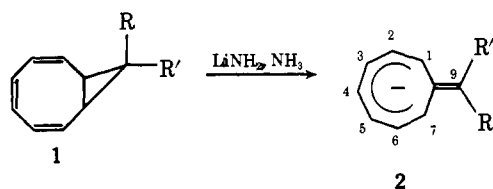


Inverse Substituent Effects and Paramagnetic Ring Currents in 9-Arylmethylenecyclooctatrienyl Anions

Sir:

According to theory, paratropism (paramagnetic ring currents) results from low-lying excited states accessible through allowed magnetic dipole transitions and is therefore inversely related to the energy gap between the highest occupied and lowest unoccupied molecular orbitals (HOMO and LUMO, respectively).¹ We now report evidence that substituents in methylenecyclooctatrienyl anions can significantly influence the magnitude of ring currents, a result which provides direct support for the foregoing theoretical basis for paratropism.

A series of *anti*-9-aryl and 9,9-diaryl derivatives of *cis*-bicyclo[6.1.0]nona-2,4,6-triene (**1a**) was prepared, either by treatment of dilithium cyclooctatetraene dianion with the corresponding benzal chloride at -33° (**1b-g**) or by photolysis (through Pyrex) of the corresponding diazo compound in the presence of cyclooctatetraene (**1h-l**). The *anti* stereochemistry was assigned on the basis of the value of J_{18} and J_{89} (5.8 Hz); in one case (**1**, R = 2-naphthyl, R' = H) the *syn* isomer ($J_{18} = J_{89} = 10.2$ Hz) was also isolated. The corresponding

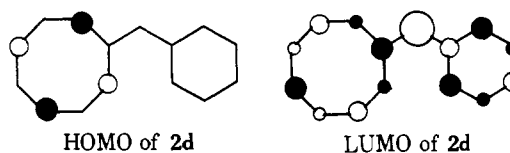


- a**, R = R' = H
b, R = H; R' = *p*-C₆H₄OCH₃
c, R = H; R' = *p*-C₆H₄CH₃
d, R = H; R' = Ph
e, R = H; R' = *p*-C₆H₄Cl
f, R = H; R' = *p*-C₆H₄Br
g, R = H; R' = *p*-C₆H₄CF₃
h, R = H; R' = 2-naphthyl
i, R = H; R' = 1-naphthyl
j, R = H; R' = 9-anthryl
k, R = R' = Ph
l, R = R' = 9,9-fluorenyl

methylenecyclooctatrienyl anions (**2**) were generated by the treatment of **1** derivatives with lithium amide in liquid ammonia or with *n*-butyllithium in hexamethylphosphoramide (HMPA). NMR and uv spectral data are given in Tables I and II, respectively.²

Two significant points emerge from the data in Tables I and II. First, the chemical shifts of the protons on the eight-membered ring (H₂-H₇) give excellent linear plots with the σ_p values⁵ of the phenyl substituents. All protons display essentially the same slope (-2.0 ± 0.1 ppm/ σ unit)⁶ in **1b-f**, but with slopes which have signs opposite to those of all other such correlations which have been reported for protons.^{7,8} Second, the trend of λ_{\max} values⁹ relative to σ_p is opposite to that found for *para*-substituted styrenes,¹⁰ i.e., donors cause a shift to shorter wavelengths rather than to longer wavelengths.

Both sets of data can be understood on the basis of the distribution of the wave function in the HOMO and LUMO in **2d**. It has already been shown that **2a** is atropic, i.e., it shows no evidence for a ring current.³ Apparently any diatropic effects associated with the occupied orbitals are more or less balanced by paratropic effects associated with the HOMO and LUMO.



Because of its symmetry, the HOMO of **1a** vanishes at C₉ and consequently will not be influenced by substituents at this position. Therefore, only the LUMO (of the two frontier orbitals) will be affected by substituents. As indicated by polarographic reduction potentials, donors raise the LUMO whereas acceptors lower it.¹¹ The fact that plots of the chemical shifts of H₂-H₇ vs. σ_p values for the phenyl substituents all

Table I. Chemical Shift Data for (Lithium) 9-Arylmethylenecyclooctatrienyl Anions in Liquid Ammonia at ca. -60°

Anion	Chemical shift (δ) ^a							
	H ₁	H ₂	H ₃	H ₄	H ₅	H ₆	H ₇	H ₉
2a ^b	4.42	5.38	3.80	5.20	3.80	5.38	4.42	5.00
2b	4.67	5.37	3.78	5.12	3.70	5.30	4.30	6.22
2c	4.62	5.28	3.73	5.06	3.63	5.24	4.23	6.18
2d ^c	4.53	5.23	3.66	5.00	3.56	5.19	4.18	6.17
2e	4.30	5.12	3.55	4.86	3.44	5.06	4.03	5.95
2f	4.28	5.09	3.53	4.86	3.43	5.05	4.03	5.95
2h ^d	4.57	5.15	3.62	4.93	3.51	5.15	4.15	6.19
2i ^e	4.47	5.33	3.74	5.07	3.60	5.33	4.37	6.66
2k	3.94	4.99	3.44	4.87	3.44	4.99	3.94	—

^a Trimethylamine ($\delta_{\text{NH}_3}^{\text{Me}_4\text{Si}} 2.135$) was employed as an internal standard. ^b Reference 3. ^c The NMR spectrum of the potassium salt is reported in ref 4. ^d At -29° . ^e At -40° .

Table II. Uv Spectral Data for (Lithium) 9-Arylmethylenecyclooctatrienyl Anions in *n*-Butyllithium-HMPA at 25° .

Anion	Color	λ_{\max} (nm)	ϵ_{\max}	Extinction coefficient (ϵ) at various wavelengths (nm)			
				460	500	540	600
2b	Pale orange	$\sim 465^a$	500	515	330	170	~ 0
2c	Orange	$\sim 465^a$	680	695	540	385	230
2d	Red	468	705	700	650	450	210
2e	Dark red	482	905	895	905	720	275
2h	Red	$\sim 485^a$	175	180	170	155	130
2i	Red	$\sim 485^a$	280	340	240	190	80
2k	Green	485	790	800	735	655	560

^a This value is only approximate due to the broadness of the peak.

have essentially the same slope is evidence that *we are primarily observing a ring current effect which is a function of the HOMO-LUMO energy gap*. The phenyl and naphthyl groups in **2d**, **2h**, **2i**, and **2k** lower the LUMO relative to the parent anion (**2a**) due to their higher density of π energy levels. These results, when coupled with the uv spectral data (which give an independent measure of the trend in the HOMO-LUMO energy difference), give strong support to the theoretical interpretation of paramagnetic ring currents.¹

Finally, it is interesting to note that the chemical shifts of H_1 and H_9 in **2b-f** do not correlate as well with σ_p as do those of the other protons. This can be explained by a greater degree of coplanarity of the 9-aryl ring with the eight-membered ring in the case of donor substituents due to greater π -electron delocalization.¹² The chemical shifts of H_1 in **2i** and **2k** (relative to **2d**) also suggest a twisting of the 9-aryl ring, probably for steric reasons. Interestingly, the signals for H_2-H_7 in **2i** ($R' = 1$ -naphthyl) are shifted *downfield* from the corresponding signals in **2d** ($R' = \text{phenyl}$) and **2h** ($R' = 2$ -naphthyl), even though the calculated HOMO-LUMO energy gap in planar **2i** is smaller than those in the latter anions. This is best explained by a greater degree of twisting of the 1-naphthyl group compared to the phenyl and 2-naphthyl groups.¹³

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Nitrogen to Nitrogen Proton Transfer. The Significance of Large Negative Entropies of Activation

Sir:

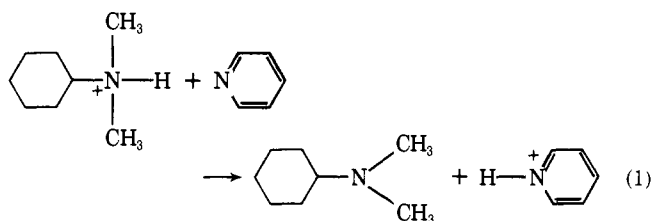
The activation entropies for transfer of a proton from H_3O^+ to H_2O and from H_2O to ^-OH are -5.8 eu and -0.1 eu, respectively.¹ These values are among the few available for fast proton transfers in protic solvents.²⁻⁴ Corresponding data for

Table I. Rate Constants at 25° and Activation Parameters for Catalyzed Proton Transfer of *N,N*-Dimethylaminocyclohexylamine Hydrochloride in Chloroform

Catalyst	$\text{p}K_a^a$	$10^{-2}k_2$, $\text{M}^{-1} \text{s}^{-1}$	ΔH^* , kcal/mol	ΔS^* , eu ^b
2,4-Lutidine	6.72	700	2.6	-28
4-Picoline	6.02	110	3.2	-29
Pyridine	5.21	13	3.9	-31
2,6-Di- <i>tert</i> -butylpyridine	4.91	8.7	3.4	-34
Aniline	4.63	4.3	3.9	-33
Dimethylaminoaceto- nitrile	4.20	1.7	5.2	-31
2-Methoxypyridine	3.28	0.11	5.5	-36
3-Bromopyridine	2.85	0.030	5.0	-40

^a In water. ^b Calculated from k_2 values at 25° with an uncertainty of ± 2.5 eu.

the reactions in aprotic solvents are found even more infrequently.^{5,6} We have measured ΔS^* for proton transfer from an aliphatic amine salt to several substituted pyridines in chloroform (eq 1). By using an amine salt/amine system we



hoped to detect subtle orientation or solvation effects which are unobservable in reactions where charge production or destruction dominates ΔS^* .⁷ Unexpectedly, an effect was uncovered which can hardly be called subtle: ΔS^* for eq 1 in chloroform equals -28 to -40 eu depending on the substituents on the pyridine ring (Table I). Such large negative entropies fall in the same range as those for bimolecular reactions which create charge (e.g., $\Delta S^* = -35$ eu for formation of *N*-methylpyridinium iodide from pyridine and methyl iodide in chloroform⁸). The present communication is devoted to explaining the magnitude of the ΔS^* for eq 1.

Most of our runs were carried out with 0.10 M *N,N*-dimethylcyclohexylamine hydrochloride (**I**) using a tenfold concentration range of basic catalyst. Observed rate constants were deduced from the slow-passage NMR signal of the *N*-methyl protons^{9,10} which changed from a doublet to a singlet as the catalyst concentration and temperature were raised. If the hydrochloride salt was not free from traces of unprotonated amine, the *N*-methyl signal gave a singlet even in the absence of added catalyst. Second-order rate constants, calculated from the slopes of linear plots of k_{obsd} vs. [catalyst], are listed in Table I. These k_2 's represent proton abstraction by the catalysts against a severe $\text{p}K_a$ gradient and were used to obtain the activation entropies. Three different concentrations of **I** (0.31 M, 0.11 M, and 0.057 M) treated with the same amount of pyridine (4.9×10^{-3} M) all yielded the same k_2 ($1360 \pm 120 \text{ M}^{-1} \text{ s}^{-1}$ at 25°). The poor solubility of **I** in many aprotic solvents prompted the choice of chloroform for this study. Chloroform was not the ideal solvent because it contained 0.8% ethanol as a preservative, and removal of the ethanol led to immediate solvent decomposition and erratic kinetics. However, ethanol did not appear to be a serious problem because 8.9% ethanol purposely added to the chloroform changed ΔS^* only slightly (3 eu). Moreover, when 1% ethanol was added to a system containing highly purified methylene chloride as the solvent, the kinetics were not perturbed. Spectra were traced in the internal lock mode after temperature equilibration of the sample for 20 min in a Jeol-JNM-MH-100 spectrometer