The heat changes for process C were obtained from the data of Kleppa, et al.,[17] and the standard free energy change for C for the dissolution of AgNO$_3$ in NaNO$_3$ from the data of Laity.[18] For the dissolution of AgNO$_3$ in KNO$_3$ the reasonable assumption was made that the standard free energy of solution could be well approximated by the standard heat of solution. In Table III are listed the values of the estimates for steps A, B, and C.

The sum of the standard heats or free energy changes A, B, and C are listed in Table III and are compared to the measured values of the heat of solution or of $-RT \ln K_{sp}$ listed in Table II. The average of these quantities in pure NaNO$_3$ and in pure KNO$_3$ is listed for the Na-

NO$_3$–KNO$_3$ solutions and should be a good approximation. The errors in the calculated values are probably about 0.5 kcal./mole. The calculated values can be seen to correspond to the measurements well within the expected errors for the ΔH_{soln} and $-RT \ln K_{sp}$ of the bromide and for ΔH_{soln} of the iodides. The deviations of the calculated values from the measured values of $-RT \ln K_{sp}$ for AgI, although not very large, are greater than the estimated errors. This deviation may possibly be due to a metastable but reproducible form of AgI in our measurements (as well as those of Flengas and Rideal) or to a small error in the literature values of the thermodynamic properties of AgI. In any case, our results confirm the fact that the FFG cycle is potentially useful in the prediction of thermodynamic properties in reciprocal salt systems.

(17) O. J. Kleppa, R. B. Clarke, and L. S. Hersh, J. Chem. Phys., 35, 175 (1961).

(18) R. Laity, J. Am. Chem. Soc., 79, 1849 (1957).

Hydrogen Exchange of Azulenes. I. Structure of the Conjugate Acids of Azulenes[1,2]

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Studies with fifteen azulenes, all but two substituted at the 1-position, show that all of them reversibly form a conjugate acid in strongly acidic aqueous solutions. Conductivity studies with azulene in 100% sulfuric acid indicate only monoprotonation. The ultraviolet and n.m.r. spectra of the azulenium ions measured in hydrogen and deuterium acids show that there are two principal structures for the cations. Protonation occurs on the 3- (or equivalent 1-) position for azulene and 4,6,8-trimethylazulene; it occurs on the unsubstituted 3-position for the following azulenes: 1-methyl-, 1-chloro-, 1-cyano-, 1-p-dimethylaminobenzyl-, 1-cyano-4,6,8-trimethyl-, and guaiazulene. Protonation occurs on the oxygen of the 1-substituent for the azulenes: 1-nitro-, 1-formyl-, 1-trifluoroacetyl-, and 1-formylguaiazulene, while it occurs on the nitrogen of 1-phenyl-azoazulene. 1-Nitro-4,6,8-trimethylazulene is unique in that protonation occurs on the 1- rather than the 3-position, presumably because of the resulting relief from steric interference between the nitro and the 8-methyl group. For this compound as well as for the four which protonate on the 1-substituent, the n.m.r. spectra in deuterium acids show there is facile exchange of the hydrogens at the 3-position, suggesting that minute amounts of the conjugate acid with protonation on the latter position are also formed in strong acids.

Introduction

The kinetics and reaction mechanism of acid-catalyzed aromatic hydrogen exchange have been studied by several authors using organic compounds labeled with deuterium or tritium.[3-6] Colapietro and Long[7] showed that azulene is a suitable compound for this type of study, particularly at low acidities. They investigated the acid-catalyzed deuterium loss of azulene-d_2 (1,3) in buffer solutions using an infrared technique. Azulene in acid exchanges the two hydrogens attached to the 1- and 3-carbons.[8] The conclusion of this early study was that the exchange reaction exhibited general acid catalysis.

A more extensive investigation of the hydrogen exchange of azulenes seemed desirable as a variety of substituted azulenes have become available. Thus it is possible to study the influence of the substituents on the rate and mechanism. These substituted azulenes have been reviewed in detail in recent publications as has the basic theory of the azulene molecule and its conjugate acid.[9,10] A variety of techniques may be used

to study the reaction; for instance, n.m.r. and ultraviolet spectra give information on the position of protonation; liquid scintillation counting applied to the rate of detritiation offers increased accuracy.

This paper and those which follow give results of a broad study of the aqueous azulene system; they supplement and modify the results quoted in a preliminary publication.[11] In this preliminary publication it was noted that the dependence of the rate of detritiation of azulene and of 1-nitroazulene on acidity was essentially the same; in contrast, the acidity dependence of the equilibrium protonation of the two compounds differed sharply. The present study gives further information on this different behavior and summarizes information for several other azulenes.

Experimental

Compounds.—Samples of four compounds, listed by name and symbol, were generously supplied by Professor K. Hafner: 4,6,8-trimethylazulene, TMAz; 1-cyano-4,6,8-trimethylazulene, CNTMAz; 1-nitro-4,6,8-trimethylazulene, NO$_2$TMAz; 1-(p-dimethylaminobenzyl)-azulene, pDMABAz. Samples of 1-cyanoazulene, CNAz; 1-phenylazoazulene, PhN$_2$Az; and 1-trifluoro-acetyl-azulene, CF$_3$COAz, were supplied by Professor A. G. Anderson; samples of 1-formylazulene, CHOAz; and 1-formyl-guaiazulene, CHOGuAz, by Professor D. H. Reid; samples of 1-methylazulene, MeAz, and 1-nitroazulene, NO$_2$Az, were supplied by Professor E. Heilbronner. Commercial azulene, Az, and guaiazulene, GuAz, were purchased from the Aldrich Chemical Co., Inc., Milwaukee, Wis. 1-Chloroazulene, ClAz; 1-carboxy-azulene, COOHAz; and another sample of 1-nitroazulene, NO$_2$-Az, were prepared in this laboratory by known methods.[12,13] The compounds were purified by recrystallization, vacuum sub-

(1) Work supported by a grant from the Atomic Energy Commission.

(2) Presented in part at the 139th National Meeting of the American Chemical Society, St. Louis, Mo., April, 1961.

(3) F. A. Long and M. A. Paul, Chem. Rev., 57, 935 (1957), for a review of earlier work.

(4) L. Melander, "Isotope Effects on Reaction Rates," Ronald Press Co., New York, N. Y., 1960.

(5) A. J. Kresge and Y. Chiang, J. Am. Chem. Soc., 83, 2877 (1961).

(6) V. Gold, R. M. Lambert, and D. P. N. Satchell, J. Chem. Soc., 2461 (1960).

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(8) A. van Tets and Hs. H. Günthard, Helv. Chim. Acta, 46, 457 (1962).

(9) E. Heilbronner, in "Nonbenzenoid Aromatic Compounds," Interscience Publishers, Inc., New York, N. Y., 1959, Chapter 5.

(10) T. Nozoe, Fort. Chem. Org. Natur., 19, 32 (1961).

(11) F. A. Long and J. Schulze, J. Am. Chem. Soc., 83, 3340 (1961).

(12) A. G. Anderson, Jr., J. A. Nelson, and J. I. Tazuma, ibid., 75, 4980 (1953).

(13) A. G. Anderson, Jr., R. G. Anderson, and L. L. Replogle, Proc. Chem. Soc., 72 (1960).

limation, and by chromatography on alumina. Purification was checked by the absorption spectra and by the melting points, both of which agreed within experimental error with published values.

Symbols.—Throughout this series of papers, the symbols given above are used for the unprotonated compounds with the monoprotonated species being denoted by the same symbols, inclosed in brackets with a plus sign. Substituent position is denoted by the conventional numbering system

Reagents.—All chemicals were reagent grade and were used without further purification except when otherwise noted. Trifluoroacetic acid was distilled before use. The 100% sulfuric acid was prepared by mixing oleum and 96% H_2SO_4 until a minimum in conductivity was reached. Deuterated sulfuric acid, D_2SO_4, was prepared by mixing SO_3 ("Sulfon B" General Chemical Division, New York, N. Y.) with the calculated amount of D_2O. Deuterated trifluoroacetic acid, CF_3COOD, was prepared by mixing trifluoroacetic anhydride (Eastman Organic Chemicals, Rochester 3, N. Y.) with the calculated amount of D_2O.

The conductivity measurements were made in a cell of 5-ml. capacity whose cell constant, 2.906 cm.$^{-1}$, was determined with solutions of potassium chloride. The electrodes were lightly platinized. The electrical apparatus comprised a 1-kc. oscillator, a Campbell–Shackleton ratio bridge, a Leeds and Northrup precision a.c. resistance box, an amplifier, and earphones. The compounds were weighed into a 10-ml. volumetric flask and the volumetric flask was filled with 100% H_2SO_4 in a drybox under nitrogen. The carefully dried conductivity cell was filled with this solution in a drybox. The absorption spectra were measured on a Cary Model 14 recording spectrophotometer. The proton magnetic resonance spectra were taken with a Varian A-60 spectrometer operating at 60 Mc./sec. The peak positions are given in p.p.m. (δ) multiplied by minus one to avoid negative numbers and are relative to an internal standard, tetramethylsilane. In solutions with a high sulfuric acid concentration, in which tetramethylsilane is not applicable, no reference was used.

Results

The information which bears on the structure of the conjugate acids of several azulenes is summarized in Fig. 1 through 4 and Tables I and II.

TABLE I

INFRARED SPECTRA IN 1% CS_2 SOLUTION OF 1-NITROAZULENE AND 1-NITROAZULENE-$d_1(3)$

Cell was 0.5 mm. NaCl; symbols after band maxima give relative intensities

NO₂Az band maxima, cm.⁻¹		NO₂Az-$d_1(3)$ band maxima, cm.⁻¹	
732 m	1040 m	750 s	1050 w
760 s	1155 vw	767 s	1110 w
785 s	1200 m	805 s	1185 m
819 s	1225 m	865 m	1220 m
880 w	1280 s	900 m	1280 s
915 vw	1330 s	965 w	1330 s
965 w	1400 s	990 w	1400 s
	3000 vw		2900 vw

TABLE II

SITE OF PROTONATION OF AZULENES

Compound	N.m.r.	Ultra-violet	Compound	N.m.r.	Ultra-violet
Az	C	C	pDMABAz	..	C
MeAz	C	C	NO₂TMAz	C	C
ClAz	C	C	NO₂Az	O	O
CNAz	C	C	CHOAz	O	O
TMAz	C	C	CF₃COAz	O?	O
GuAz	C	C	CHOGuAz	O	O
CNTMAz	..	C	PhN₂Az	N	N
COOHAz	C?	C?			

Figure 1 gives the specific conductivities of azulene and of several previously studied compounds in 100% sulfuric acid. The specific conductivities of azulene closely parallel those of p-nitroaniline and benzoic acid, compounds which are known to monoprotonate in this solvent. The data do not at all parallel the results
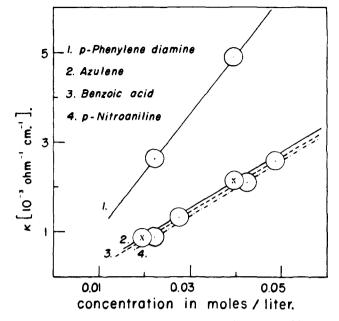

Fig. 1.—Specific conductivities in 100% sulfuric acid.

for p-phenylenediamine, a compound which is known to diprotonate. The very similar conductance behavior for the first three compounds is to be expected if they all monoprotonate, since the predominant carrier of current for this solvent is the bisulfate ion and as a consequence conductivities of bisulfate salts are virtually independent of the size and character of the cation. The conclusion that only monoprotonation occurs with azulene confirms and extends an earlier study by Plattner, Heilbronner, and Weber.[14]

Table I summarizes the infrared bands of nitroazulene and deuterated nitroazulene. The infrared spectrum is significantly different for the deuterated compound. Studies on azulene give corresponding differences.[8] With azulene it is well established that even in relatively concentrated acids deuteration occurs only at the 1- and 3-positions. With nitroazulene the position of deuteration is not so firmly established.[15] However, the n.m.r. spectra of Fig. 3 for the conjugate acid of nitroazulene in deuterated acid shows clearly that only the 3-hydrogen is exchanged. Similar studies with other 1-substituted azulenes also show that exchange is restricted to the 3-position.

The ultraviolet spectra of the azulene cations divide into two distinct groups. The spectra of the first group, which includes azulene and the next nine substituted azulenes of Table II, are characterized by three absorption maxima between 200 and 400 mμ with virtually no absorption at longer wave lengths. Details of these, as reported in Table III of the following paper, reveal a marked similarity in both the position and intensity for the three bands. The second group consists of the cations of 1-nitroazulene, 1-formalyazulene, 1-trifluoroacetylazulene, and 1-formylguaisazulene. These cations are characterized by a more com-

(14) P. A. Plattner, E. Heilbronner, and S. Weber, Helv. Chim. Acta, **35**, 1036 (1952).

(15) Some evidence that deuteration occurs only on the 3-position has been reported by F. W. McLafferty (private communication) as a result of mass spectrometric studies with the undeuterated and deuterated compounds. The mass spectrometric studies show that a sample of the nitro compound which has been prepared by deuteration in D_2SO_4 is essentially monodeuterated with no evidence of dideuteration. The best interpretation of the mass spectra is obtained by assuming that there is no deuterium on the 2-carbon and that carbon 3 is fully deuterated; but that accompanying the ionic decomposition reactions which result in the loss of fragments such as C_2HNO_2, some rearrangement of deuterium to the other positions occurs. Because of this indication of rearrangement, the evidence for deuteration only at the 3-position is suggestive but not conclusive.
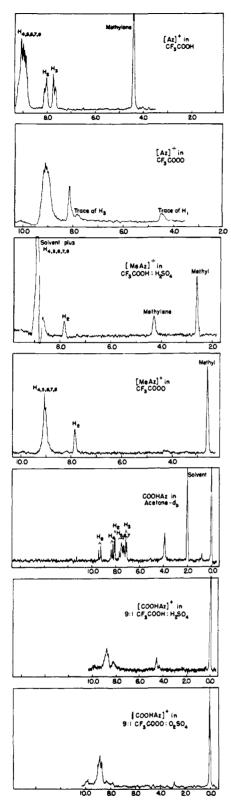
Fig. 2.—N.m.r. spectra of azulenes in various solvents.

Fig. 3.—N.m.r. spectra of azulenes in various solvents.

plex spectra in the 200–500 mμ region. Again the spectra are quite similar to each other, but distinctly different from the spectra that characterizes the first group of cations.

Figures 2 and 3 summarize the proton magnetic resonance spectra for a number of azulenium cations. The spectra are normally given for solutions in both hydrogen acids and deuterium acids; in a few cases n.m.r. spectra of the neutral compounds in acetone-d_6 or CDCl$_3$ are given for comparison. The proton assign-
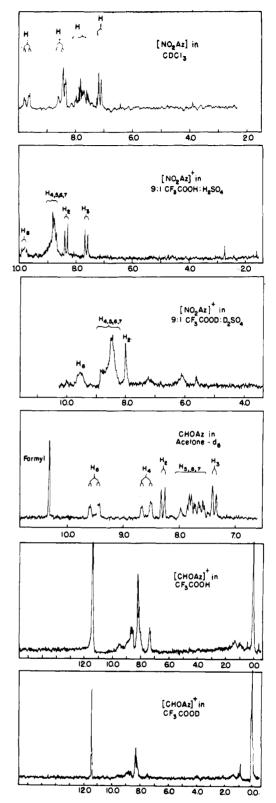
ments which are given in these figures were made with the assistance of the work of Danyluk and Schneider[16] and Heilbronner and Meuche.[17]

Discussion

All of the azulenes studied show marked color changes when dissolved in aqueous acids, most frequently from

(16) S. S. Danyluk and W. G. Schneider, *J. Am. Chem. Soc.*, **82**, 997 (1960).

(17) E. Heilbronner and D. Meuche, *Helv. Chim. Acta*, to be published. We are indebted to the authors for the opportunity to study this paper in advance of publication.

either blue or red to yellow. The reaction is reversible and the original azulene can be recovered by neutralization. All available evidence supports the proposal that the reaction in acid is a typical acid–base reaction leading to formation of the conjugate acid. As noted earlier, data on conductivities in 100% sulfuric acid show that azulene itself only monoprotonates and it is reasonable to assume that this is true of the other azulenes. The problem to which this discussion is addressed concerns the actual site of protonation. In discussing this it is convenient to do so in terms of two principal groups.

The first group consists of the compounds: Az, MeAz, COOHAz, ClAz, CNAz, TMAz, GuAz, pDMABAz, and CNTMAz. The available evidence indicates that all of these protonate at the 3-position. This type of protonation was established for the parent compound some time ago. Heilbronner and Simonetta first showed by molecular orbital calculations that the most basic site of the azulene molecule is the 1- (or 3-) position and that the most probable structure for the conjugate acid is a vinyltropylium ion.[18] Deuterium exchange studies confirmed that the 1- (or 3-) position was the point of protonation,[19] and the n.m.r. studies of Danyluk and Schneider confirm the vinyltropylium ion structure for the azulenium ion.[16]

The n.m.r. spectra for the conjugate acids of the first seven of the above compounds were taken in hydrogen and deuterium acids. The results for the first three of these are presented in Fig. 2. These spectra and those for the conjugate acids [ClAz]+, [CNAz]+, [TMAz]+, and [GuAz]+ are strikingly similar, the chief characteristics being: (a) peaks due to the seven-member ring protons at lowest field, about $\delta = 9$ p.p.m. relative to the tetramethylsilane standard; (b) peaks due to the five-member ring protons at about 8 p.p.m.; (c) a peak due to the methylene protons at about 4 p.p.m.; (d) peaks from the methyl protons at highest field, about 2 p.p.m. Careful integration of peak areas was performed for most of these conjugate acids and in every instance the numbers of protons were as expected. Specifically the peak area for the methylene groups invariably indicated two protons. In deuterated acidic solvent the methylene peaks disappear, evidently due to exchange of the protons at the site of protonation. Since the ultraviolet spectra of the conjugate acids of the above nine compounds are also strikingly similar, it seems safe to conclude that for all of these protonation occurs on the 1- or 3-carbon of the azulene skeleton.[20,21]

The substituents for most of this group of compounds are such that carbon protonation is the expected result, but for two of them, COOHAz and NO₂TMAz, this type of behavior is surprising. These special cases are, however, more easily discussed after the characteristics of compounds which protonate on a substituent are established. To do this we turn to the second group of compounds: NO₂Az, CHOAz, CF₃COAz, CHOGuAz, and PhN₂Az.

The ultraviolet spectra of the conjugate acids of the first four compounds of this second group are

(18) E. Heilbronner and M. Simonetta, *Helv. Chim. Acta,* **35**, 1049 (1952).

(19) A. Bauder and H. H. Günthard, *ibid.,* **41**, 889 (1958).

(20) Because of the smallness of our samples, we were unable to make n.m.r. studies for [pDMABAz]++ and [CNTMAz]+. However, in view of their ultraviolet spectra, there is no reason to doubt but that these two also are protonated on the 3-carbon.

(21) An initial protonation of 1-(*p*-dimethylaminobenzyl)-azulene occurs at very low acidities and results in only a slight spectral change. This is undoubtedly to be attributed to protonation of the *p*-amino group of the benzyl substituent. In concentrated aqueous acids there is a further color change leading to a product whose spectrum is typical of the "first group" of azulenes. We attribute this to a second protonation, this time on the 3-carbon.
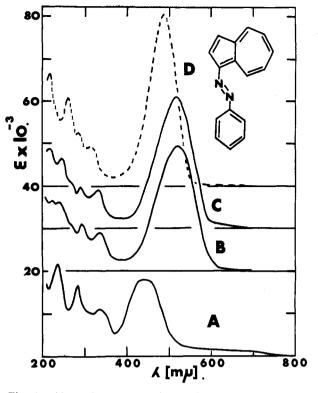

Fig. 4.—Absorption spectra of PhN₂Az in the solvents: A, water; B, 8:2 ethanol–1 N aqueous HCl; C, 70% aqueous HClO₄; D, oleum (15% SO₃). Zero lines shifted as indicated.

very similar and quite different from those of compounds which protonate on carbon. The spectra for these conjugate acids give no evidence for the presence of the vinyltropylium ion structure; in fact the spectra are sufficiently similar to those for the parent neutral molecules as to suggest that the basic ring resonance has not been greatly modified.

The n.m.r. spectra for the conjugate acids of the five compounds of this group have been studied in both hydrogen and deuterium acids, and the results for two of them, [NO₂Az]+ and [CHOAz]+, are given in Fig. 3. The spectra for [CHOGuAz]+ and [CF₃COAz]+ are similar to these in all important respects and are not given explicitly.[22] The significant point is that none of these ions exhibits the characteristic methylene peak of carbon protonation. These similarities, as well as the known basicity of the carbonyl, nitro, and azo groups, lead to the conclusion that for all five of these compounds the principal structure of the conjugate acid is one with protonation on the substituent, specifically on the oxygen of the formyl and nitro groups and nitrogen of the azo group. A more extensive study of the n.m.r. spectra of 1-nitroazulene and its conjugate acid has recently been made by Heilbronner and Meuche[17] who also conclude that protonation is on the substituent. These same authors additionally report that the n.m.r. spectrum of the conjugate acid of lactaroviolin (1-formyl-4-methyl-7-isopropenylazulene) also indicates protonation on the formyl group.[23] Finally, preparative evidence has been cited by Hafner and Bernhard[24] to support the proposal that protonation of 1-formyl-4,6,8-trimethylazulene occurs on the formyl group.[25]

(22) N.m.r. studies with [PhN₂Az] were less satisfactory owing to the low solubility of its salts. However, the spectra were good enough to show definitely the absence of a methylene signal at $\delta = 4$ p.p.m. This, combined with the close similarity of its ultraviolet spectrum to the other conjugate acids of this group, makes it evident that substituent protonation occurs.

(23) E. Heilbronner and D. Meuche, private communication.

(24) K. Hafner and C. Bernhard, *Ann.,* **625**, 108 (1959).

Phenylazoazulene differs from the other members of this second group in as much as the azo group is sufficiently basic to protonate at low acidities. The ultraviolet spectra for this species in several solvents are shown in Fig. 4. Monoprotonation is complete in solution B, which is 0.2 N hydrochloric acid. This protonation is accompanied by a bathochromic shift of 80 mμ, causing a visible color change from yellow to red.[27] As is evident from the similarity of spectra B, C, and D, further protonation does not occur even in oleum of H_0 acidity of -12. The slight hyposochromic shift of the long wave length peak of spectrum D is due to a solvent effect. Further evidence obtained at lower acidities, for the absence of second protonation, is that the n.m.r. spectrum in trifluoroacetic acid exhibits no "methylene" signal.

For all members of this second group of compounds, the n.m.r. signal from the 3-proton disappears in deuterated acid. The implication is that the 3-position is second in basicity only to the substituent. One must therefore assume that at equilibrium the predominant form of the conjugate acid is accompanied by minute amounts of the conjugate acid with the methylene structure. However, there is no evidence from either the n.m.r. or ultraviolet spectra for measurable amounts of this latter structure, i.e., protonation on substituent seems complete within experimental error.

Table II summarizes the available evidence on the site of protonation for all the azulenes studied. In this table the question marks which follow after the assignment from the n.m.r. results refer primarily to uncertainties in detailed interpretations; the conclusions on site of protonation are reasonably firm. There are, however, two special cases, COOHAz and NO$_2$TMAz, which are listed in Table II as protonating on carbon, even though other carbonyl and nitro substituted azulenes protonate on the oxygen of the substituent.

The ultraviolet spectrum of [COOHAz]$^+$ is very similar to that of the first group of azulenium ions;

(25) We do not know the origin of the n.m.r. signal occurring at about 1 p.p.m. for 1-formylazulene and its conjugate acid. The signal from a formyl proton is expected to occur at about 10 p.p.m.,[26] and by direct experiments with benzaldehyde in various acids we have established that this is true for polar acidic solvents as well as for organic solvents. The signal from the formyl hydrogen of [CHOAz]$^+$ appears to shift somewhat in acidic solvents (Fig. 3). However, this shift cannot be the explanation of the peak at 1 p.p.m.
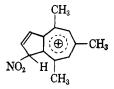
(26) R. E. Klinck and H. B. Stothers, Can. J. Chem., 40, 1071 (1962).

(27) Protonation presumably occurs on the nonbonding electron pair of one nitrogen, the orbital involved lying in the plane of the molecule. Molecular orbital calculations indicate that the protonation is on the nitrogen adjacent to the phenyl group.[28]

(28) F. Gerson and E. Heilbronner, Helv. Chim. Acta, 42, 1883 (1959).

i.e., those which are protonated on carbon. The n.m.r. spectrum of [COOHAz]$^+$ is complex in that there appear to be two signals in the methylene region. Both signals disappear in a deuterated acid. We do not have an explanation for the presence of two signals. The character and position of these n.m.r. signals and the character of the ultraviolet spectrum both suggest carbon protonation, presumably at the 3-position. However, data to be presented in part II are not consistent with this and we conclude that some uncertainty exists in the results for this compound.

The behavior of 1-nitrotrimethylazulene is unique among the compounds studied and has been the subject of a preliminary report.[29] The ultraviolet spectrum of this compound in the neutral form is very similar to that of 1-nitroazulene. However, the conjugate acid, [NO$_2$TMAz]$^+$, gives a spectrum very like azulene itself and quite unlike that for [NO$_2$Az]$^+$. The n.m.r. spectrum of [NO$_2$TMAz]$^+$ is remarkable for a peak of $\delta = 6.7$ p.p.m. relative to the tetramethylsilane standard.[29] This peak on integration is due to one proton and disappears in deuterated acid. The obvious explanation of these facts is that, owing to a gain in energy from relief of steric interference, protonation in this case occurs on the 1-carbon leading to the cation

The possibility of this type of protonation was suggested some time ago, again for steric reasons, for the conjugate acid of 1,8-dimethylazulene.[30] In the present case it permits a straightforward explanation of both the ultraviolet and n.m.r. spectra as well as the observed acid strength of [NO$_2$TMAz]$^+$. The unusual chemical shift for the peak due to the hydrogen at the 1-position can be qualitatively ascribed to a strong deshielding effect by the adjacent nitro group. In a deuterated acid this peak disappears and so does the contribution from the hydrogen at the 3-position. The implication of the latter fact is that, although less basic, the 3-carbon is sufficiently basic as to permit facile hydrogen exchange by the normal acid-catalyzed mechanism.

(29) J. Schulze and F. A. Long, Proc. Chem. Soc., 364 (1962).

(30) L. H. Chopard-dit-Jean and E. Heilbronner, Helv. Chim. Acta, 35, 2170 (1952).