	5.34	3.76	5.08	3.62	5.21	4.48	6.63	2.69
−7	4.36	5.31	3.73	5.05	3.59	5.18	4.45	6.57	2.69
11	4.34	5.29	3.71	5.03	3.57	5.17	4.43	6.54	2.69
31	4.31	5.29	3.69	5.02	3.56	5.14	4.41	6.52	2.68

[a] Trimethylamine ($\delta_{NH_3}{}^{Me_4Si}$ 2.135) was used as an internal standard.

Table IV. Chemical Shifts of H_1–H_9 of the Lithium and Potassium Salts of **2a** and **2c** in Liquid Ammonia

			chemical shift,[a] δ							
compd	X	*T*, °C	H_1	H_2	H_3	H_4	H_5	H_6	H_7	H_9
Li^+ **2a**	OCH_3	−71	4.56	5.44	3.85	5.17	3.73	5.32	4.56	6.70
K^+ **2a**	OCH_3	−72	4.57	5.43	3.85	5.17	3.72	5.33	4.57	6.73
Li^+ **2c**	H	−25	4.40	5.33	3.76	5.08	3.61	5.23	4.48	6.65
K^+ **2c**	H	−33	4.33	5.27	3.71	5.02	3.62	5.17	4.45	6.62

[a] Trimethylamine ($\delta_{NH_3}{}^{Me_4Si}$ 2.135) was used as an internal standard.

Table V. Experimental Data and Free Energies of Activation ($\Delta G^{\ddagger}$) for 9-Arylmethylenecyclooctatrienyl Anions

anion	X	cation	solvent	T_c,[a] °C	$\Delta G^{\ddagger}$[b]	$\Delta G^{\ddagger}$(DNMR)[c]	*T*,[d] °C
1		Li	NH_3	27[e]	14.9	15.1[e]	27
2a	OCH_3	Li	NH_3	*g*	>17.0[h]		
2b	CH_3	Li	NH_3	38	16.4	16.4	38
2c	H	Li	NH_3	5[e]	14.4	14.4[e]	4
2d	Cl	Li	NH_3	−38 (−45)[f]	12.1	12.2	−38
2e		Li	NH_3	*g*		16.4	38
2a	OCH_3	K	NH_3	*g*	>17.0[h]		
2c	H	K	NH_3	27[e] (12)[f]	14.9	15.1[e]	27
2b	CH_3	Li	HMPA	31	16.1	16.2[i]	31

[a] "Coalescence" temperature of H_1 and H_7 at 90 MHz; ±2 °C. [b] Calculated from eq 1 and the Eyring equation; ±0.3 kcal mol^{-1} for H_1 and H_7. [c] Calculated from rate constants obtained from DNMR-3A line shape syntheses; ±0.2 kcal mol^{-1}. [d] Temperature at which the data chosen for line shape synthesis studies was obtained. [e] Values are based on ^1H NMR spectra obtained at 100 MHz. [f] "Coalescence" temperature of H_3 and H_5 at 90 MHz; ±2 °C. [g] The "coalescence" temperature of H_1 and H_7 was not observed. [h] Estimated from the frequency difference between H_1 and H_7 at the highest temperature of observation. For Li^+ and K^+ **2a**, the temperatures are 47 and 52 °C, respectively. [i] ±0.3 kcal mol^{-1}.

the desired anions (probably the 9-amido adducts) were noted. The consequent uncertainty of the concentrations of K^+ **2a** and K^+ **2c**, as well as magnetic anisotropy effects due to the other species in solution, makes interpretation of the counterion effect on the chemical shift of the eight-membered ring protons difficult. The ^1H NMR spectrum of K^+ **2a** remained in the slow-exchange limit below 52 °C, whereas that of K^+ **2c** exhibited coalescence phenomena (Table V).

The effect on rotation of a more ionizing solvent was investigated by generating Li^+ **2b** in HMPA (Table II). The signals due to H_3 and H_5 were obscured by the solvent peaks centered at δ 2.6, whereas those of H_1 and H_7 appeared as a single doublet throughout the temperature range of observation. The apparent triplets due to H_3 and H_5 coalesced to a single apparent triplet at 43 °C at 90 MHz.

Ground States of the Anions. The general upfield shifts of the eight-membered ring protons of the lithium salts of **2a–d** with increasingly powerful electron-withdrawing groups have been shown to result from substituent-dependent changes in the paramagnetic ring current in the eight-membered ring.[6] The upfield shift of H_9 in **1** and **2c** relative to model compounds was taken as evidence for twisting of the ring systems about the C_9–aryl bond.[1] The similar chemical shifts of H_9 in **2a–d** suggest that all of these systems are twisted by about the same amount.

The small upfield shifts of H_1–H_9 in the lithium salts of **2a–d** (see Table III) as well as in the potassium salts of **2a** and **2c** with increasing temperature are indicative of contact ion pairs.[8] Additional evidence for contact ion pairs is provided by the upfield shifts of the eight-membered ring protons of Li^+ **2b** in HMPA relative to those in ammonia at a similar temperature (cf. Li^+ **2b** in Tables *II* and III), which are expected for a change from contact ion pairs in the former solvent to solvent-separated ion pairs or free ions in the latter. We conclude that in the ground state the lithium and potassium salts of **2a–d** form predominately contact ion pairs above −60 °C in liquid ammonia and are mostly solvent-separated ion pairs or free ions in HMPA. The cation in the contact ion pairs is probably located over the eight-membered ring since the negative charge is clearly confined to this portion of the molecule.[6,9]

Substituent Effects on Rates of Rotation. Rate constants for exchange in **2b–d** were obtained by line shape synthesis using the DNMR-3 program[10] (Table V) and also from the relationship

$$k_c = \pi \Delta\nu / 2^{1/2} \qquad (1)$$

where k_c is the rate of exchange at the coalescence temperature and $\Delta\nu$ is the frequency difference in hertz between the coalescing signals in the slow-exchange limit.[11] In general, this frequency difference is a function of temperature, and values of $\Delta\nu$ at the coalescence temperature were obtained by extrapolation from a linear correlation of $\Delta\nu$ (as measured at various temperatures in the slow-exchange limit (Table V) vs. temperature). Free energies of activation ($\Delta G^\ddagger$) were then calculated from the Eyring equation in which the transmission coefficient is assumed to be one.[12] These values are presented in Table V, along with the values of $\Delta G^\ddagger$ previously obtained for **1** and **2c**.[1]

The use of eq 1 for "coalescing" multiplets has been considered to be somewhat problematical.[13] However, comparison of $\Delta G^\ddagger$ values derived from the values of k_c obtained from eq 1 and also from the line shape synthesis studies shows them to be in excellent agreement with each other.

From inspection of Table V it is evident that electron donors raise the activation barrier for rotation about the C_8–C_9 double bond, whereas electron-withdrawing groups lower it. If $\Delta G^\ddagger$ is assumed to be essentially independent of temperature over a range of 80 °C, it becomes possible to determine the rate constant for rotation of **2b** and **2d** at the coalescence temperature of **2c** through the use of the Eyring equation. This in turn allows construction of a three-point $\sigma\rho$ plot, by employing previously determined 1-(4-X-naphthyl) σ values.[14] The ρ value thus determined is +8.1 with a correlation coefficient of 0.99. The activation barrier for **2a** can then be estimated to be ca. 18 kcal mol^{-1} on the basis of the methoxy σ value[14] which is consistent with the experimentally established lower bound of 17.0 kcal mol^{-1}.

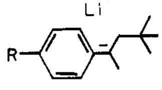
The order of substituent effects as reflected by this ρ value indicates that the substituents interact with an electron-rich transition state. This clearly eliminates transition states **3a–d**. It is also possible to exclude the diradical transition states **4a–d**, since electron donors accelerate the rate of reactions which form benzyl radicals from closed-shell precursors.[15] Furthermore, the absolute value of ρ is considerably larger than those found for the foregoing reactions, which are generally less than one.[15] Only transition states **5a–d**, which are expected to be strongly stabilized by electron-withdrawing groups, are compatible with the experimental data.

Several factors combine to render **5a–d** lower in free energy than **3a–d** and **4a–d**. First, the resonance stabilization of **3a–d** due to formation of a cyclooctatetraene dianion and an α-methylnaphthyl cation will be offset by the energy required for charge separation. In addition, **5a–d** will be stabilized relative to **3a–d** and **4a–d** by ca. 14 kcal mol^{-1} due to release of strain energy as the eight-membered ring becomes nonplanar.[16] This is a noteworthy feature of this mechanism. Finally, the more localized negative charge distribution in **5** relative to **3** and **4** will be accompanied by a more stabilizing cation–anion interaction.

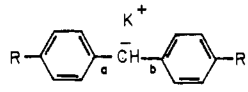
Although the ^1H NMR spectra of the para-substituted phenyl analogues of **2a–c** do not exhibit exchange phenomena at temperatures up to ca. 35 °C, **2e** exhibits an exchange-broadened spectrum on warming to 38 °C. The acceleration of the rate of rotation by an electron-withdrawing substituent indicates that rotation in this series occurs through transition states similar to **5a–d**.

Line shape synthesis reveals that $\Delta G^\ddagger$ for **2e** is 4.2 kcal mol^{-1} greater than that for **2d** (see Table V). Rotational activation barriers in the 9-phenylmethylenecyclooctatrienyl anions are expected to be larger than those for **2a–d** both because **2a–d** are twisted to a greater extent about the C_9–aryl bond than are the corresponding phenyl anions,[1] causing a destabilization of the ground state of the former relative to the latter, and, more importantly, because the greater ability of the naphthyl group to delocalize charge stabilizes transition states **5a–d** relative to similar transition states involving substituted phenyl groups. The same effects also explain the lower activation barrier in **2c** relative to **1** (Table V).

Comparison of $|\Delta\Delta G^\ddagger|$ (the absolute difference in activation barriers between otherwise equivalent *p*-hydrogen- and *p*-alkyl-substituted anions) gives the following order: $|\Delta\Delta G^\ddagger|_{\mathbf{2b}-\mathbf{2c}} = 2.0$ kcal/mol (in ammonia) > $|\Delta\Delta G^\ddagger|_{\mathbf{12a}-\mathbf{12b}} = 1.5$ kcal/mol or $|\Delta\Delta G^\ddagger|_{\mathbf{12a}-\mathbf{12c}} = 1.6$ kcal/mol (in TMEDA–isooctane)[17] > $|\Delta\Delta G^\ddagger|_{\mathbf{13b}(\text{bond a})-\mathbf{13a}} = 0.8$ kcal/mol or $|\Delta\Delta G^\ddagger|_{\mathbf{13c}-\mathbf{13b}(\text{bond b})} = 0.6$ kcal/mol (in HMPA–THF).[18] It is interesting that this order correlates very well with the change in HMO (ω technique) π-charge density at the para position upon rotation (Δq): $\Delta q_{\mathbf{5c}}$ (0.17) > $\Delta q_{\mathbf{12a}}$ (0.09) > $\Delta q_{\mathbf{13a}}$ (0.04). However, solvent and counterion also play a role as indicated by the different values obtained for $\Delta G^\ddagger_{\mathbf{13b}(\text{bond b})}$ the potassium salt in HMPA–THF[18] and the lithium salt in THF.[19]

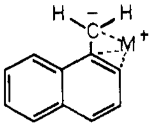


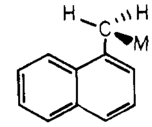
12a R=H
12b R=i-Pr
12c R=t-Bu



13a R=R'=H
13b R=H, R'=CH$_3$
13c R=R'=CH$_3$

Counterion and Solvent Effects on Rotation. As noted previously, **2a–d** form contact ion pairs in the ground state. As negative charge is transferred from the eight-membered ring to the naphthylmethyl moiety upon rotation, the cation is expected to change its position so as to remain closely associated with this charge. An extensive study of the 1-methylnaphthyl anion (**14**) in THF led to the conclusion that the counterion coordinates not





M = Li, Na, K

14

15

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only with the exocyclic carbon but also with two adjacent ring positions as well.[20] Ground-state **14** possesses a charge distribution similar to those which we propose for rotational transition states **5a–e**, and it is likely that the cation interacts with the latter in the same way as it does with the former.

On replacing lithium with potassium in **2c**, $\Delta G^{\ddagger}$ increases from 14.4 to 15.1 kcal mol^{-1}. This is a small change when compared to the estimated 4.9 kcal mol^{-1} increase in $\Delta G^{\ddagger}$ for rotation about the exocyclic π bond in **14** in THF-d_8 for the same pair of cations. The relative insensitivity to a change of the cation on the activation barrier in **2c** can be explained by a comparison of the cation–anion interactions in the ground and transition states. Due to the localization of charge on the exocyclic carbon atom for **14** → **15**, the harder[21] lithium cation stabilizes **15** relative to **14** more than does the softer[21] potassium cation. In contrast, the magnitude of the cation–anion interactions in **2c** and **5c** are expected to be similar since charge is extensively delocalized in both.

This analysis is supported by the observation that $\Delta G^{\ddagger}$ for rotation in the lithium salt of **2b** is approximately the same in ammonia as in HMPA (Table V). The change in ground-state energy due to the shift from contact to solvent-separated ion pairs or free ions is apparently balanced by a similar change in the transition state, as expected if the degree of charge delocalization in transition-state **5b** is similar to that in ground-state **2b**.

Summary

Determination of the effect of substituents on the rate of rotation around the C_8–C_9 bond in **2a–d** has led to the conclusion that this process occurs through transition states **5a–d**. The small observed counterion and solvent effects are also satisfactorily accomodated by these transition states. The low barriers to rotation are explained in part by the unusual driving force provided by a folding of the eight-membered rings in the transition states.

Experimental Section

General Data. Infrared (IR) spectra were recorded on a Perkin-Elmer Model 337 or Model 283 infrared spectrophotometer in 1-mm NaCl cells or on KBr pellets. NMR spectra were recorded on a Varian EM-390 spectrometer equipped with an internal lock and a variable-temperature probe. Preparative high-pressure liquid chromatography (HPLC) was performed on a Waters Prep 500 liquid chromatograph. All melting points are uncorrected. Elemental analyses were performed by either Galbraith Laboratories or by Dr. Franz Kasler of the University of Maryland.

4-Methoxy-1-naphthaldehyde Azine (7). To a solution of 20 g (0.11 mol) of 4-methoxy-1-naphthaldehyde (Aldrich) in 120 mL of 1-butanol was added 15 mL of 85% hydrazine hydrate. The solution was stirred and refluxed for 4 h, poured into 300 mL of methanol, and concentrated (rotary evaporation) to ca. 100 mL. When the solution was left standing in a refrigerator overnight, 16 g (0.043 mol, 79%) of yellow crystals (mp 192–193 °C) of **7** were isolated. (Refluxing a sample of **7** with a 12 M excess of 95% hydrazine hydrate in ethanol failed to produce the corresponding hydrazone.) IR 3010, 1577, 1322, 1269, 1226 cm^{-1}; ^{1}H NMR ($DCCl_3$) δ 9.39 (2 H, s, H_9), 9.09 (2 H, d, aromatic, J = 8 Hz), 8.38 (2 H, m, aromatic), 8.06 (2 H, d, aromatic, J = 8 Hz), 7.65 (4 H, m, aromatic), 6.94 (2 H, d, aromatic, J = 8 Hz), 4.10 (6 H, s, methoxy). Anal. Calcd for $C_{24}H_{20}N_2O_2$: C, 78.26; H, 5.44; N, 7.61. Found: C, 78.04; H, 5.52; N, 7.65.

4-Methoxy-1-(dichloromethyl)naphthaldehyde (9a). A stirred solution of 7.5 g (40 mmol) of 4-methoxy-1-naphthaldehyde in 50 mL of ether under nitrogen was cooled to ca. 0 °C with an ice bath and phosphorous pentachloride (16.1 g, 77 mmol) was added in one portion. After 5 min the ice bath was removed and stirring was continued for 1 h at room temperature. The solution was filtered and concentrated by rotary evaporation. Phosphoryl oxychloride was removed by heating the product to 100–110 °C in vacuo until a constant weight was attained. (Attempts to purify the product by distillation caused decomposition and formation of a black resin.) The yield of product (as an amber oil) was 9.75 g (40.4 mmol), 100% of theory: ^{1}H NMR ($DCCl_3$) δ 8.21 (2 H, m, aromatic), 7.59 (1 H, d, aromatic, J = 8 Hz), 7.44 (2 H, m, aromatic), 7.19 (1 H, s, H_9), 6.48 (1 H, d, J = 8 Hz), 3.76 (3 H, s, methoxy).

***anti*-9-(1-(4-Methoxynaphthyl))-*cis*-bicyclo[6.1.0]nona-2,4,6-triene (6a).** To a stirred solution of 0.60 g (87 mmol) of lithium in 100 mL of refluxing anhydrous ammonia was added, over a ca. 5-min period, a solution of 4.51 g (43.3 mmol) of cyclooctatetraene in 10 mL of anhydrous ether. The resulting red-brown solution contained a tan precipitate. To this solution was added dropwise over 5 min a solution of 9.75 g (40.4 mmol) of 4-methoxy-1-(dichloromethyl)naphthalene in 15 mL of anhydrous ether. The chocolate brown solution was stirred for 0.5 h, and then 50 mL of ether was added, followed by dropwise addition of 50 mL of saturated aqueous NH_4Cl. Ammonia was allowed to evaporate at room temperature, the organic layer was separated, and the aqueous layer was extracted with 50-mL portions of ether until the extracts were almost colorless. All subsequent operations were performed at temperatures below 30 °C. The combined organic layers were dried over $MgSO_4$, filtered, and concentrated by rotary evaporation. The red-black concentrate was chromatographed on 30 g of Baker 60–200 mesh silica gel with 3% ether–hexane in 75-mL fractions. The first four fractions were combined and concentrated by rotary evaporation to give a thick yellow oil. This oil was chromatographed on 85 g of E. Merck silica gel 60 (activity 2–3) with 3% ether–hexane. The first fraction was 100 mL and all the rest were 40 mL. Fractions 4–10 were combined and concentrated by rotary evaporation to give a yellow oil. The oil solidified after trituration with 1 mL of hexane and on standing in a refrigerator for 2 h. The solid was transferred to a Buchner funnel and washed repeatedly with cold (dry ice–acetone) pentane. After the mixture was dried, 0.597 g (2.18 mmol, 5%) of **6a** was obtained as fine white needles: mp 79.5–80.0 °C; IR 3080, 1590, 1468, 1380, 1270, 1099 cm^{-1}; ^{1}H NMR ($DCCl_3$) δ 8.2–8.4 (2 H, m, aromatic), 7.4–7.7 (2 H, m, aromatic), 7.24 (1 H, d, J = 7.8 Hz), 6.70 (1 H, d, J = 7.8 Hz), 4.9–5.5 (6 H, m, olefinic), 3.96 (3 H, s, methoxy), 1.99 (1 H, A of AB_2, H_9, $J_{19} = J_{18}$ = 5.6 Hz), 1.83 (2 H, B of AB_2, H_1 and H_8). Anal. Calcd for $C_{20}H_{18}O$: C, 87.56; H, 6.62. Found: C, 87.74; H, 6.66.

1,2-Bis(1-(4-methoxynaphthyl))-3,5,7-cyclooctatetraene. In an earlier run using a procedure similar to that employed for the synthesis of **6a**, but with hexane as eluant for the initial column, 76 mg (0.17 mmol, 1% based on 4-methoxy-1-(dichloromethyl)naphthalene) of **10** was isolated by cooling the oil obtained from fractions 11–20 (20 mL each) to dry ice temperatures: mp 130–131.5 °C; IR 3002, 1589, 1467, 1391, 1097 cm^{-1}; ^{1}H NMR ($DCCl_3$) δ 8.20–8.29 (2 H, m, aromatic), 7.79–7.87 (2 H, m, aromatic), 7.38–7.55 (4 H, m, aromatic), 7.15 (2 H, d, aromatic, J = 7 Hz), 6.68 (2 H, d, aromatic, J = 7 Hz), 6.00 (2 H, d, H_4 and H_7, $J_{34} = J_{78}$ = 10 Hz), 5.62 (2 H, s, H_5 and H_6), 5.24 (2 H, d of d, H_3 and H_8, $J_{18} = J_{23}$ = 6 Hz), 3.96 (6 H, s, methoxy), 3.04–3.52 (6 H, m, H_1, H_2, and exocyclic protons). Anal. Calcd for $C_{32}H_{30}O_2$: C, 86.06; H, 6.77. Found: C, 86.07; H, 6.80.

***syn*- and *anti*-9-(1-(4-Methylnaphthyl))-*cis*-bicyclo[6.1.0]nona-2,4,6-triene (11b and 6b).** A flame-dried flask containing 20 mL of ether and 0.60 g (86.5 mmol) of lithium wire (cut into small pieces) under a nitrogen atmosphere was cooled in an ice bath. A solution of 20 mL of ether containing 5.48 g (39.9 mmol) of 1-bromobutane was added dropwise over 1 h. The solution was warmed to room temperature, stirred for 2 h, and then cooled in an ice bath, and 2,2,6,6-tetramethylpiperidine (5.53 g, 39.2 mmol) was added over 5 min. After being stirred at room temperature for 0.5 h, this solution was transferred by syringe to an addition funnel and added dropwise (at a rate sufficient to maintain a gentle reflux) to a solution of 40 mL of ether, 40 mL of freshly distilled cyclooctatetraene, and 7.84 g (41.1 mmol) of 4-methyl-1-(chloromethyl)naphthalene[22] under a nitrogen atmosphere. The solution became bright orange and contained a white precipitate. After the solution was stirred for 1.5 h at room temperature, 30 mL of H_2O was added, the layers were separated, the organic layer was washed with 2 × 25 mL of water, and the combined aqueous layers were washed with 25 mL of ether. The temperature of the products in subsequent operations was not allowed to exceed 30 °C. The combined organic layers were dried over $MgSO_4$ and filtered, the ether was removed by rotary evaporation, and cyclooctatetraene was removed by vacuum distillation. Crystals of **11b** formed in the residue when cooled overnight and were collected by filtration. The remaining oil was chromatographed on 130 g of neutral alumina in 100-mL fractions of hexane for fractions 1–5 and 1% ether–hexane for fractions 6–10. After analysis of the fractions by TLC, fractions 5–9 were combined and concentrated to give an oily solid consisting of a mixture of **6b** and **11b**. This solid was dissolved in 7 mL of methylene chloride, and the solution was injected onto a preparative HPLC silica gel cartridge. Elution with hexane revealed two overlapping major peaks, the second of which was partially separated from the first by using the recycle technique. Concentration of the fractions containing material giving rise to the second peak produced **11b** as a white solid whereas concentration of the fractions containing material giving rise to

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the first peak afforded a green oil containing some crystalline material consisting mostly of **6b** and some **11b**. The latter material was rechromatographed by preparative HPLC using conditions similar to those used in the first run, the only exception being the use of hexane to dissolve the oil and solid before injection. Recycling permitted complete separation of **6b** from **11b**. The **11b** collected from the two HPLC runs plus that which had crystallized from the crude reaction product was recrystallized from hexane to give 2.07 g (8.01 mmol, 20%) of **11b** as pure white crystals: mp 119–120 °C; IR: 3009, 1597, 1033, 833 cm^{-1}; ^{1}H NMR ($DCCl_3$) δ 8.34–8.46 (1 H, m, aromatic), 7.96–8.07 (1 H, m, aromatic), 7.49–7.64 (2 H, m, aromatic), 7.41 (1 H, d, aromatic, $J = 7$ Hz), 7.18 (1 H, d, aromatic, $J = 7$ Hz), 5.87–5.94 (6 H, m, olefinic), 2.82 (1 H, t, H_9, $J_{19} = J_{89} = 9.2$ Hz), 2.64 (3 H, s, methyl), 2.17 (2 H, d, H_1 and H_8). Anal. Calcd for $C_{20}H_{18}$: C, 92.98; H, 7.02. Found: C, 92.87; H, 7.14.

The fractions from the second HPLC run containing **6b** were combined and concentrated to give a green oil. This was triturated with pentane, cooled to dry ice temperatures, and allowed to warm while being scratched with a glass rod. A fine white powder appeared at temperatures below 0 °C which, when rapidly collected by suction filtration, remained solid at room temperature. Several crops were collected. Analytically pure material was obtained by low-temperature (−20 °C) recrystallization from hexane. The product (0.480 g, 1.86 mmol, 5%) was isolated as fine white crystals: mp 53–54 °C; IR 3075, 3005, 2860, 1598, 1381, 1065, 927 cm^{-1}; ^{1}H NMR ($DCCl_3$) δ 8.30–8.44 (1 H, m, aromatic), 7.96–8.12 (1 H, m, aromatic), 7.52–7.66 (2 H, m, aromatic), 7.20 (2 H, s, aromatic), 5.90–6.46 (6 H, m, olefinic), 2.68 (3 H, s, methyl), 2.06 (1 H, A of AB_2, H_9, $J_{19} = J_{89} = 4.8$ Hz), 1.85 (2 H, B of AB_2, H_1 and H_8). Anal. Calcd for $C_{20}H_{18}$: C, 92.76; H, 7.20. Found: C, 92.76; H, 7.20.

4-Chloro-1-naphthaldehyde Hydrazone. Nitrogen was bubbled for 20 min through a stirred solution of 1.5 g (7.9 mmol) of 4-chloro-1-naphthaldehyde[23] in 60 mL of ethanol. After addition of 3.5 mL of 85% hydrazine hydrate, the solution was refluxed for 4.5 h under nitrogen and cooled to room temperature and 5 g of $MgSO_4$ was added. After 5 min, the solution was filtered and ethanol removed by rotary evaporation. (An earlier attempt to recrystallize the hydrazone led to formation of the corresponding azine). The crude hydrazone was used immediately in the next reaction.

4-Chloro-1-(diazomethyl)naphthalene. The crude 4-chloro-1-naphthaldehyde hydrazone obtained from the previous experiment was dissolved in 80 mL of ether under nitrogen. To this solution was added 8.75 g (4.04 mmol) of yellow mercuric oxide, 10.00 g (73.5 mmol) of calcium sulfate, and 0.55 g (10 mmol) of sodium methoxide. The solution was stirred overnight and then filtered through a Celite bed. Ether was removed by rotary evaporation at room temperature. The red oil thus obtained was used immediately in the next step.

***syn*- and *anti*-9-(1-(4-Chloronaphthyl))-*cis*-bicyclo[6.1.0]nona-2,4,6-triene (11d and 6d).** The 4-chloro-1-(diazomethyl)naphthalene obtained from the previous experiment was dissolved in 80 mL of freshly distilled cyclooctatetraene. This solution was placed in a Pyrex photolysis well, purged with nitrogen for 20 min, and then irradiated with a 450-W medium-pressure Hanovia lamp for 3 h. All subsequent operations were carried out at temperatures below 30 °C. The excess cyclooctatetraene was removed in vacuo, and the residue was chromatographed with 1% ether–hexane (100 mL fractions) on 75 g of E. Merck silica gel 60 (activity 2–3). Fractions 6 and 7 were combined and concentrated by rotary evaporation to give oily crystals consisting of a mixture of **6d** and **11d**.

The combined product from three such reactions (involving a total of 4.5 g of 4-chloro-1-naphthaldehyde) was dissolved in 5 mL of methylene chloride and injected onto a silica gel cartridge in a preparative liquid chromatograph. Elution with hexane and application of the recycle technique allowed several minor contaminants to be removed, but **6d** and **11d** coeluted. Concentration of the fractions containing the isomers by rotary evaporation afforded a white solid and some oil. When the solid was carefully washed with hexane, the oil could be separated from it. Recrystallization of the solid from hexane afforded 83 mg (0.30 mmol, 1.3% based on starting aldehyde) of **11d**: mp 144–145 °C; IR 3068, 3007, 1589, 1507, 1372, 1035, 922, 890, 638 cm^{-1}; ^{1}H NMR ($DCCl_3$) δ 8.26–8.48 (2 H, m, aromatic), 7.56–7.66 (2 H, m, aromatic), 7.43 (2 H, s, aromatic), 6.90 (6 H, br s, olefinic), 2.83 (1 H, t, H_9, $J_{19} = J_{89} = 8.6$ Hz), 2.21 (2 H, d, H_1 and H_8). Anal. Calcd for $C_{19}H_{15}Cl$: C, 81.65; H, 5.63. Found: C, 81.65; H, 5.63.

Removal of hexane from the washings by rotary evaporation gave a green oil. This was triturated with hexane and cooled to dry ice temperatures. When the solution was warmed and scratched with a glass rod, a white powder appeared which could be collected by rapid filtration below 0 °C. Several crops were collected. The powder was recrystallized from hexane at −20 °C to give 157 mg (0.563 mmol, 2.4% based on starting aldehyde) of **6d**: mp 62–62.5 °C; IR 3076, 3020, 1508, 1372, 686, 630 cm^{-1}; ^{1}H NMR ($DCCl_3$) δ 8.20–8.47 (2 H, m, aromatic), 7.50–7.73 (2 H, m, aromatic), 7.45 (1 H, d, $J = 8$ Hz), 7.19 (1 H, d, $J = 8$ Hz), 5.85–6.40 (6 H, m, olefinic), 2.06 (1 H, A of AB_2, H_9, $J_{19} = J_{89} = 5.1$ Hz), 1.85 (2 H, B of AB_2, H_1 and H_8). Anal. Calcd for $C_{19}H_{15}Cl$: C, 81.86; H, 5.42. Found: C, 81.66; H, 5.46.

Preparation of Anions in Liquid Ammonia. Samples of anions for ^{1}H NMR spectrometry were prepared in thick-walled NMR tubes containing 0.50 mL of anhydrous liquid ammonia according to our previously published method.[24] Anion spectra (except for that of Li^+ **2e**) are recorded in Table II. The amount of lithium or potassium wire as well as the amount of precursor used to prepare each anion is given below.

(9-(1-(4-Methoxynaphthyl))methylenecyclooctatrienyl)lithium (Li^+ **2a**). Treatment of 45.5 mg (0.166 mmol) of **6a** with lithium amide (from 8.2 mg (1.2 mmol) of lithium) afforded a reddish green solution of Li^+ **2b**.

(9-(1-(4-Methoxynaphthyl))methylenecyclooctatrienyl)potassium (K^+ 2a). Treatment of 45.5 mg (0.166 mmol) of **6a** with potassium amide (from 12.2 mg (0.31 mmol) of potassium) afforded a reddish green solution of (K^+ **2b**).

(9-(1-(4-Methylnaphthyl))methylenecyclooctatrienyl)lithium (Li^+ 2b). Treatment of 39 mg (0.15 mmol) of **6b** with lithium amide (from 18 mg (2.6 mmol) of lithium) afforded a dark green solution of Li^+ **2b**.

(9-(1-Naphthyl)methylenecyclooctatrienyl)potassium (K^+ 2c). Treatment of 60 mg (0.26 mmol) of **6c**[1] with potassium amide (from 12.0 mg (0.307 mmol) of potassium) afforded a dark green solution of K^+ **2c**.

(9-(1-(4-Chloronaphthyl))methylenecyclooctatrienyl)lithium (Li^+ 2d). Treatment of 46.1 mg (0.165 mmol) of **6d** with lithium amide (from 8.0 mg (1.2 mmol) of lithium) afforded a dark green solution of Li^+ **2d**.

(9-(1-(4-Chlorophenyl))methylenecyclooctatrienyl)lithium (Li^+ 2e). Treatment of 38.0 mg (0.167 mmol) of *anti*-9-(1-(4-chlorophenyl))-*cis*-bicyclo[6.1.0]nona-2,4,6-triene[6] with lithium amide made from 8.0 mg (1.2 mmol) of lithium afforded a dark green solution of Li^+ **2d**. The ^{1}H NMR spectrum of this sample was identical with that previously reported.[6]

(9-(1-(4-Methylnaphthyl))methylenecyclooctatrienyl)lithium in HMPA (Li^+ 2b). To a 5-mm NMR tube was added 41 mg (0.16 mmol) of **11b**, 0.50 mL of dry HMPA, and 40 μL of tetramethylsilane. Addition of 0.1 mL of a ca. 5.3 M solution of lithium dimethylamide in HMPA afforded an emerald green solution of Li^+ **2b** whose ^{1}H NMR spectrum is listed in Table II.

Acknowledgment. We thank the National Science Foundation (Grant CHE78-12218) for support of this work. We also acknowledge support by the University of Nebraska Computing Network.

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