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9-Naphthylmethylenecyclooctatrienyl Anions. Conformational Analysis and Bond Rotation

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Abstract: Treatment of *anti*-9-naphthylbicyclo[6.1.0]nona-2,4,6-trienes (*anti*-**2b,c**) with lithium amide in liquid ammonia causes the formation of the corresponding lithium 9-naphthylmethylenecyclooctatrienyl anions (**3b,c**). A conformational analysis was made of these anions on the basis of their ^{1}H NMR spectra. The spectra of anions **3b** and **3c** display a temperature dependence associated with rotation around the C_8–C_9 π bond. The free energies of activation ($\Delta G^{\ddagger}$) were determined by line-shape analysis to be 15.1 kcal/mol (at 27 °C) and 14.4 kcal/mol (at 4 °C), respectively. The lack of a dependence of the rate of this process on the concentration of anion **3c** or of lithium amide, as well as the absence of an observable incorporation of deuterium into **3c** in ammonia-d_3, demonstrates that this bond rotation is a unimolecular process.

Dynamic nuclear magnetic resonance (DNMR) spectrometry has become an important technique for the detection and study of processes in solution possessing free energies of activation lying between 6 and 25 kcal/mol. The activation energies for rotation about partial double bonds in a variety of polar molecules[2] as well as in delocalized cations[2b] and anions[3] fall within this range, and such systems have been extensively investigated by DNMR spectrometry. Some of the lowest activation barriers are associated with molecules which are highly polarized both in the ground and transition states or with bonds possessing relatively low π bond orders. In this paper we report the preparation of several 9-naphthylmethylenecyclooctatrienyl anions, an analysis of their conformations, and the observation of an unusually low barrier to rotation about the highly localized C_8–C_9 π bond, and we discuss evidence for the mechanism of rotation.

Results and Discussion

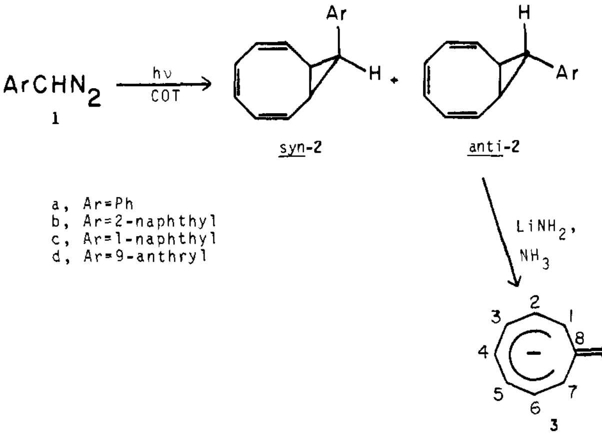
Preparation of Anions. The 9-naphthylbicyclo[6.1.0]nona-2,4,6-trienes *anti*-**2b** and -**2c** which served as precursors to **3b** and **3c**, respectively, were prepared by photolysis of the corresponding aryldiazomethanes (**1**) in the presence of a large excess of cyclooctatetraene (COT) (Scheme I). Equal quantities of the anti and syn isomers (*anti*-**2b** and *syn*-**2b**, respectively) were isolated in the case of the 2-naphthyl derivative whereas no syn isomer was isolated for the 1-naphthyl derivative. Purification of the 1- and 2-naphthyl products was difficult in some of the preparations but was successfully effected by chromatography on silver nitrate impregnated silica gel.

Treatment of **2b** and **2c** with lithium amide in liquid ammonia at ca. −60 °C immediately afforded emerald green solutions of the corresponding methylenecyclooctatrienyl anions (**3b** and **3c**). NMR data for these anions are given in Table I.

The *anti*-9-anthryl derivative **2d** was also prepared by the route in Scheme I. This compound immediately produced a deep purple solution on treatment with lithium amide–ammonia, but an interpretable NMR spectrum was not obtained. The 9-phenyl derivatives (**2a** and **3a**) have been reported previously.[4]

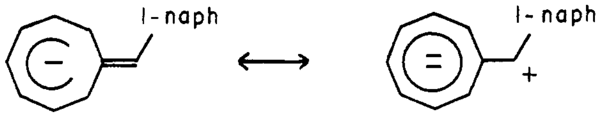
Conformational Analysis. The key observation in this study is that of the temperature dependence of the NMR spectra of **3b** and **3c** (vide infra). In order to determine whether the relative rates for the observed process arise from energy differences in the ground states or transition states, or both, it is necessary to analyze steric effects in the ground state. Low activation energy bond rotations have been shown to arise from steric strain in the ground state[5] as well as from electronic stabilization of the transition state.[6]

Scheme I



The chemical shift of H_9 (δ 5.00) in the parent methylenecyclooctatrienyl anion (lithium salt in liquid ammonia) (**3**, Ar = H) indicates that there is little or no negative charge at C_9.[7] This is consistent with an HMO ω-technique calculation[8] which shows essentially no charge at C_9 and a high π bond order for the C_8–C_9 bond (0.79).

In this context, the large downfield shift of H_9 in **3c** (δ 6.65) relative to **3a** and **3b** (δ 6.18 and 6.17, respectively) is of interest. A priori, this could result either from the magnetic anisotropy of the naphthyl ring or from a contribution of dipolar resonance form **4b** due to a steric-induced twisting about the C_8–C_9 bond.



4a **4b**

So that this question could be resolved, the chemical shifts of **3a–c**

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[1] To whom correspondence should be addressed at the University of Nebraska.

[2] Reviews: (a) H. O. Kalinowski and H. Kessler, *Top. Stereochem.*, **7**, 295 (1972); (b) L. M. Jackman in "Dynamic Nuclear Magnetic Resonance Spectroscopy", L. M. Jackman and F. A. Cotton, Eds., Academic Press, New York, 1975, Chapter 7.

[3] Reviews: (a) S. W. Staley in "Pericyclic Reactions", Vol. 1, A. P. Marchand and R. E. Lehr, Eds., Academic Press, New York, 1977, Chapter 4; (b) D. H. Hunter in "Isotopes in Organic Chemistry", Vol. 1, E. Buncel and C. C. Lee, Eds., Elsevier, Amsterdam, pp 135 ff.

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

[5] I. Agranat and Y. Tapuhi, *J. Org. Chem.*, **44**, 1941 (1979).

[6] U. Berg and U. Sjostrand, *Org. Magn. Reson.*, **11**, 555 (1978).

[7] S. W. Staley and G. M. Cramer, *J. Am. Chem. Soc.*, **95**, 5051 (1973).

[8] A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists", Wiley, New York, 1961, pp 115–116.

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Table I. NMR Data for 9-Arylmethylenecyclooctatrienyl Anions (Lithium Salts) in Liquid Ammonia

		chemical shift[a] (J, Hz)				
anion	T, °C	H_1, H_7	H_2, H_6	H_3, H_5	H_4	H_9
3a	−60	4.53, 4.18; two d ($J = 13.0$)	5.24, 5.20; two d of d ($J_{12} = 13.0, J_{23} = 10.8$)	3.66, 3.56; two t ($J = 10.8$)	5.00; t ($J = 11.0$)	6.17; s
3b	−29	4.56, 4.14; two d ($J = 13.0$)	5.18, 5.14; two d of d ($J_{12} = J_{23} = 13$)	3.62, 3.51; two t ($J = 10.5$)	4.92; t ($J = 10.5$)	6.18; s
3c-1[b]	−25	4.48, 4.40; two d ($J = 12.8$)	5.33, 5.23; two d of d ($J = 13$)	3.76, 3.61; two t ($J = 11$)	5.08; t ($J = 11.5$)	6.65; s
3c-2[c]	−33	4.43, 4.33	5.25, 5.14	3.66, 3.52	5.00	6.59
3c-4[d]	−25	4.38, 4.26	5.21, 5.07	3.66, 3.51	4.95	6.56

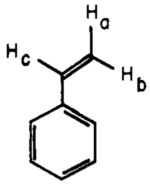
[a] Chemical shift given in δ. Trimethylamine (δ_{NH_3} (Me_4Si) = 2.135) was used as an internal standard. [b] 0.33 M. [c] 0.068 M. [d] 0.24 M in ammonia-d_3.

Table II. Chemical Shifts of the Vinyl Protons in Vinylaryl Compounds

	chemical shift (δ)			
compd	H_a	H_b	H_c	ref
5	5.16	5.66	6.65	*a*
6	5.25	5.75	6.80	*a*
7	5.36	5.65		*a*
7	5.33	5.62	7.25	*b*

[a] Reference 11; in $CDCl_3$. [b] This work; in CCl_4.

were analyzed with reference to NMR data for the corresponding vinylaryl compounds **5**–**7**.



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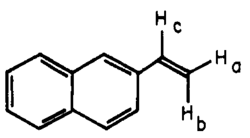

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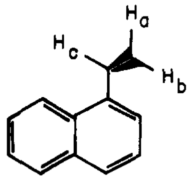

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By analogy to styrene,[9] **6** is probably planar, whereas **7** is undoubtedly nonplanar. The structures for **6** and **7** show what we have concluded to be the dominant conformations.

As the vinyl group is twisted out of the plane of the aryl ring, H_b will undergo a greater decrease in deshielding due to the anisotropy of the aryl ring than will H_a or H_c. Thus the *upfield* shift of H_b in **7** relative to H_b in **5** (Table II), which occurs despite the greater anisotropy of the naphthyl ring in **7** compared to the phenyl ring in **5**, must result primarily from a twisting of the vinyl group out of the plane of the naphthyl ring due to an interaction between H_c and H_{peri} in conformation **7**.[10]

As seen in Table I, H_2–H_7 in **3a** are downfield from the corresponding protons in **3b** but are upfield from those in **3c**. This has been explained as resulting from changes in the paramagnetic ring current in the eight-membered ring.[12] This ring current, which we believe to be primarily dependent on the HOMO–LUMO energy gap, is increased as the LUMO is lowered in **3b** (relative to **3a**) due to the larger π system of the substituent at C_9 and is reduced as the LUMO is raised in **3c** due to extra twisting about the C_9–aryl bond compared to those in **3a** and **3b**. Further evidence for this twisting (which results from interactions analogous to those in **7**) is provided by the chemical shifts of H_1 (Table I). These protons shift in directions opposite to those experienced by H_2–H_7 on comparing **3a**, **3b**, and **3c** but in the *same* direction (and for the same reasons) as H_b in **5**–**7** (Table II). Consequently, H_1 in **3c** is upfield of H_1 in **3a** or **3b** because of a greater degree of twisting in the C_9–1-naphthyl bond compared to the C_9–phenyl or C_9–2-naphthyl bond.

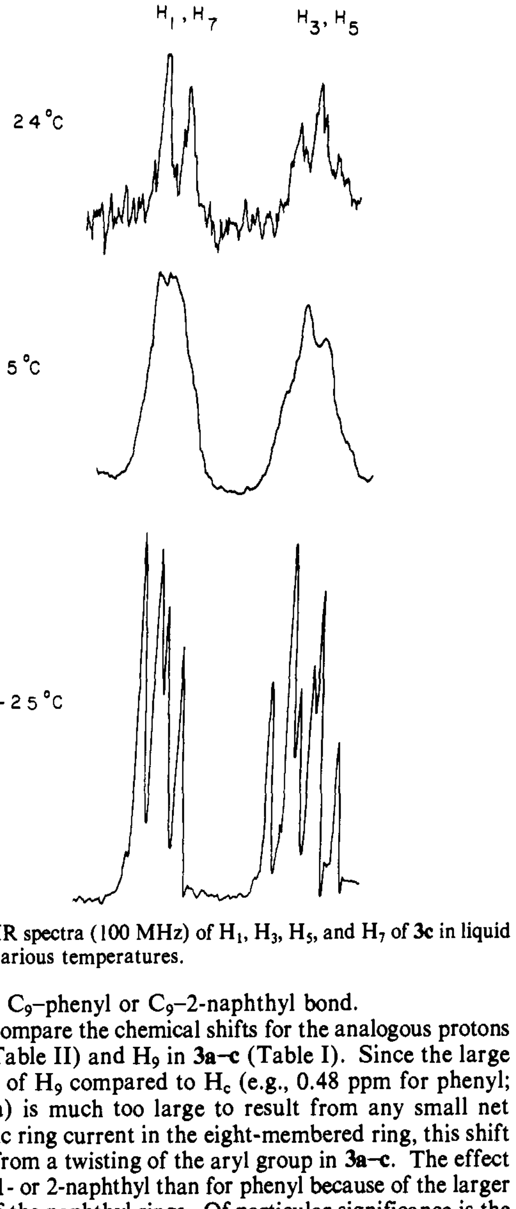

Figure 1. NMR spectra (100 MHz) of H_1, H_3, H_5, and H_7 of **3c** in liquid ammonia at various temperatures.

We next compare the chemical shifts for the analogous protons H_c in **5**–**7** (Table II) and H_9 in **3a**–**c** (Table I). Since the large upfield shift of H_9 compared to H_c (e.g., 0.48 ppm for phenyl; cf. **5** and **3a**) is much too large to result from any small net paramagnetic ring current in the eight-membered ring, this shift must result from a twisting of the aryl group in **3a**–**c**. The effect is larger for 1- or 2-naphthyl than for phenyl because of the larger anisotropy of the naphthyl rings. Of particular significance is the observation that the large downfield shift of H_9 in **3c** (δ 6.65) relative to **3a** and **3b** is also reflected in a similar downfield shift of H_c in **7** (δ 7.25) relative to **5** and **6**. This indicates that the former shift is due to the anisotropy of the 1-naphthyl ring and not to a contribution of resonance form **4b**.

In summary, the foregoing analysis has led us to conclude that (a) anions **3a**–**c** are twisted at the C_9–aryl bonds, (b) the C_9–1-naphthyl bond in **3c** is twisted more than the corresponding bonds in **3a** and **3b**, and (c) resonance form **4b** does not contribute significantly to the ground state of **3c**. This information will be

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[9] J. Sühnel, K. Gustav, and U. P. Wild, *Z. Chem.* **17**, 342 (1977).

[10] Cf. L. H. Klemm, H. Ziffer, J. W. Sprague, and W. Hodes, *J. Org. Chem.* **20**, 190 (1955).

[11] D. F. Church and G. J. Gleicher, *J. Org. Chem.*, **41**, 2327 (1976).

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

Table III. Coalescence Temperatures (T_c) and Free Energies of Activation ($\Delta G^{\ddagger}$) for 9-Naphthylmethylenecyclooctatrienyl Anions (Lithium Salts) in Liquid Ammonia at 100 MHz

anion	exchanging protons	$T_c{}^a$	$\Delta G^{\ddagger b}$	$\Delta G^{\ddagger}$ (DNMR)^c	T, °C
3b^d	H_1 and H_7	27	14.9	15.1	27
3b^d	H_3 and H_5	12	14.8		
3c^e	H_1 and H_7	5	14.4	14.4	4
3c^e	H_3 and H_5	7	14.5		

^{a} ±2 °C for H_1 and H_7; ±3 °C for H_3 and H_5. ^{b} Calculated from eq 1 and the Eyring equation. ±0.3 kcal/mol for H_1 and H_7; ±0.4 kcal/mol for H_3 and H_5. ^{c} Calculated from rate constants obtained from DNMR-3A line-shape synthesis; ±0.2 kcal/mol. ^{d} 0.44 M. ^{e} Sample 3c-1 (0.33 M).

useful in analyzing the temperature-dependent NMR data in the next section.

Temperature Dependence of NMR Spectra. The NMR spectrum of the 9-phenyl anion **3a** is essentially unchanged on warming the solution to 34 °C. In contrast, increasing the temperature of **3c** causes the doublets for H_1 and H_7 to coalesce to a single doublet at δ 4.35 while the apparent triplets for H_3 and H_5 coalesce to a single triplet at δ 3.64. Representative spectra are presented in Figure 1. These changes may be reversed by cooling the sample. Similarly, warming **3b** causes coalescence of the doublets for H_1 and H_7 into a broad absorption at δ 4.64–4.09 whereas the apparent triplets due to H_3 and H_5 coalesce to a single triplet at δ 3.64. Cooling the sample allowed recovery of the original spectrum. In both cases the overlap of the doublet of doublets for H_2 and H_6 with the triplet for H_4 precluded accurate detection of their coalescence. These phenomena are best explained by the pairwise exchange averaging of the chemical shifts of the eight-membered ring protons by rotation of the naphthyl group about the exocyclic double bond of **3b** and **3c** at a rapid rate on the NMR time scale.

Rate constants and activation energies for these processes were determined from the "coalescence"[13] (see Figure 1) of the doublets for H_1 and H_7 and the apparent triplets for H_3 and H_5 since these were the most clearly resolved signals. The rate constant (k_c) corresponding to the rate necessary to produce coalescence for a two-site exchange process may be determined from the relationship

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

where $\Delta\nu$ is the frequency difference in Hz for the signals which undergo coalescence.[14] The $\Delta\nu$ values of H_1 and H_7 in both **3b** and **3c** were temperature dependent, becoming larger as the temperature was increased. The actual value of $\Delta\nu$ at coalescence was extrapolated from a linear correlation of $\Delta\nu$ (as measured at various temperatures in the slow exchange limit) vs. temperature. The $\Delta\nu$ values of H_3 and H_5 were treated in the same manner. Free energies of activation ($\Delta G^{\ddagger}$) were calculated from the Eyring equation with a transmission coefficient of 1[15] and are presented in Table III.

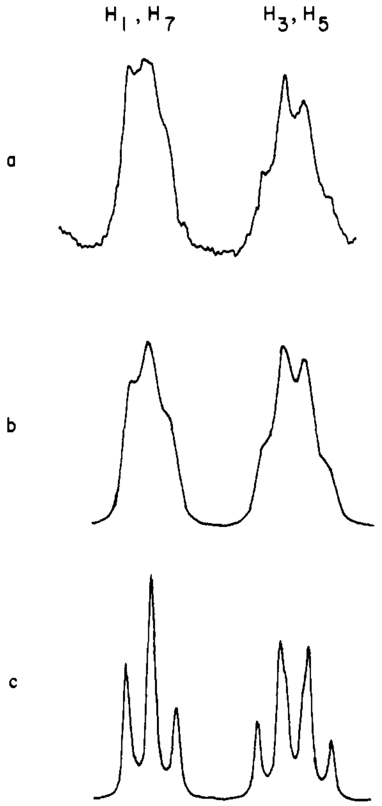
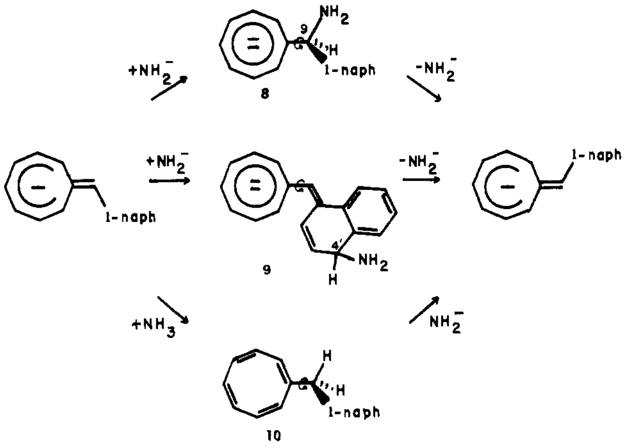


Figure 2. (a) NMR spectrum (100 MHz) of H_1, H_3, H_5, and H_7 of **3c** at 4 °C. (b) Calculated line shape for k = 25.96 s^{-1}. (c) Calculated line shape with the rate constant decreased by a factor of 4.9 (k = 5.30 s^{-1}).

Scheme II



The accuracy of approximate relationships such as eq 1 is problematical.[13] Equation 1 was originally derived for a two-site exchange process between singlets of equal intensity,[14] but it has been shown both theoretically[16] and experimentally[17] to apply reasonably well to various first- and second-order multiplets. To our knowledge, however, it has not been compared with line-shape synthesis methods in the case of second-order doublets or first-order doublets of doublets such as are present in the spectra of **3b** and **3c**. The rate of exchange just before coalescence was therefore obtained by line-shape synthesis utilizing the DNMR-3A computer program[18] (Figure 2). The free energies of activation determined from these rates are also presented in Table III for comparison with those calculated from eq 1. The respective values are seen to be in excellent agreement with each other and show that the use of eq 1 may be extended to the analysis of coalescing second-order doublets and first-order doublets of doublets.

Mechanism of Rotation. As discussed above, the present NMR data show that the exocyclic double bond of **3b** is nonpolar. This deduction is supported by self-consistent HMO ω-technique calculations[8] which indicate that this bond is highly localized. The C_8–C_9 π bond order for **3b** is calculated to be 0.70, and the π charge densities at C_8 and C_9 are −0.016 and −0.013, respectively.

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(13) G. Binsch and H. Kessler, *Angew. Chem., Int. Ed. Engl.*, **19**, 411 (1980).

(14) H. S. Gutowsky and C. H. Holm, *J. Chem. Phys.*, **25**, 1228 (1956).

(15) G. Binsch, *Top. Stereochem.*, **3**, 97 (1968).

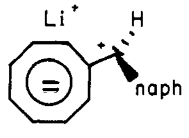
(16) (a) D. Kost, E. H. Carlson, and M. Raban, *J. Chem. Soc. D*, 656 (1971); (b) K.-I. Dahlqvist, S. Forsén, and T. Alm, *Acta Chem. Scand.*, **24**, 651 (1970).

(17) (a) W. Egan, R. Tang, G. Zon, and K. Mislow, *J. Am. Chem. Soc.*, **93**, 6205 (1971); (b) S. E. Potter and I. O. Sutherland, *J. Chem. Soc., Chem. Commun.*, 754 (1972); (c) M. Bernard and M. St.-Jacques, *Tetrahedron*, **29**, 2539 (1973); (d) M. Bernard, L. Canuel, and M. St.-Jacques, *J. Am. Chem. Soc.*, **96**, 2929 (1974).

(18) D. A. Kleier and G. Binsch, *QCPE*, **11**, 165 (1970). We thank Dr. H. L. Ammon for a copy of this program.

This combination of a high π bond order and a low activation barrier for rotation is inherently interesting. In order to reconcile these seemingly incompatible observations, it is important to determine the mechanism of rotation.

A priori, two classes of mechanism must be considered. As exemplified for **3c**, they are the bimolecular (Scheme II) and unimolecular (**11–13**) classes. Similar mechanisms may be envisaged for **3b**. Rotation could occur via a transition state involving two molecules of **3c**. Inversion of primary Grignards has been found to occur by such a transition state.[19] In addition, since the anions are generated in solutions containing excess lithium amide, reversible amide attack at C_9 or at C_4 of the naphthyl ring could lead to intermediates **8** and **9**, respectively. Rotation about the exocyclic single bond in these intermediates followed by expulsion of amide would lead to the observed phenomena. Although *potassium* amide is known to attack the methylenecyclooctatrienyl anion at C_9 rapidly and irreversibly at −65 °C,[4,20] the anion generated from lithium amide is stable up to 0 °C.[7] No evidence for reversible amide attack on this type of anion has been reported, but the possibility cannot be ignored. A third potential mechanism involves proton transfer from solvent to **3c** to give intermediate **10**, followed by rotation and deprotonation. Reversible protonation has been previously observed (by deuterium exchange) at the negatively charged positions of the cyclononatrienyl anion.[21]



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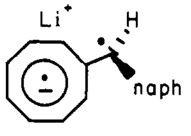

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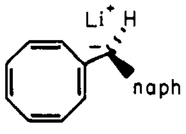

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The possible transition states (**11–13**) for unimolecular mechanisms differ in the distribution of charge. Transfer of the exocyclic π electrons into the eight-membered ring produces the dipolar transition state **11**, whereas homolytic fission of the π bond leads to the diradical transition state **12**. A third possibility involves transfer of the exocyclic π electrons to C_9 to produce transition state **13**.

The occurrence of a transition state involving two molecules of **3c** can be detected by varying the concentration of **3c**.[19,22] As seen in Figure 2, for such a transition state a decrease in the concentration of **3c** by a factor of 4.9 would produce a dramatic change in the appearance of the spectrum at the coalescence temperatures for sample **3c**-1. This is equivalent to an increase in T_c for H_1 and H_7 from 5 to ca. 15 °C at 100 MHz.

To test this mechanism we prepared a sample of **3c** in which the anion concentration was decreased by a factor of 4.9 from that of the original sample while using a sufficient excess of lithium amide to ensure that the solution remained saturated with amide after generation of the anion. The ^1H NMR spectrum of the low concentration sample of **3c** is recorded in Table I as entry **3c**-2. The eight-membered ring protons of sample **3c**-2 exhibit an upfield shift with respect to those of **3c**-1. This can be attributed either to decreased intermolecular deshielding and/or to a shift in the ion-pairing equilibrium toward solvent-separated ion pairs[23] in the lower concentration sample at lower temperatures. When sample **3c**-2 is warmed, the signals due to H_1 and H_7 coalesce at 5 °C, the same value of T_c as observed for sample **3c**-1. The rate of exchange was found to be identical with that of sample **3c**-1 by computer line-shape synthesis.[18] From the invariance of the exchange rate with changes in concentration of **3c** and the probable existence of **3c** as a monomeric species in liquid ammonia, we conclude that rotation occurs by a transition state which is unimolecular with respect to **3c**.

The rate of exchange due to pathways leading to intermediates **8** and **9** will be dependent on the amide concentration. A change in amide concentration by a factor of 4.9 would affect the appearence of the spectrum in the same way as that discussed above for a bimolecular transition state of **3c**.[24] A saturated solution of lithium amide in ammonia at 23 °C is 3×10^{-4} M in lithium amide.[25] Hence, for 0.50 mL of such a solution, the addition of 12 mg of *anti*-**2c** will produce an *anti*-**2c**:lithium amide molar ratio of 330:1. This is probably a conservative estimate since any common ion effects will tend to increase this ratio. Accordingly, a solution of **3c** in 0.50 mL of ammonia saturated with lithium amide was prepared and 12 mg of *anti*-**2c** was added to it (sample **3c**-3). The presence of excess *anti*-**2c** in the final solution was indicated by observation of its olefinic proton resonances. Under these conditions, the concentration of amide was undoubtedly reduced by a factor of >5 by irreversible reaction with *anti*-**2c**, yet there was no observable effect on the rate of exchange. We therefore conclude that rotational processes proceeding via intermediates **8** and **9** do not make a significant contribution to the total rate of exchange.

Solvent participation in rotation leading to intermediate **10** was tested by generating **3c** in ca. 98% ammonia-d_3 (sample **3c**-4). The resonance due to H_9 should rapidly (<1 s) disappear at the coalescence temperature if H_9 were to exchange with solvent deuterium. However, no detectable deuterium incorporation into **3c** occurred in 4.5 h at temperatures above 0 °C. An estimate of the maximum rate of deuterium incorporation leads to the conclusion that it is at least 10^6 times slower than that for rotation. Clearly rotation proceeding through intermediate **10** makes no contribution to the overall rate of exchange.

Interestingly, T_c for H_1 and H_7 of **3c** in ammonia-d_3 was determined to be 6 °C higher than that in ammonia-d_0 at 90 MHz. This corresponds to a slightly higher rotational activation barrier ($\Delta G^{\ddagger}_{ND_3}$ = 14.6 kcal/mol). It is known that ammonia can hydrogen bond to the π electron clouds of cyclooctatetraene anions, producing a stabilization of the dianion relative to the radical anion.[26] The higher activation barrier measured in ammonia-d_3, while just within the experimental error, is probably real and reflects differing differential solvation effects on the anion and/or cation in the ground and transition states of **3c** in ammonia-d_0 and ammonia-d_3.

In summary, spin exchange in **3c** has been shown to occur by a chemically unimolecular process, i.e., by simple rotation around the C_8–C_9 bond. This is the first case in which this kinetic point has been tested in such detail for a dynamic process in a carbanion. However, the above data do not permit one to distinguish between transition states **11**, **12**, and **13**. Studies directed toward the resolution of this problem will be reported in a future publication.

Experimental Section

General Procedures. Routine IR and NMR spectra were obtained on a Perkin-Elmer Model 337 infrared spectrophotometer in 1-mm NaCl cells or on a Varian A60-D NMR spectrometer. The NMR spectra of anions **3b** and **3c** were obtained on an XL-100 NMR spectrometer equipped with a variable-temperature probe and an external lock and on a Varian EM-390 NMR spectrometer equipped with a variable-temperature probe and an internal lock. Melting points are uncorrected. Microanalyses were performed by Dr. Franz Kasler of the University of Maryland.

2-Naphthyldiazomethane (1a). In a 500-mL round-bottomed flask equipped with a magnetic stirring bar was placed 3.0 g (17 mmol) of 2-naphthaldehyde hydrazone,[27] 3.7 g (17 mmol) of yellow mercuric oxide, 5.0 g (3.7×10^{-2} mol) of anhydrous calcium sulfate, and 0.4 g (7.4 mmol) of sodium methoxide in 100 mL of anhydrous ether. The flask was stoppered and stirred vigorously for ca. 24 h. The dark red solution was filtered and then concentrated by rotary evaporation. It was used immediately in the next experiment. (**Caution**: *An attempt to store the*

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[19] G. Frankel, C. E. Cottrall, and D. T. Dix, *J. Am. Chem. Soc.*, **93**, 1704 (1971).

[20] G. M. Cramer, Ph.D. Dissertation, University of Maryland, 1974.

[21] S. W. Staley and N. J. Pearl, *J. Am. Chem. Soc.*, **95**, 3437 (1973).

[22] G. Fraenkel, J. G. Russell, and Y. H. Chen., *J. Am. Chem. Soc.*, **95**, 3208 (1973).

[23] J. B. Grutzner, J. M. Lawlor, and L. M. Jackman, *J. Am. Chem. Soc.*, **94**, 2306 (1972); C. Gooijar and N. H. Velthorst, *Org. Magn. Reson.*, **12**, 684, (1979).

[24] W. C. Gardiner, "Rates and Mechanisms of Chemical Reactions", W. A. Benjamin, Menlo Park, CA, 1972, p 234.

[25] D. C. Jackman and C. W. Keenan, *J. Inorg. Nucl. Chem.*, **30**, 2047 (1968).

[26] G. R. Stevenson and A. Vassos, *J. Phys. Chem.*, **81**, 1526 (1977).

[27] T. Nakaya, T. Tomomoto, and M. Imoto, *Bull. Chem. Soc. Jpn.*, **40**, 691 (1967).

solid hydrazone resulted in an explosion.)

***syn*- and *anti*-9-(2-Naphthyl)-*cis*-bicyclo[6.1.0]nona-2,4,6-triene (2a).** 2-Naphthyldiazomethane from the previous preparation was dissolved in 50 g (0.45 mol) of freshly distilled cyclooctatetraene. This solution was placed in a Pyrex photolysis well and agitated by a stream of N_2 admitted by a needle which extended to the bottom of the well. After a wait of 10 min, the solution was irradiated for 5 h with a 450-W medium-pressure Hanovia lamp. Unchanged cyclooctatetraene was removed by distillation in vacuo. The brown residue was chromatographed on 100 g of neutral alumina with pentane, and 100 mL fractions were collected. Fractions 6–11 were combined and rechromatographed on 20 g of silica gel impregnated with 40% $AgNO_3$ with use of 50:1 pentane–ether (50-mL fractions). Concentration of fractions 15–30 yielded crystalline material. Fractions 15–20 were combined and chromatographed on 30 g of neutral alumina with pentane (25-mL fractions). The crystalline material from fractions 15–20 was combined and recrystallized from pentane to yield 50 mg (1.2% on the basis of 2-naphthaldehyde hydrazone) of *syn*-9-(2-naphthyl)-*cis*-bicyclo[6.1.0]nona-2,4,6-triene: mp 57–58 °C; IR (CCl_4) 3055, 3010, 1630, 1600, 1510 cm^{-1}; NMR ($DCCl_3$) δ 7.11–8.04 (7 H, naphthyl), 5.40–6.30 (6 H, m, olefinic), 2.51 (1 H, A of AB_2, H_9, $J_{19} = J_{89} = 10.2$ Hz), 2.09 (2 H, B of AB_2, H_1 and H_8). Anal. Calcd for $C_{19}H_{16}$: C, 93.40; H, 6.60. Found: C, 93.51; H, 6.67.

The anti isomer was obtained by chromatographing the material isolated from fractions 25–30 of the silica gel–$AgNO_3$ column on 30 g of neutral alumina with pentane (25-mL fractions). The material obtained from fractions 25–30 was recrystallized from pentane to yield 55 mg (1.3% on the basis of 2-naphthaldehyde hydrazone) of *anti*-9-(2-naphthyl)-*cis*-bicyclo[6.1.0]nona-2,4,6-triene (*anti*-**2b**): mp 119.5–120.5 °C; IR (CCl_4) 3060, 3010, 1630, 1600, 1500 cm^{-1}; NMR ($DCCl_3$) δ 7.03–7.82 (7 H, naphthyl), 5.87–6.30 (6 H olefinic), 1.95 (2 H, B of AB_2, H_1 and H_8, $J_{19} = J_{89} = 5.8$ Hz), and 1.70 (1 H, A of AB_2, H_9). Anal. Calcd for $C_{19}H_{16}$: C, 93.40; H, 6.60. Found: C, 93.12; H, 6.69.

9-(2-Naphthyl)methylenecyclooctatrienyllithium (3b). Our published general technique for obtaining NMR spectra of samples in liquid ammonia was employed.[28] Treatment of 52.5 mg (0.22 mmol) of *anti*-**2b** with lithium amide (from 6.0 mg (0.86 mmol) of lithium) afforded an emerald green solution of **3b** whose NMR spectrum is listed in Table I. Temperature-dependent NMR data are given in Table III.

***anti*-9-(1-Naphthyl)-*cis*-bicyclo[6.1.0]nona-2,4,6-triene (2c).** 1-Naphthyldiazomethane (**1c**)[27] was dissolved in 59 g (0.58 mol) of freshly distilled cyclooctatetraene and the solution placed in a Pyrex photolysis well. The solution was agitated by passing N_2 through a needle which extended to the bottom of the well. The solution was purged with N_2 for 15 min and then irradiated by a 450-W medium-pressure Hanovia lamp for 8 h. Excess cyclooctatetraene was removed in vacuo. (All operations were carried out at temperatures less than 30 °C.) The amber residue was chromatographed (100-mL fractions) on neutral alumina with 0.5 L of hexane, 0.3 L of 1% ether–hexane, and 0.9 L of 2% ether–hexane. Fractions 5–16 were combined and concentrated to give a pale green oil which rapidly crystallized. Recrystallization from pentane gave 1.64 g (27% on the basis of 1-naphthaldehyde hydrazone) of *anti*-**2c**: white needles; mp 72–73 °C; IR (CCl_4) 3055, 3010, 1640, 1597, 1505 cm^{-1}; NMR ($DCCl_3$) δ 8.24–8.47 (1 H, m, H_8 of naphthyl), 5.83–6.50 (6 H, H_2–H_7 of naphthyl), 6.35–5.50 (6 H, m, olefinic), 2.07 (2 H, B of AB_2, H_1 and H_8, $J_{19} = J_{89} = 5.8$ Hz), 1.84 (1 H, A of AB_2, H_9). Anal. Calcd for $C_{19}H_{16}$: C, 93.40; H, 6.60. Found: C, 93.14; H, 6.89.

9-(1-Naphthyl)methylenecyclooctatrienyllithium (Sample 3c-1). Treatment of 40.1 mg (0.166 mmol) of **2c** with lithium amide (from 61 mg (8.8 mmol) of lithium) in 0.50 mL of ammonia afforded in ca. 5 min an emerald green solution of **3c** whose NMR spectrum is listed in Table I. Temperature-dependent NMR data are given in Table III.

Sample 3c-2. Treatment of 8.2 mg (0.034 mmol) of **2c** with lithium amide (from 61 mg (8.8mmol) of lithium) in 0.50 mL of ammonia afforded a solution whose NMR spectrum is listed in Table I. The coalescence temperature of the H_1 and H_7 signals was the same as that observed in sample **3c**-1 (Table III).

Sample 3c-3. Treatment of 40.2 mg (0.166 mmol) of *anti*-**2c** with lithium amide (from 8.3 mg (1.2 mmol) of lithium) in 0.50 mL of ammonia afforded an emerald green solution of **3c**. The tube was inverted, the NMR spectrum of **3c** was recorded, and the tube was reinverted. The anion solution was frozen, the end of the tube *above* the filter plug was opened and thoroughly cleaned, and 12 mg (4.9×10^{-2} mmol) of *anti*-**2c** was added. (This represents a $>10^2$-fold excess with respect to the amount of lithium amide in solution; see text.) The tube was then sealed, the solution thawed, and the tube inverted again, thereby allowing the amide–anion solution to mix with the additional *anti*-**2c**. The ^{1}H NMR spectrum of this sample displayed signals for *both anti*-**2c** and **3c**. The spectrum of **3c** in this sample and its temperature dependence was identical with that for **3c**-1. T_c for H_1 and H_7 was determined to be 3 °C at 90 MHz.

Sample 3c-4. Treatment of 29.3 mg (0.120 mmol) of *anti*-**2c** with lithium amide-d_2 (from 17 mg (2.0 mmol) of lithium) in 0.50 mL of ammonia-d_3[29] at 0 °C afforded a reddish green solution of **3c** over a 2-h period. (This conversion normally takes ca. 5 min in ammonia-d_0 at ca. −50 °C.) The NMR spectrum is listed in Table I. The coalescence temperature of the ^{1}H NMR signals due to H_1 and H_7 was found to be 9 °C at 90 MHz.

***anti*-9-(9-Anthryl)-*cis*-bicyclo[6.1.0]nona-2,4,6-triene (2d)** (prepared by Dr. Y. Ueno). To 100 mL of freshly distilled cyclooctatetraene was added 15.6 g (71.5 mmol) of 9-anthryldiazomethane.[27] The resulting deep red solution was transferred to a photolysis well, and N_2 was bubbled through the solution for 15 min. The solution was irradiated for 7 h through a Pyrex filter with a 450-W medium-pressure Hanovia lamp. Excess cyclooctatetraene was removed by distillation in vacuo. The brown residue was suspended in ether and chromatographed on 50 g of neutral alumina with 9:1 pentane–ether. Three fractions of 600, 350, and 600 mL were collected. Evaporation of solvent from the first 600-mL fraction afforded 2.25 g of crude product which was rechromatographed on 70 g of neutral alumina with 9:1 pentane–ether. The first 15 50-mL fractions were combined and the solvent evaporated to yield 1.49 g of a pale yellow solid. A single recrystallization from pentane afforded pure **2d** as pale yellow needles; mp 150.5–151.5 °C.

Concentration of the second fraction of 350 mL obtained from the first column yielded 0.4 g of crude product. This material was rechromatographed on 12 g of neutral alumina with 9:1 pentane–ether. Concentration of the first 10 50-mL fractions gave a pale yellow solid. A single recrystallization from pentane afforded 260 mg of pure *anti*-**2d**: pale yellow needles; total yield 1.75 g (8.3%); IR (CCl_4) 3077, 3042, 2993, 1405, 1344, 881 cm^{-1}; NMR ($DCCl_3$) δ 7.2–8.6 (9 H, m, aromatic), 5.8–6.7 (6 H, m, olefinic), 2.23 (1 H, t, $J = 5.9$ Hz, H_9), 1.80 (2 H, d, $J = 5.9$ Hz, H_1 and H_8). Anal. Calcd for $C_{23}H_{18}$: C, 93.84; H, 6.16. Found: C, 94.02; H, 6.29.

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

(29) V. I. Melczynski, *Angew. Chem.*, **74**, 32 (1962).