troscopy. In the case of diphenylmethane, the liquid hydrocarbon was isolated by concentration of the extract and glpc separation (25% Apiezon on Chromosorb W).

The base concentration was determined by quenching kinetic aliquots at various times with water and titrating with standard HCl.

The resulting base concentration was corrected to kinetic temperature with the density-temperature tables of Timmermans.[27]

(27) J. Timmermans, "Physico-Chemical Constants of Pure Organic Compounds," Elsevier, New York, N. Y., 1950, pp 303–304.

The Basic Strength of Carbazole. An Estimate of the Nitrogen Basicity of Pyrrole and Indole[1]

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Abstract: The protonation of N-methylcarbazole in strong acids was found to occur on nitrogen, as evidenced by changes in its nmr spectrum, and to be accompanied by the disappearance of strong absorption of ultraviolet light at 235 mm. Similar spectral changes occur with other carbazole bases; these were used, in conjunction with standard indicator methods, to determine extents of protonation of carbazole and eight of its derivatives. The acidity dependencies of these protonation reactions fall, on the whole, into categories expected for secondary and tertiary amines, but slopes of plots of log I vs. H_0 show enough individual variation to give a set of individually extrapolated pK_a's inconsistent with expected substituent effects. Half-protonation points, $(H_0)_{I=1}$, on the other hand, correlate very well with Hammett σ constants; these $(H_0)_{I=1}$ values were therefore used to estimate basicities by a method which gives carbazole itself a pK_a of about -6. This provides an upper limit for the basic strength of the nitrogen atom in the related heteroaromatics pyrrole and indole, substances in which equilibrium protonation occurs preferentially on carbon and for which nitrogen basicity is not directly measurable.

The N-heteroaromatics pyrrole and indole are unusual in that they undergo equilibrium protonation on carbon in preference to nitrogen and display their basic properties only in concentrated acid solution.[5,6] The nitrogen atom in these substances must therefore be very weakly basic indeed. It is not possible, of course, to measure this property of these systems directly, but it might be estimated in the following way. Under equilibrium conditions, pyrrole undergoes preferential protonation on an α-carbon atom,[5a,7] but indole protonates on β-carbon,[6b] thus trading off an additional resonance form for undisturbed conjugation in its benzene ring. This suggests that the next higher benzolog, carbazole, in which the second side of the pyrrole ring is blocked as the first is in indole, might protonate on nitrogen; determination of the gross basicity of carbazole would then furnish an estimate of nitrogen basicity in the pyrrole system.

With this objective in mind, we undertook to determine the site of protonation and the basic strength of

(2) Petroleum Research Fund Graduate Fellow.
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(5) (a) E. B. Whipple, Y. Chiang, and R. L. Hinman, J. Amer. Chem. Soc., 85, 26 (1963); (b) Y. Chiang and E. B. Whipple, ibid., 85, 2763 (1963); (c) Y. Chiang, R. L. Hinman, S. Theodoropulos, and E. B. Whipple, Tetrahedron, 23, 745 (1967).
(6) (a) R. L. Hinman and J. Lang, Tetrahedron Lett., 12 (1960); (b) R. L. Hinman and E. B. Whipple, J. Amer. Chem. Soc., 84, 2534 (1962); (c) R. L. Hinman and J. Lang, ibid., 86, 3796 (1964).
(7) R. J. Abraham, E. Bullock, and S. S. Mitra, Can. J. Chem., 37, 1859 (1959).

carbazole. In the sole previous report on this subject, the pK_a of carbazole itself was estimated only as < -1, and the site of protonation was not established.[8]

Results and Discussion

Protonation of carbazole occurs in very strong acids (e.g., half-protonation at $\sim$8.5 M sulfuric acid), as evidenced by the reversible change in the ultraviolet spectrum. The principal band in the ultraviolet spectrum of the fully protonated carbazole (Figure 1) closely resembles that of fluorene (λ_{max} 262 mm, log ϵ_{max} 4.30 M^{-1} cm^{-1})[9] in both wavelength and intensity, suggesting that protonation occurs on nitrogen. Confirmation of nitrogen as the site of protonation was established from the nmr spectra of N-methylcarbazole in strong acids. In a mixture of trifluoroacetic acid and sulfuric acid the nmr spectrum consists of a complex multiplet in the aromatic proton region and a singlet some 4 ppm further upfield. Since these bands have the relative areas of 8–3, they can be attributed to the aromatic ring protons and those of the N-methyl group, respectively. In fluorosulfonic acid at 30° the methyl-group peak appears as a doublet, $J = 6$ Hz, demonstrating that protonation occurs on nitrogen. No splitting is observed in the weaker acid because of fast proton exchange, which also accounts for the absence of an observable signal for this proton in both cases.

The intense ultraviolet absorption band of the basic form of carbazole at 235 nm, $\epsilon > 10^4$, which disappears upon protonation, is especially suited to quantitative

(8) N. F. Hall, J. Amer. Chem. Soc., 52, 5115 (1930).
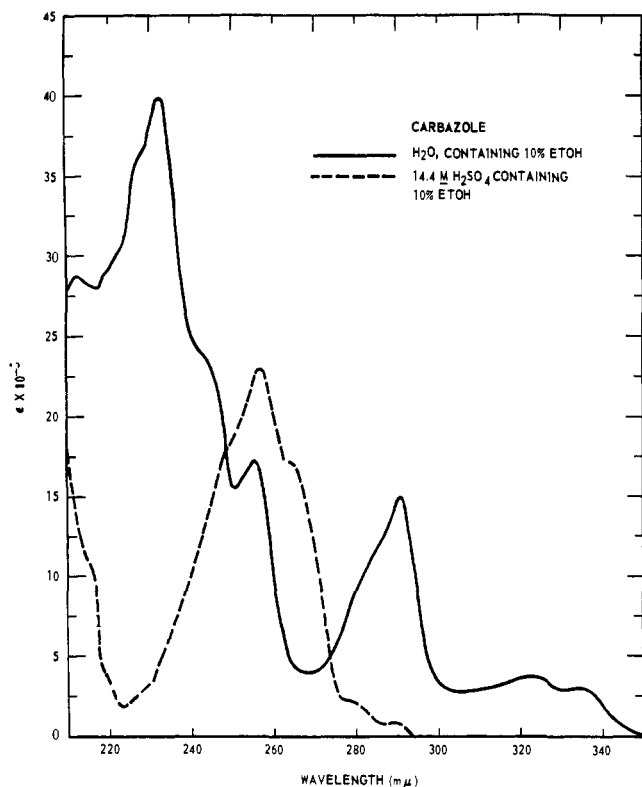(9) E. J. Moriconi, F. T. Wallenberger, L. P. Kuhn, and W. F. O'Connor, J. Org. Chem., 22, 1651 (1957).

Figure 1. The ultraviolet spectra of carbazole and its N-protonated conjugate acid.

Figure 2. Extents of protonation of carbazole and some of its derivatives in 20% ethanol–80% aqueous sulfuric acid.

determination of basic strength by the indicator method.[10] This band shows no change in intensity in going from wholly aqueous solution to 48% sulfuric acid, thus demonstrating the absence of medium effects on ϵ_B. At higher acidities the system shows good isosbestic point behavior at 205 and 250 nm. Similar spectral changes occur with the variously substituted carbazole derivatives listed in Table I. Many of these compounds, however, are exceedingly insoluble in water, not dissolving even to the extent of forming 10^{-6} M solutions, which makes accurate measurement of absorbance changes impossible. Addition of small amounts of organic solvents relieves this situation markedly, and indicator measurements were therefore carried out in a 20% ethanol–80% aqueous sulfuric acid solvent system. This is an easily prepared, reproducible medium which has been used before for basicity measurements of substances with low water solubility,[11] and for which acidity functions have been developed using both primary anilines (H_0)[12] and diphenylamines[11b] as indicators. At high acidities, a portion of the ethanol is converted to ethyl hydrogen sulfate, but that seems not to affect the utility of this mixed medium.[12] Some of the carbazoles examined here proved to be unstable in very concentrated sulfuric acid solution, as evidenced by time-dependent changes in their ultraviolet spectra. In these cases, absorbance was recorded as a function of time, and values at the time of sample preparation were determined by linear extrapolation.

The data obtained for carbazole and eight of its derivatives are displayed in Figure 2 as plots of log I ($I =$ indicator ratio $= C_{BH}/C_B$) vs. H_0.[12] The relationship between these two variables proved to be essentially linear in all cases, and the data were therefore subjected to weighted, linear least-squares analysis. H_0 was assumed to be known exactly, and weights were assigned to log I values in proportion to the reciprocals of their expected uncertainties squared;[13] relative uncertainties in log I were calculated using a recently published error function.[14] The results of this analysis are summarized in Table I.

Inspection of column three of Table I shows that none of these log I vs. H_0 plots has unit slope, and that the H_0 acidity function therefore does not correlate the protonation of any of these bases. This is hardly surprising, for carbazoles are quite different structurally from the *primary* aniline bases used to construct the H_0 function. In particular, the acidity dependence of the protonation of weak bases in concentrated acids depends strongly on the number of sites available for hydrogen bonding between the conjugate acids and the solvent,[11b,15,16] which leads to increasingly steeper acidity dependence along the series priary amines < secondary amines < tertiary amines. It is significant, therefore, that the first seven entries in Table I, all secondary amines, show values of $-d$ log I/dH_0 whose average is some 10% above unity, and that slopes for the remaining two compounds, both tertiary amines, are still greater. (However, the slopes for the secondary carbazole bases differ from those for diphenylamines, showing that factors other than the number of hydrogen bonding sites are important.) In fact, with the exception of carbazole and 2-nitrocarbazole, all secondary amines give slopes whose individual values are not significantly different from their mean, 1.11 ± 0.04. It is

(10) E. M. Arnett, *Progr. Phys. Org. Chem.*, **1**, 223 (1963).

(11) (a) H. H. Jaffe and R. W. Gardner, *J. Amer. Chem. Soc.*, **80**, 319 (1958); S. J. Yeh and H. H. Jaffe, *ibid.*, **81**, 3274 (1959); (b) D. Dolman and R. Stewart, *Can. J. Chem.*, **45**, 904 (1967).

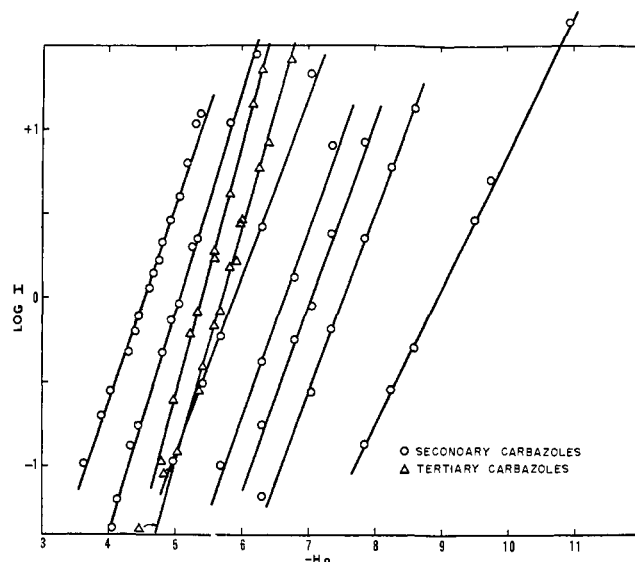(12) A. J. Kresge and H. J. Chen, *J. Amer. Chem. Soc.*, submitted for publication.

(13) A. G. Worthing and J. Geffner, "Treatment of Experimental Data," Wiley, New York, N. Y., 1943, Chapter VIII.

(14) A. J. Kresge and H. J. Chen, *Anal. Chem.*, **41**, 74 (1969).

(15) R. W. Taft, Jr., *J. Amer. Chem. Soc.*, **82**, 2965 (1960); E. M. Arnett and G. W. Mach, *ibid.*, **86**, 2671 (1964); **88**, 1177 (1966).

(16) W. M. Schubert and R. M. Quacchia, *ibid.*, **84**, 3778 (1962); **85**, 1278 (1963); A. J. Kresge, G. W. Barry, K. R. Charles, and Y. Chiang, *ibid.*, **84**, 4343 (1962).

Table I. The Protonation of Carbazoles in 20% Ethanol–80% Sulfuric Acid at 25°

| Substrate	$(E_{H^+}/I)_{I=1}{}^a$	d log I/dH_0	$(H_0)_{I=1}$	pK_a Individual extrap	Group extrap
Secondary amines					
3-Methylcarbazole	15.6	-1.17 ± 0.03	-4.44 ± 0.03	-5.4 ± 0.1	-4.9 ± 0.3
Carbazole	16.9	-1.31 ± 0.03	-4.94 ± 0.04	-6.8 ± 0.2	-5.9 ± 0.3
2-Methoxycarbazole	18.8	-1.07 ± 0.02	-5.79 ± 0.02	-6.3 ± 0.1	-6.5 ± 0.3
3-Chlorocarbazole	20.5	-1.10 ± 0.09	-6.55 ± 0.12	-7.3 ± 0.6	-7.1 ± 0.3
2-Bromocarbazole	21.4	-1.11 ± 0.07	-6.93 ± 0.09	-7.8 ± 0.5	-8.0 ± 0.3
3,6-Dichlorocarbazole	22.2	-1.09 ± 0.03	-7.41 ± 0.04	-8.2 ± 0.2	-8.4 ± 0.3
2-Nitrocarbazole	25.4	-0.82 ± 0.02	-8.81 ± 0.03	-7.0 ± 0.2	-9.8 ± 0.4
Tertiary amines					
9-Ethylcarbazole	17.4	-1.49 ± 0.03	-5.29 ± 0.03	-8.4 ± 0.2	-7.8 ± 0.7
9-Methylcarbazole	18.2	-1.40 ± 0.05	-5.60 ± 0.05	-8.3 ± 0.3	-8.2 ± 0.8

^{a} Equivalents of acid (H_2SO_4 + $C_2H_5OSO_3H$) per liter of solution at which $I = 1$.

not clear why carbazole should be different, but 2-nitrocarbazole had to be studied in very concentrated acids where decomposition problems were quite severe.

In a situation such as this where d log I/dH_0 for a series of bases is variable, assignment of even relative basicities to all members of the group is difficult, and evaluation of thermodynamic acidity constants may be impossible. The problem may be approached in two fundamentally different ways, which we have discussed previously.[5c] The first of these involves extrapolating the relationship between log I and H_0 down to the point where H_0 first becomes equal to log C_{H^+}, i.e. to $H_0 = 1.00$,[17] and then using the value of I so obtained to calculate pK_a. Acidity constants obtained in this way are listed in Table I, column 5. This procedure is equivalent to assigning an individual acidity function to each base, which in the limit must be correct, but it assumes also that each of these individual acidity functions is proportional to H_0, i.e. it requires plots of log I vs. H_0 to be linear. The latter seems to be approximately true for many different kinds of bases in aqueous sulfuric acid,[18] but it need not of course be universally true. Results obtained in this way, moreover, are particularly sensitive to systematic errors which affect one end of a log I vs. H_0 plot more strongly than the other, and uncertainties are apt to be especially large with very weak bases where the extrapolation is long.

Another approach to the problem of estimating the basicities of a group of substances with varying values of d log I/dH_0 uses the value of H_0 at half-protonation, $(H_0)_{I=1}$, as an index of basic strength.[5c] When d log I/dH_0 is itself unity, this measure of basic strength is of course equal to pK_a. With d log I/dH_0 variable, however, the numbers which the method generates have no thermodynamic significance; they do afford a measure of relative basicity, but may provide an order within a series which is different from that based on individually extrapolated pK_a's. Nevertheless, this method does have the virtue of not relying on long and often dubious extrapolation. Moreover, it ranks bases in an order which applies under conditions of appreciable extents of protonation and not in dilute solution where weak bases are essentially not protonated at all; this order, when different from the sequence based on individually extrapolated pK_a's, is very often the order of the greater practical significance. Results obtained by this method are also listed in Table I.

Comparison of these two measures of basicity, $(H_0)_{I=1}$ values and individually extrapolated pK_a's (Table I, columns 4 and 5), shows that these two quantities do, as anticipated, furnish rather different estimates of basic strength. The scale provided by $(H_0)_{I=1}$ appears, on the whole, to be the more sensible one as judged by the effect of substituents on basicity, i.e. it gives substituent effects more closely related to those experienced by two close structural analogs of carbazole (1): diphenylamine (2) and aniline (3). This can be
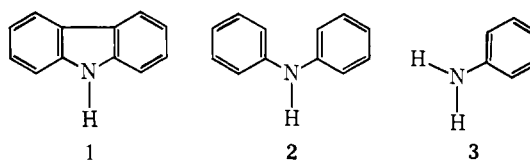
demonstrated through use of Hammett σ–ρ relationships. The anilines corresponding to the seven secondary carbazole bases listed in Table I show an excellent correlation between pK_a[19] and σ constants: r (correlation coefficient) = 0.998. The pK_a of the diphenylamine analog of 2-bromocarbazole is unfortunately not available, but those of diphenylamines corresponding to the remaining secondary carbazoles have been reported,[11b] and these also correlate very well with σ; r in this case is 0.999. The secondary carbazoles themselves give a correspondingly good correlation between $(H_0)_{I=1}$ and σ, r = 0.993 (Figure 3), but only a poor relationship between individually extrapolated pK_a's and σ, r = 0.702 (Figure 4).

In these correlations, σ_{meta} constants were used for groups in the 2 position of carbazole and σ_{para} constants for those in the 3 position. These two kinds of substituent constant mix resonance and inductive effects in different proportions: σ_{para} contains more than twice the resonance effect included in σ_{meta}.[20] The fact that this usage gave as good a correlation as it did (r = 0.993) must indicate that conjugative interactions between the nitrogen atom and substituent groups in the 2 position of carbazole, such as those shown in 4, are relatively unimportant. This, of course, is consistent with the fact that such resonance forms disrupt the aromaticity

(17) A. J. Kresge and H. J. Chen, unpublished work.
(18) K. Yates and R. A. McClelland, J. Amer. Chem. Soc., 89, 2686 (1967).
(19) A. I. Biggs, J. Chem. Soc., 2572 (1961).
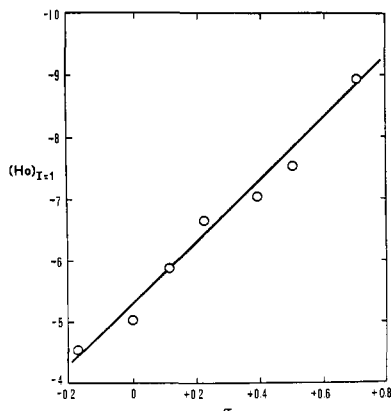(20) C. G. Swain and E. C. Lupton, Jr., J. Amer. Chem. Soc., 90, 4328 (1968).

Figure 3. The relationship between Hammett σ constants and the basicity of carbazoles as measured by half-protonation points.
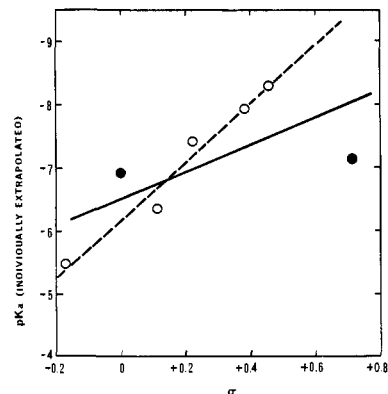

Figure 4. The relationship between Hammett σ constants and the basicity of carbazoles as measured by individually extrapolated pK_a's: solid line, correlation using all of the data; broken line, correlation omitting points (filled circles) for carbazole and 2-nitrocarbazole.

of two benzene rings, whereas conjugative effects from the 3 position affect the π system of one benzene ring only.

4
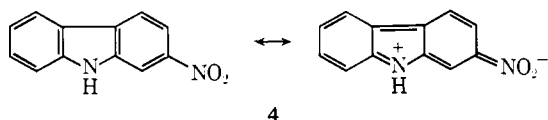
The value of ρ provided by this correlation between σ and $(H_0)_{I=1}$, 5.0 $\pm$ 0.1, is considerably greater than those for the correlations between σ and pK_a for the corresponding groups of anilines, ρ = 2.9 $\pm$ 0.1, and diphenylamines, ρ = 3.2 $\pm$ 0.1. Correcting for the fact that these $(H_0)_{I=1}$ values are not on the pK_a scale, i.e., d log $I/dH_0 \neq$ 1.00, by using the average value of d log I/dH_0, 1.10, makes the difference even greater: ρ = 5.0 $\times$ 1.10 = 5.5. The reason for this behavior is not clear, but several rationalizations may be advanced. The configuration about nitrogen in anilines and diphenylamines is pyramidal,[21] whereas in carbazole it may be more nearly planar.[22] There is also the added constraint in carbazole that both the phenyl rings and the nitrogen atom all be approximately coplanar. Both of these factors will facilitate transmission of substituent effects and thus make ρ larger.

It is significant that the correlation between individually extrapolated pK_a's and σ for carbazoles can be improved markedly by removal of the data for carbazole and 2-nitrocarbazole: r increases from 0.702 to 0.984 (Figure 4, broken line). These two substances have d log I/dH_0 values which differ markedly from those of the remaining secondary carbazoles, and, in the case of 2-nitrocarbazole, this difference can be attributed to instability of this base in the very concentrated acid solutions required for its study. 2-Nitrocarbazole, however, does not deviate at all from the correlation using $(H_0)_{I=1}$. This suggests that $(H_0)_{I=1}$ values may in general be less sensitive to effects of substrate instability than are individually extrapolated pK_a's, and that the

(21) B. M. Wepster, Recl. Trav. Chim. Pays-Bas, 72, 661 (1953); Progr. Stereochem., 2, 99 (1958).
(22) Cf. M. J. S. Dewar, "The Molecular Orbital Theory of Organic Chemistry," McGraw-Hill, New York, N. Y., 1969, p 406 ff.

former are therefore the more reliable measures of basic strength.

Although $(H_0)_{I=1}$ is the better measure of basic strength, the present values suffer from the disadvantage of not being directly comparable with acidity constants referred to dilute aqueous solution, i.e. they are not on the pK_a scale. Any attempt to put a quantity measured in concentrated acids on a scale pertaining to dilute aqueous solution must, of course, involve extrapolation. The results of such extrapolation, even when made down a supposedly self-consistent acidity function, are always dubious, for the self-consistency of any indicator acidity function which exceeds the range of applicability of one indicator cannot be verified. Nevertheless, valid pK_a's for many bases are known, and it is worthwhile, for the sake of comparison, to attempt to relate the data obtained here to other values.

It was demonstrated above that individually extrapolated values using variable d log I/dH_0 provide a poor set of carbazole pK_a's; $(H_0)_{I=1}$ values, on the other hand, do furnish a sensible measure of basicity. This substantiates our earlier inference that it is probably safer to ignore small differences in d log I/dH_0 among structurally similar bases than to extrapolate these variations over large concentration ranges. It does appear, however, that the slopes of the indicator ratio plots for the group of carbazole bases as a whole differ significantly and consistently from those of the H_0 bases, and that this occurs over a wide enough concentration range to imply that they are differently solvated. If one, therefore, requires estimates of thermodynamic pK_a's, it is probably better to allow for the difference in solvent effects by basing the extrapolation to dilute solution not on properties of individual bases but rather on parameters determined by the group as a whole, i.e., on an average value of d log I/dH_0 plus $(H_0)_{I=1}$ values calculated from the correlation with σ (Figure 3). The last column of Table I presents pK_a's determined this way. $(H_0)_{I=1}$ values interpolated from the σ–ρ correlation of Figure 3, $(H_0)_{I=1}$ = $(-5.18 \pm 0.95) - (5.01 \pm 0.26)\sigma$, were used together with d log I/dH_0 = 1.11 $\pm$ 0.04 (the average of the values for the five "normal" secondary carbazoles) to calculate values of log I at H_0 = 1.00 for each base; these were then translated into pK_a's by subtracting -1.00, the value of log C_{H^+} at H_0 = 1.00.

The two tertiary carbazoles listed in Table I cannot be treated in the same way, for these could not be expected to conform to a σ–ρ relationship constructed with secondary bases. Estimates of basic strength for these substances were therefore obtained by adopting d log $I/dH_0 = 1.4$ for tertiary carbazoles and performing extrapolations using observed values of $(H_0)_{I=1}$, recognizing that this group slope is rather high in comparison to the known differences in the slopes of primary and tertiary anilines.[15] The results are listed in the last column of Table I.[23]

It must be emphasized that even these numbers obtained by group extrapolation (Table I, last column) are subject to all of the uncertainties inherent in the acidity function method of estimating pK_a.[12,17] They are, however, the best estimates that we can make and are, we feel, considerably superior to individually extrapolated pK_a's.

All of these pK_a's are referred to the same standard state as the H_0 scale used in their calculation: dilute solution in 20% ethanol–80% water.[12] Since the medium effect on the pK_a's of a group of amine bases averages -0.2 pK unit,[24] the present numbers can be translated into constants referred to a wholly aqueous standard state by adding 0.2.

These results indicate that the nitrogen-protonated conjugate acid of carbazole has a pK_a of about -6 in dilute aqueous solution. This makes it very much less basic than its analog, diphenylamine ($pK_a = 0.78$),[11b] which is a consequence of the fact that protonation of carbazole disrupts an aromatic system. It is also possible that more significant rehybridization of the nitrogen orbitals occurs, but this is difficult to evaluate in the absence of quantitative data on bond angles.[22] The difference in basicity of 7 pK units gives 10 kcal/mol as the resonance stabilization obtained in forming an additional ring through joining two ortho positions in diphenylamine, which is the same as the relationship shown by diphenylmethane (pK_a 33) and fluorene ($pK_a = 25$).[25]

This pK_a of -6 is also appreciably less than values obtained for the carbon-protonated conjugate acids of pyrrole[5b] and indole.[6c] (Pyrrole and indole are of about the same basicity but the actual numbers obtained as "pK_a" vary from -2 to -4 depending on the method of treating the data.) This suggests that no more than ca. 1% of the conjugate acids of pyrrole and indole can be the nitrogen-protonated species, but even this is probably high, for the basic strength of benzologs generally increases with the addition of benzene units. For example, the pK_a's of cyclopentadiene, indene, and fluorene are 16, 21, and 25, respectively,[25] and anthracene is more basic than naphthalene which is in turn more basic than benzene.[26] This is consistent with some preliminary work we have done on the basicity of pyrrole and indole as judged by hydrogen bond strength;[27] these

results suggest that nitrogen-protonated pyrrole and indole would have pK_a's in the vicinity of -10.

Experimental Section

Materials. N-Methyl- and N-ethylcarbazole were prepared by treating acetone solutions of carbazole with dimethyl or diethyl sulfate. 3,6-Dichlorocarbazole was the gift of Dr. H. M. Grotta of the Battelle Memorial Institute and the other secondary carbazoles were generously supplied by Dr. P. A. S. Smith of the University of Michigan. These substances were purified by recrystallization to constant melting points which agreed with accepted literature values.

All other materials were best available commercial reagents and were used without further purification.

Indicator Measurements. Indicator measurements were made in a solvent system consisting of one volume of commercial 95% ethanol plus enough aqueous sulfuric acid to give a final volume exactly five times as great. Acid solutions were prepared by pipetting 10-ml quantities of ethanol into 50-ml volumetric flasks and then filling the flasks to the mark with sulfuric acid of the appropriate concentration. In the case of concentrated acids, considerable heat was evolved during this dilution; the acid was therefore added in small quantities while the flask was being cooled externally. In all cases, final volume adjustments were made with the flasks and their contents in thermal equilibrium with a bath operating at 25°. The precision in pipetting ethanol was determined by weighing to be $\pm 0.04\%$ (standard deviation of nine determinations).

Sample solutions for spectral measurements were prepared by adding 50-ml aliquots of approximately 10^{-3} M ethanolic solutions (95% ethanol) of indicator to 50-ml quantities of these 20% ethanolic acids while the latter were being stirred in the 25° bath. Stirring was accomplished mechanically using glass- or Teflon-coated stirring bars and a stirring motor immersed in the bath but encased in a large plastic bag. In the case of unstable substrates, a stopwatch was started when the two solutions were brought together. When mixing was complete (20–30 sec), indicator solutions were transferred to 10-cm quartz cells and their absorbances were measured against reference solutions consisting of ethanolic sulfuric acid of the same concentrations. Absorbance measurements were made with a Cary Model 11 spectrometer operating in the time-scan mode whose cell compartment was thermostated at 25 $\pm$ 0.1° by water circulating from the constant temperature bath. This procedure for mixing indicator and sulfuric acid solutions was adopted when it was discovered that mixing by manual shaking of the cuvette produced tiny air bubbles which, in the case of viscous solutions, persisted for 10–20 min; this, of course, confused the extrapolation to zero time which was necessary for unstable substrates.

All indicator solutions were prepared and measured in duplicate; each of the log I values presented in Figure 2 is therefore the

Table II. Ultraviolet Spectra of Carbazoles

| Carbazole | B | | BH+ | |
	λ_{max}, nm	$10^{-3}\epsilon_{max}$, M^{-1} cm^{-1}	λ_{max}, nm	$10^{-3}\epsilon_{max}$, M^{-1} cm^{-1}
3-Chloro	235[a]	39.8	259[b]	24.2
3-Methyl	232[c]	36.2	259[d]	22.5
2-Methoxy	234[c]	47.3	271[d]	28.1
2-Bromo	237[f]	41.3	267[e]	32.2
3,6-Dichloro	239[a]	46.0	258[e]	22.8
2-Nitro	251[h]	16.5	320[b]	16.5
2-Methoxy-9-methyl	238[c]	48.1	274[d]	30.9
9-Ethyl	236[g]	40.7	258[d]	19.4
9-Methyl	235[h]	40.6	258[b]	20.2
3-Chloro-9-methyl	239[a]	40.7	260[e]	18.1

[a] 62% H_2SO_4 + 20 vol % EtOH. [b] 96% H_2SO_4. [c] 40% H_2SO_4 + 20 vol % EtOH. [d] 81% H_2SO_4. [e] 90% H_2SO_4. [f] 52% H_2SO_4 + 20 vol % EtOH. [g] 30% H_2SO_4 + 10 vol % EtOH. [h] 95% EtOH.

(23) It is particularly interesting that N-alkylcarbazoles are uniformly less basic than their nonalkylated analogs. This is consistent with the generally observed effect of addition of an alkyl group to the site of protonation of secondary amines or carbon-protonated bases such as pyrroles, indoles, and enamines (R. L. Hinman, *Tetrahedron*, **24**, 185 (1968)).

(24) B. Gutbezahl and E. Grunwald, *J. Amer. Chem. Soc.*, **75**, 559 (1953).

(25) For the most recent data and a review of previous work see A. Streitwieser, Jr., E. Ciuffarin, and J. H. Hammons, *ibid.*, **89**, 63 (1967).

(26) H. H. Perkampus, *Advan. Phys. Org. Chem.*, **4**, 195 (1966).

(27) W. Gordy, *J. Chem. Phys.*, 7, 93 (1939); W. Gordy and W. C. Stanford, *ibid.*, 9, 204 (1941).

average of two independent determinations. Acid concentrations were measured by titrating aliquots of indicator solutions; the primary determination was equivalents of acid per kilogram of solution, and this was then converted to equivalents of acid per

liter when needed by calculations using the recently measured[12] densities of these solutions.

Principal features of the ultraviolet spectra of the carbazole bases and their conjugate acids are given in Table II.

Relative Heats of Formation of Cyclic Oxonium Ions in Sulfuric Acid[1]

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Abstract: The relative heats of formation of a series of 2-substituted 4,4-dimethyl-1,3-dioxolenium ions have been measured calorimetrically in concentrated sulfuric acid. The relative heats of formation of some tetrahydrofuryl-, -pyryl, and 1,3-dioxenium ions have also been measured. A significant Baker–Nathan order has been observed. Replacement of a methyl group by phenyl or vinyl results in a less exothermic heat of formation for the ion. The effects of substituents and ring size on the relative thermodynamic stabilities of the cations are discussed. Linear relationships between the relative heats of formation of dioxolenium ions and the chemical shift of the ring protons and solvolysis rates of *trans*-2-aroyloxycyclohexyl tosylates have been observed.

As part of our studies of the thermodynamics of formation of organic intermediates, we have been investigating the relative heats of formation of cationic intermediates formed *via* anchimeric assistance. One of the best established and most thoroughly studied members of this class of ions is the 1,3-dioxolenium ion (I). Our studies of this ion have led us to gather data on the six-membered ring analog II, and the tetrahydrofuryl (III) and -pyryl (IV) ions.
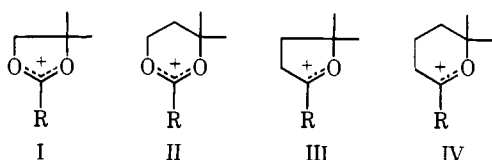
The first demonstration of a dioxolenium ion as an intermediate in a solvolysis reaction was due to Winstein[2] who observed participation by the acetoxy group in the solvolysis of *trans*-2-acetoxycyclohexyl tosylate. The early solvolytic studies of this intermediate have been reviewed.[3] More recently a variety of preparations of stable 1,3-dioxolenium salts have been reported.[4-10] Several groups have also studied the nmr spectra of these ions in strong acids. Pittman[11] has prepared a variety of 2-substituted 3,3-dimethyldioxolenium ions in strong acids. Hart and Tomalia have

studied the nmr spectra of a variety of dioxolenium ions in acidic media[8] including several dications.[12] A variety of five- and six-membered ring unsaturated monooxonium ions have been prepared by Brouwer using a procedure analogous to that of Pittman[11,13] and their nmr spectra reported.[14] Dioxolenium ions are important intermediates in carbohydrate chemistry and have been observed from acetylated carbohydrates in liquid hydrogen fluoride.[15] Pedersen has also studied dioxolenium ions in anhydrous hydrogen fluoride.[16]

A great deal of information about the spectra, formation, and chemical reactivity of cyclic five- and six-membered ring mono- and dioxonium ions is available but thermodynamic data on this series have not been available. This series of compounds seemed to provide a system in which thermodynamic stability and chemical reactivity could be compared. The effect of substituents and ring size on the thermodynamic stability is also of interest. To these ends we have measured calorimetrically the relative heats of formation of a series of ions having the general structures illustrated in I–IV.

Experimental Section

The calorimeter and its operation have been described previously.[17] The sulfuric acid was Baker Analyzed Reagent grade. Several bottles of this acid were mixed, stirred, and rebottled to ensure constant composition throughout the work. The strength of the acid was determined by measuring the heat of solution of water in the acid and determining the strength from Giauque's data.[18] The methallyl esters were prepared by treating the necessary carboxylic acid with methallyl chloride in trimethylamine using the procedure of Mills.[19] Reaction of an acid chloride with

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