

¹³C NMR Chemical Shifts in 1- and 2-Substituted Azulenes. Transmission of Electronic Effects in Nonalternant π Systems^{1a}

Tadeusz A. Holak,^{*1b} Shahla Sadigh-Esfandiary,^{1c} Frederick R. Carter,^{1c} and D. J. Sardella^{*1c}

Department of Chemistry, Boston College, Chestnut Hill, Massachusetts 02167, and Department of Organic Chemistry, Jagiellonian University, Krakow, Poland

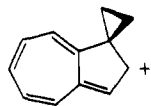
Received November 27, 1979

The transmission of electronic effects through nonalternant π systems has been investigated via substituent effects on ¹³C NMR chemical shifts of 1- and 2-substituted azulenes and CNDO molecular orbital calculations. Dual substituent parameter analysis of the chemical shifts permitted separation of the resonance and field/inductive components, while comparison of the regression coefficients with theoretically derived resonance- and field/inductive-induced electron-density variations showed the regression coefficients to be adequate indicators of substituent-induced electron redistribution. In the five-membered ring, resonance and field/inductive effects oppose one another, while they reinforce each other in the seven-membered ring. Implications for the chemistry of azulenes are discussed.

Introduction

It has long been appreciated that there exists a significant difference between the electronic structures of alternant and nonalternant molecular π systems,² as illustrated by the C₁₀H₈ isomers naphthalene and azulene. In contrast to the colorless nonpolar naphthalene, azulene is deep blue and has a dipole moment of 0.8 D.³ This latter property, indicative of nonuniform π -electron distribution, derives from the fact that the theorem requiring all carbon atoms in alternant π systems to have π -electron densities of 1.000 does not hold for nonalternant systems.⁴ This is illustrated by the π -densities, calculated by the CNDO method, shown in Figure 1. (Appreciable variations also occur in σ -densities.)

As a consequence, nonalternant compounds are very susceptible to attack by polar reagents; azulene, for example, is acylated virtually instantaneously at room temperature by acetic anhydride in tin(IV) chloride⁵ and protonated in dilute acid.⁶ More dramatically, the azulene π -system is enormously effective in stabilizing carbocations. Thus, 2-(1-azulyl)ethyl tosylate undergoes solvolysis via the cation 1, with a rate acceleration of about 10⁵ relative



to solvolysis of 2-phenylethyl brosylate for the k_A process at 25 °C.⁷ By contrast, only slight accelerations are observed for other isomeric 2-(azulyl)ethyl tosylates.⁸

To understand the detailed manner in which the azulene π -system is influenced by substitution, we have studied substituent effects on its ¹³C NMR chemical shifts, since ¹³C NMR chemical shifts are generally conceded to be at least indicative of (and often linearly related to) electron-density variations in π systems.⁹⁻¹¹

Results

We obtained ¹³C NMR spectra, both coupled and proton noise decoupled, of several 1- and 2-substituted azulenes, as well as of 1,3-diacetyl- and 1,3-dibromoazulenes. In general, all protonated-carbon resonances were unambiguously assignable on the basis of approximate position in the spectrum, one-bond ¹³CH couplings and further multiplicity induced by longer-range ¹³CH couplings. For 1-chloroazulene, T₁ data afforded an independent check of the assignments and clarified two ambiguities. Non-protonated carbons were observed in many, but not all, cases.

The general approach used in making assignments is typified by the case of 1-chloroazulene. Resonances due to all ten carbons were easily discernable in the noise-decoupled spectrum and like those of azulene, whose spectrum has been reported previously,^{12,13} fall into three regions: around δ 116, 120-125, and 130-140. Considerably more information is present in the coupled spectrum (Figure 2) which shows, besides the characteristically large (ca. 160 Hz) directly bonded ¹³CH couplings, further multiplicity due to long-range two-bond (²J_{CH} = 5-6 Hz) and three-bond (³J_{CH} = 10-11 Hz) couplings.

A nonprotonated carbon, assigned to C-1, resonates at δ 115.9, while a protonated-carbon resonance (¹J_{CH} = 171.9 Hz) at δ 116.2 is due to C-3. A pair of lines at δ 123.3 (¹J_{CH} = 158 Hz) and 124.0 (¹J_{CH} = 158 Hz) correspond closely to C-5 and C-7 of azulene (δ 122.8) and were so assigned. The remaining six resonances (due to carbons 2, 4, 6, 9, and 10) occur in the region δ 130-140, with the bridgehead carbons (C-9 and C-10) at the extremes (δ 133.5 and 139.6). Carbon 6 is easily assignable since it alone exhibits long-range coupling to two nearly equivalent protons (³J_{CH} = 11 Hz).

The doublet centered at δ 134.9 (¹J_{CH} = 169 Hz) is split further into doublets (²J_{CH} = 5.4 Hz), and similarity to the couplings observed for C-3 (¹J_{CH} = 172, ²J_{CH} = 5.7) allows its assignment to C-2.^{14a} The remaining resonances at δ 132.3 (¹J_{CH} = 157, ³J_{CH} = 10.7) and 138.2 (¹J_{CH} = 154, ³J_{CH}

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(14) (a) We observe generally, in agreement with previous reports,^{14b} that within the five-membered ring ¹J_{CH} \approx 170 Hz, while in the seven-membered ring ¹J_{CH} = 150-160 Hz. On this basis, we were forced to reverse the assignments for C-2 and C-6 in azulene made by Grant et al.¹³ (b) Spiesecke, H.; Schneider, W. G. *Tetrahedron Lett.* **1961**, 468. (c) Data for 1,3-disubstituted azulenes are included with those for 1-substituted compounds, for reasons outlined in the Discussion.

Table I. ^{13}C NMR Chemical Shifts (δ) of 1-Substituted Azulenes

carbon	CH_3^a	H	Cl	CH_3CO	NO_2	1,3- Br_2	1,3- $(\text{CH}_3\text{CO})_2$
2	137.9	137.0	134.9	140.0	134.2	138.2	143.0
3	116.5	118.3	116.2	118.4	117.1	102.4	-
4	135.9	136.7	138.2	140.0	141.4	136.9	142.4
5	121.7	122.9	124.0	128.0	130.2	124.9	133.9
6	137.0	137.4	139.3	141.0	141.9	140.8	145.4
7	120.9	122.9	123.3	130.0	131.4	124.9	133.9
8	133.4	136.7	134.3	139.0	137.8	136.9	142.4

^a Braun, S.; Kinkeldei, J. *Tetrahedron* 1977, 33, 1827.

Table II. ^{13}C NMR Chemical Shifts (δ) of 2-Substituted Azulenes

carbon	CH_3O	CH_3^a	H	Cl	CN	I
1	102.3	118.4	118.3	116.4	121.3	125.5
2	170.7	150.2	137.0	139.8	116.3	98.6
4	132.6	134.0	136.7	136.7	141.7	135.9
5	125.1	122.9	122.9	125.7	126.3	125.5
6	133.2	135.2	137.4	138.3	142.7	139.0

^a See Table I, footnote a.

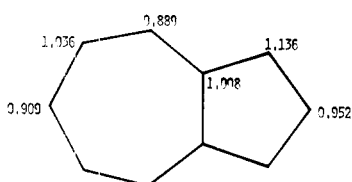


Figure 1. π -Electron densities in azulene, calculated via the CNDO method.

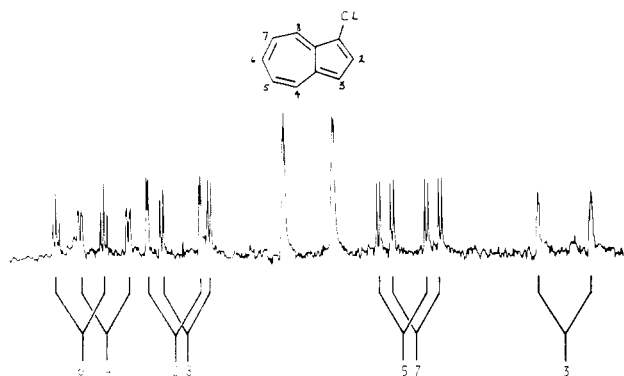


Figure 2. Coupled ^{13}C NMR spectrum of 1-chloroazulene. The unmarked doublet is benzene.

= 10.7) are due to C-4 and C-8.

The pairs of carbons 4,8 and 5,7 were differentiated by their spin-lattice relaxation times. 1-Chloroazulene should tumble anisotropically about an axis roughly parallel to its long axis but tilted somewhat toward chlorine at one end and toward C-5 at the other. Carbons lying closest to this axis, such as C-2, C-5, and C-6, should thus have the shortest T_1 's, consistent with our assignments for C-2 and C-6. Within the otherwise difficult-to-distinguish pairs C-4, C-8 and C-5, C-7, the inclination of the tumbling axis suggests $T_1(8) > T_1(4)$ and $T_1(7) > T_1(5)$, allowing assignment of the resonances at δ 123.3 ($T_1 = 11.5$ s), 124.0 (10.6 s), 134.3 (13.7 s), and 138.2 (13.3 s) to C-7, C-5, C-4, and C-8, respectively.

Chemical shifts for all compounds included in this study are summarized in Tables I and II.^{14c} The chemical shifts are plotted vs. Hammett's σ_p constants in Figures 3 and 4.

In order to provide a theoretical model for electron withdrawal from the five-membered ring of azulene, we performed CNDO/2 calculations on azulene, 1-azulyl-

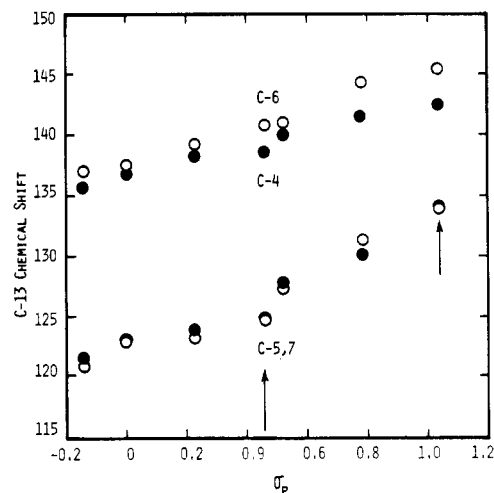


Figure 3. Correlation of the ^{13}C NMR chemical shifts in the seven-membered rings of 1-substituted azulenes with Hammett's σ_p . Points indicated by arrows are those for 1,3-dibromo- and 1,3-diacetylazulenes.

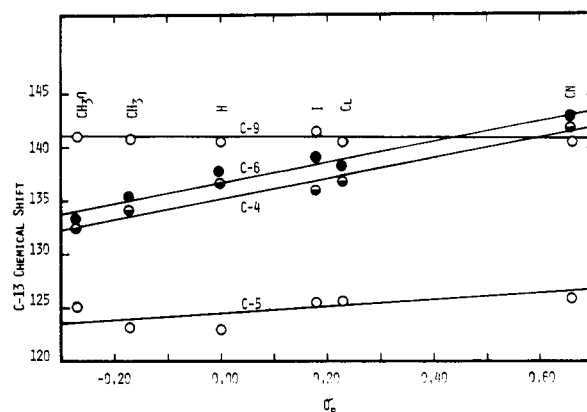


Figure 4. Correlation of the ^{13}C NMR chemical shifts in the seven-membered rings of 2-substituted azulenes with Hammett's σ_p .

Table III. π -Electron Densities of Planar and Orthogonal 1- and 2-Azulylmethyl Cations

carbon	1-azulylmethyl		2-azulylmethyl	
	coplanar	orthogonal	coplanar	orthogonal
1	1.060	1.258	1.012	1.180
2	0.905	0.984	1.020	1.060
3	0.989	1.005	1.012	1.180
4	0.913	0.853	0.778	0.856
5	0.888	0.987	1.047	0.998
6	0.897	0.855	0.760	0.848
7	0.904	0.995	1.047	0.998
8	0.898	0.887	0.778	0.856
9	0.919	1.047	1.038	1.008
10	0.861	0.994	1.038	1.008

methyl cation (two calculations, with the azulyl and methylenidene moieties coplanar and mutually perpendicular,

Table IV. DSP Correlations for 1-Substituted Azulene ^{13}C NMR Shifts (Swain-Lupton Parameters)

carbon	f	r	% r	correlation coefficient
2	-4.131	9.250	69	0.805
3	-1.356	6.232	82	0.921
4	3.319	6.089	65	0.999
5	4.369	12.353	74	0.996
6	3.214	5.314	62	0.988
7	4.489	19.431	81	0.997
8	-0.082	13.855	99	0.970

respectively), and 2-azulymethyl cation (also in coplanar and orthogonal conformations). The π -electron densities are summarized in Figure 1 and Table III. The orthogonal conformations serve as a model for field and/or inductive effects, while the planar ones should include field, inductive, and resonance effects. Since twisting does not alter the radial and angular disposition of the "carbonium ion" center relative to the azulene π system, the difference between the planar and orthogonal conformations should correspond only to resonance effects.

Discussion

The data show clearly that, as indicated above, ^{13}C H coupling constants in the five- and seven-membered rings of both series of compounds behave differently, with one-bond couplings in the five-membered rings being substantially larger than those in the seven-membered ones. This observation is consistent with the idea that opening out the C-C-C angle reduces the s character in the carbon orbital used to form the CH bond, thereby reducing the coupling constant.¹⁵ Similarly, the fact that $^2J_{\text{CH}}$ values in the five-membered rings are much larger than those in the seven-membered rings (actually undetectable) agrees with calculations showing increasing H-C-C bond angles leading to larger couplings.¹⁶ Both $^1J_{\text{CH}}$ and $^2J_{\text{CH}}$ may be used to differentiate carbons within the two rings.

The main significance of this study derives from the chemical-shift data which exhibit considerable sensitivity to substitution, electron-withdrawing substituents leading to downfield shifts. Surprisingly, however, *the greatest sensitivity occurs in the seven-membered ring, remote from the site of substitution*, a type of behavior not encountered in alternant aromatic systems such as naphthalene.¹⁷

A second point of interest is that, in the 1-substituted azulenes, carbons 5 and 7 respond identically to substitution, despite their nonequivalent relationship to the site of substitution. If substituents in the 1- and 3-positions are assumed to act independently, then the ^{13}C NMR shifts of the 1,3-di-X-azulenes should correlate with $2\sigma_p(\text{X})$, as observed (Figure 3). Carbons 4 and 6 also respond identically while carbon 8 is virtually unaffected, perhaps due to approximate cancellation of electronically induced downfield and sterically induced upfield shifts.

A similar situation occurs in the 2-substituted azulenes where carbons 4, 6, and 8 are all equally sensitive to substitution (Figure 4), while carbons 5 and 7 are considerably less so.

The above observations seemed to suggest a significant resonance component in the substituent effect. This was further investigated by analysis of the data by the dual

Table V. DSP Correlations for 2-Substituted Azulene ^{13}C NMR Shifts (Swain-Lupton Parameters)

carbon	f	r	% r	correlation coefficient
1	1.659	24.401	94	0.719
2	-28.635	-57.801	67	0.719
4	3.555	11.382	76	0.988
5	3.904	-0.723	16	0.994
6	4.573	10.981	71	0.988
1 ^a	-3.198	28.708	90	0.945
2 ^a	-11.66	-72.852	86	0.997

^a Data for 2-iodoazulene excluded.

Table VI. DSP Correlations for 1-Substituted Azulenes ^{13}C NMR Shifts (Taft Parameters)

carbon	ρ_I	ρ_R	% r	correlation coefficient
2	-5.76	6.34	52	0.794
3	-1.46	4.48	75	0.854
4	5.89	6.12	51	0.999
5	8.06	11.88	60	0.998
6	5.65	5.43	49	0.988
7	8.93	17.75	67	0.998
8	1.36	11.09	89	0.942

Table VII. DSP Correlations for 2-Substituted Azulene ^{13}C NMR Shifts (Taft Parameters)

carbon	ρ_I	ρ_R	% r	correlation coefficient
1	-0.091	27.53		0.952
2	-29.76	-70.59	70	0.997
4	7.58	10.90	59	0.991
5	5.76	-0.51	8	0.997
6	8.01	11.20	58	0.999

substituent parameter approach, using equations of the form $\delta_c = f\mathcal{F} + r\mathcal{R} + C$ and $\delta_c = \rho_I\sigma_I + \rho_R\sigma_R + d$, where \mathcal{F} and \mathcal{R} are the Swain-Lupton field and resonance parameters and σ_I and σ_R are the Taft inductive and resonance parameters. The results are summarized in Tables IV-VII. In all cases, carbons in the seven-membered rings gave excellent correlations (correlation coefficients > 0.988), the single exception being C-8 in the 1-azulenes (correlation coefficient 0.94-0.97). By contrast, correlations in the five-membered rings were only fair to poor (correlation coefficients 0.72-0.92, with one exception), with the poorest fits being those for carbons adjacent to the site of substitution. To test the possibility that the shifts of these carbons are experiencing a steric shift, we performed three-parameter fits, incorporating the steric parameter Q^{18} , on the shifts for C-2 and C-8 in the 1-substituted azulenes. Improvement was only slight and did not affect the relative importance of \mathcal{F} and \mathcal{R} . In the 2-substituted series, exclusion of the data for 2-iodoazulene led to very good correlations for all carbons. Here, however, a significant variation in the other parameters did occur ($f = -3.20$, $r = 28.71$), bringing f into line with the results in the 1-substituted series.

Several interesting features emerge from the DSP analyses. First, the ^{13}C NMR shifts in both azulene series are much more sensitive to substitution than those of the analogous naphthalene series, with both field and resonance effects contributing significantly to the observed variations. Second, the relative unresponsiveness of five-membered-ring carbons to substitution is seen to derive from opposing field and resonance effects, whereas in

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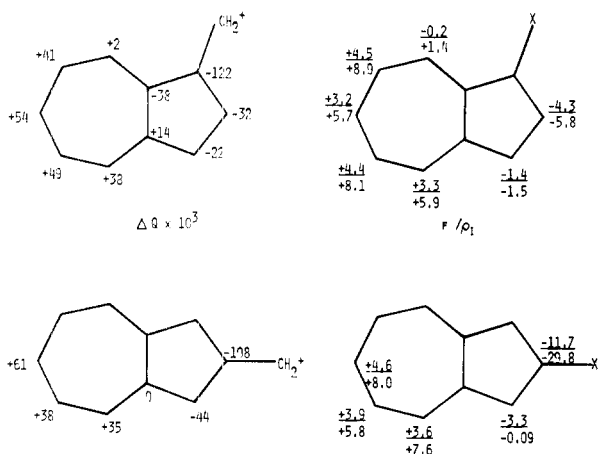


Figure 5. Comparison between the regression coefficients f and ρ_I and the electron-density differences between the orthogonal conformations of 1- and 2-azulymethyl cations and azulene.

the seven-membered rings the two effects more often operate in concert, leading to the observed large substituent-induced shifts. Third, the patterns exhibited by f and ρ_I on the one hand and r and ρ_R on the other appear, in general, to reflect substituent-induced charge development.

Patterns of Electron-Density Redistribution. Substituent-induced ^{13}C NMR chemical shifts are generally agreed to faithfully reflect π -electron-density variations in alternant π systems, especially at carbons not adjacent to the site of substitution.¹⁹ Thus, if this is also true for nonalternant systems, the regression coefficients should afford an experimental insight into the mode of electron redistribution by the substituent via its field (f or ρ_I) and resonance (r or ρ_R) effects. This point was tested by using CNDO/2 calculations, as mentioned earlier.

To assess the field and/or inductive effects of substituents, we show in Figure 5 a comparison between the regression coefficients f and ρ_I and the electron-density differences between the orthogonal conformations of 1- and 2-azulymethyl cations and azulene. Clearly there is a close correspondence between the experimentally derived and theoretical data, demonstrating that the regression coefficients reflect electron-density redistribution by the field and/or inductive effect. In both series, electron-withdrawing substituents cause a drift of electron density from the seven-membered ring to the five-membered one, with the single node being in the vicinity of the ring juncture. This pattern corresponds to what has been termed by Topsom²⁰ the π_F (or field) effect and is similar to the behavior observed in 1- and 2-substituted naphthalenes.

In a fashion similar to that described above, the regression coefficients r and ρ_R should provide insight into the "resonance" component of the substituent effect. The analogous theoretical quantity appropriate for the comparison should be the difference between the π -electron densities in the planar conformation (which should include all types of effects) and those in the orthogonal conformation (where conjugation has been destroyed while preserving the distance and angular relationships between the "carbonium" center and the azulene π -system). The results for the 2-substituted azulenes (Figure 6) are consistent with expectation: carbon atoms conjugated to the substituent group (C-1, C-3, C-4, C-6, and C-8) are all depleted of electron density and deshielded. Interestingly, nonconjugated carbons (C-2, C-5, C-7, C-9, and C-10) are

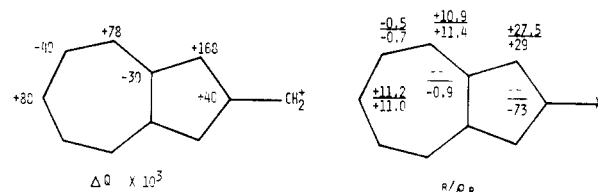


Figure 6. Comparison between the regression coefficients r and ρ_R and the electron-density differences between the planar and orthogonal conformations of 2-substituted azulenes.

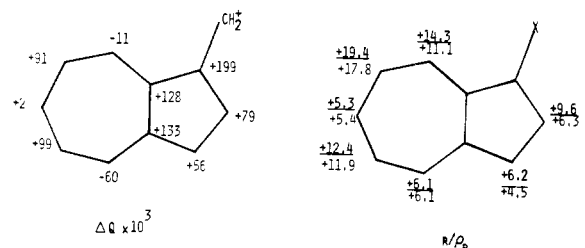


Figure 7. Comparison between the regression coefficients r and ρ_R and the electron-density differences between the planar and orthogonal conformations of 1-substituted azulenes.

predicted by the CNDO/2 calculations to acquire *additional* electron density. Concomitantly, their regression coefficients are negative (albeit small). This alternation of signs is characteristic of what Topsom has described as π_{orb} (nonconjugative electrostatic interaction between an orbital on the substituent and the π -orbital at the site of substitution). However, the fact that the calculations indicate a significant loss of π -electron density from the azulene π system and the enormous disparity in magnitudes between coefficients of conjugated and unconjugated carbons indicate this effect to be far less important than the classical R (resonance) effect.

The situation in the 1-substituted azulene series is somewhat less clear (Figure 7), the patterns of theoretically and experimentally derived descriptors differing significantly.

The CNDO-derived electron-density variations for the 1-azulymethyl cation indicate a fairly uniform loss of π -electrons from the five-membered ring, as well as from carbons 5 and 7 in the seven-membered ring. Carbons 4, 6, and 8, formally unconjugated, are either unaffected or experience an increase in π density, a pattern reminiscent of that observed in the 2-substituted series. The regression coefficients, r and ρ_R , however, exhibit a different pattern: electron withdrawal by resonance leads to downfield shift of all carbons, with C-5 and C-7 much more sensitive to electron demand than any others. In addition, the sign alternation observed in the other series and in the CNDO calculations is absent.

The pattern can be rationalized by invoking a combination of resonance (R), field (π_F), and orbital-orbital interaction (π_{orb}) effects. However, an alternative and conceptually simpler explanation is suggested by the π -bond orders (Figure 8). In the planar 2-azulymethyl cation, bond orders alternate, with the alternation increasing on going from the orthogonal to the planar conformation. The resulting ion is thus best described as a polyenic cation, with positive charge developing at all conjugated carbons.

The structure of the planar 1-azulymethyl cation is quite different, exhibiting strong bond alternation in the five-membered ring, but very little in the seven-membered one. Indeed, alternation increases in the five-membered and decreases in the seven-membered ring, on going from the orthogonal to the planar conformation, suggesting the

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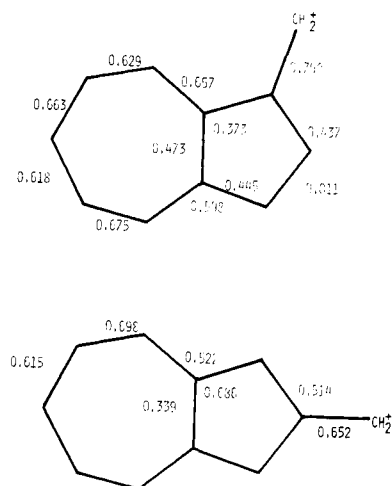


Figure 8. π -Bond orders of the planar 2-azulymethyl cation (bottom) and the planar 1-azulymethyl cation (top).

onset of a fundamental change in the nature of the π system. At this point, the molecule is probably best described as beginning to resemble contiguous tropylium and butadienic subsystems.

The general correspondence between the experimentally derived and theoretical results suggests that variations in ^{13}C NMR chemical shifts in azulenes can serve as an index of π -electron-density redistribution effected by substituents. Nonetheless, the lack of a complete correspondence does signal caution in their interpretation. Subject to this caveat, however, our observations are consistent with a variety of data on the kinetic and equilibrium behavior of azulene systems.

Our CNDO calculations indicate that 1-substituted azulenes should be much more efficient at stabilizing an adjacent positive charge than 2-substituted ones. Consistent with expectation, McDonald and Richmond have reported that 2-(1-azulyl)ethyl arenesulfonates undergo acetolysis via the ethyleneazulenium ion approximately 2000 times faster than the corresponding 2-(2-azulyl)ethyl arenesulfonates.⁸

Our observation that attachment of a substituent to the 1-position of azulene affects primarily the 5- and 7-positions is also consistent with the report that the acid-weakening effect of methyl substitution on the $\text{p}K_a$ of 1-azuloic acid is greatest at positions 5 and 7 and considerably weaker at C-3, C-4, C-6, and C-8.²¹

The 3-position in 1-azuloic acid exhibits behavior intermediate between a meta and a para position,²¹ again

Table VIII. Comparison of Regression Parameters of 1-Substituted Azulene 3-Positions with 1-Substituted Naphthalene 3- and 4-Positions

series	position	ρ_I	ρ_R
1-X-azulene	3	-1.46	+4.48
1-X-naphthalene	3	-1.80	-1.63
1-X-naphthalene	4	+5.92	+19.98

consistent with the ^{13}C NMR spectral results. Table VIII compares the values of ρ_I and ρ_R for 1-substituted azulenes with those for C-3 and C-4 of 1-substituted naphthalenes. Interestingly, ρ_R is moderately large and positive, as expected for a para-like position, while ρ_I is negative, as expected for a meta-like position (although much larger in magnitude). The relative insensitivity of C-3 to substitution thus appears to be due partly to cancellation of inductive and resonance effects.

Experimental Section

All compounds were prepared by literature procedures²² and had physical constants consistent with those reported in the literature. Product identity was also checked by proton NMR spectroscopy.

NMR spectra were recorded on one of three different instruments: Bruker WH-90 spectrometers (Brandeis University and University of Lodz, Poland) or a Bruker HFX-270 spectrometer (Florida State University). Samples were dissolved in acetone- d_6 (ca. 1 M solutions in 10-mm tubes) containing a small amount of Me_4Si .

Dual parameter fits were performed on a PDP-11 computer by using the statistical analysis program COSAP.

CNDO calculations were performed by using the program CNINDO (program no. 141, Quantum Chemistry Program Exchange) on an IBM 370/145 computer, using the electron-diffraction geometry for azulene reported by Bastiansen.²³

Acknowledgment. D.J.S. and F.R.C. gratefully acknowledge support from Grant No. CA 23454, awarded by the National Cancer Institute, DHEW.

Registry No. Azulene, 275-51-4; 1-methylazulene, 769-31-3; 1-chloroazulene, 23306-02-7; 1-acetylazulene, 7206-57-7; 1-nitroazulene, 7206-56-6; 1,3-dibromoazulene, 14658-95-8; 1,3-diacetylazulene, 10487-55-5; 2-methoxyazulene, 36044-37-8; 2-methylazulene, 769-86-8; 2-chloroazulene, 36044-31-2; 2-cyanoazulene, 58081-28-0; 2-iodoazulene, 36044-41-4; 1-azulymethyl cation, 73274-81-4; 2-azulymethyl cation, 73274-82-5.

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Basic Methanolysis of *N*-Aryl-*N*-phenylbenzamides

Trevor J. Broxton,* Leslie W. Deady, and Jeffrey E. Rowe

Department of Organic Chemistry, La Trobe University, Bundoora, Victoria 3083, Australia

Received November 8, 1979

The mechanism of basic methanolysis of a series of *N*-aryl-*N*-phenylbenzamides in methanol and in 80% Me_2SO -methanol has been studied. Comparison of Hammett ρ values with results in the literature suggest that in methanol the rate-determining step is solvent-assisted C-N bond breaking while in 80% Me_2SO -methanol the rate-determining step is methoxide attack. The mechanism of basic methanolysis in a given case is shown to depend both on the relative basicity of methoxide ion and the arylamine anion and on steric effects in the intermediate complex.

The mechanism of basic methanolysis of anilides is finely balanced, with several possible rate-determining

steps (Scheme I).¹ The rate-determining step in any particular case is governed by the relative rates of loss of