Conformational Analysis. XII. The Chemical Shifts of Methylarenes[1,2]

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The chemical shifts of the methyl group of methylarenes have been determined for 29 compounds in dimethyl sulfoxide-d_6 as solvent. The compounds include all the isomeric methyl derivatives of benzene, naphthalene, anthracene, phenanthrene, 1,2-benzanthracene, and benzo[c]phenanthrene. A good correlation is obtained relating the chemical shifts of the compounds containing three or fewer rings to the summation of the inverse cubes of the distances (ΣR^{-3}) which separate the methyl group and the centers of the aromatic rings. This correlation indicates the anisotropy of the diamagnetic susceptibility of the aromatic rings as a result of circulating interatomic currents and implicitly assumes that ring currents in each hexagon of polynuclear aromatic hydrocarbons are equal to that of benzene. For those compounds containing three or fewer rings and in which there is no significant steric compression of the methyl group, the ring systems are planar and the correlation line is acceptable with a correlation coefficient, $r = 0.986$. However, chemical shift contributions as a result of nonplanarity of rings or steric compression of hydrogen decrease the correlation coefficient. In addition, compounds containing more than three rings do not correlate as well with ΣR^{-3}. A significantly better and more general correlation is obtained using previously calculated ring current intensities (I) and evaluating ΣIR^{-3}. This function correlates the data for phenyl, naphthyl, anthryl, and phenanthryl with $r = 0.997$. For those molecules whose individual ring current intensities are not known, the proper number of experimental chemical shifts permits their evaluation from the established correlation line. The ring current intensities of 1,2-benzanthracene have been calculated from the best experimental fit of four chemical shifts. The resultant correlation of all of the methyl-1,2-benzanthracenes and the other ring systems is excellent with $r = 0.995$. An extension of the ΣIR^{-3} function to nonplanar rings has been achieved for the methylbenzo[c]phenanthrenes.

The anisotropy of the diamagnetic susceptibility of aromatic compounds as a result of circulating interatomic currents constitutes one of the most dramatic contributions to proton chemical shifts of organic molecules. The differences in the field position of the proton chemical shift in benzene and ethylene have been estimated by a point dipole approximation.[4] In this approximation the π electrons in benzene are considered to move in a circular path lying in the plane of the ring and containing all carbon atoms.

$$\Delta\delta = \frac{-e^2a^2}{2mc^2R^3} \qquad (1)$$

The magnitude of the anisotropy contribution to the chemical shift of a bound proton is calculated as −1.4 ppm for a ring radius (a) of 1.25 Å. The term R is the distance from the center of the ring to the affected proton.

In polynuclear aromatic hydrocarbons the radius of each ring is approximately equal to that of benzene. Therefore, the chemical shifts of ring bound protons could be calculated by summing individual ring terms operating at the proper distance, R.[5] The relative shifts of ring bound protons within a given molecule are more reliable than the absolute chemical shifts which are predicted using a ΣR^{-3} expression. The function is useful, however, in predicting the general spectral features of a planar molecule.

An alternative model for the induced ring current involves two closed paths at equal distances above and below the plane of the aromatic ring.[6] The improvement between calculated and observed chemical shifts, however, does not compensate for the increased complexity of the derived expression. Exact agreement between calculated and observed chemical-shift differences of ethylene and benzene can be obtained by adjusting the separation of the current loops. The same procedure does not provide consistent values for benzene and the 1 and 2 positions in naphthalene.[7]

Quantum mechanical methods for calculating chemical shifts due to ring currents have been developed.[8-10] The assumption that the current flowing in each hexagon of polynuclear hydrocarbons is equal is not valid. The variance in ring current intensities (I) increases with the number of rings and is a function of molecular structure.

The determination of the chemical shifts of aromatic protons in compounds containing more than two rings is difficult because the splitting patterns are complex. In many molecules there are no known values[11] for comparison with ones calculated from ring current intensities. An experimentally convenient approach to the solution of this problem is the use of a methyl substituent as a magnetic probe. The methyl proton resonance is easily identified and experiences a positional chemical shift difference which is somewhat smaller than for ring protons,[12] but which is sufficiently different to be experimentally meaningful.

Results

The chemical shifts of the methyl protons of 29 methylarenes are listed in Table I. These values were determined at 40° at concentrations of 0.025 mol fraction solute, where possible, in dimethyl sulfoxide-d_6. The chemical shifts are reported in hertz below TMS and were determined relative to the center of the quintuplet at 153 Hz resulting from dimethyl sulfoxide-d_5 which is approximately 0.05 mol fraction in the com-

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[1] Paper X: R. J. Ouellette, K. Liptak, and G. E. Booth, *J. Org. Chem.*, **32**, 2394 (1967).

[2] This research was carried out with the support of a grant from the Petroleum Research Fund of the American Chemical Society.

[3] Taken from the Ph.D. Thesis of B. G. van L., The Ohio State University, 1968.

[4] J. A. Pople, *J. Chem. Phys.*, **24**, 1111 (1956).

[5] J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p 251.

[6] C. E. Johnson, Jr., and F. A. Bovey, *J. Chem. Phys.*, **29**, 1012 (1958).

[7] N. Jonathan, S. Gordon, and B. P. Dailey, *ibid.*, **36**, 2443 (1962).

[8] J. A. Pople, *Mol. Phys.*, **1**, 175 (1958).

[9] R. McWeeney, *ibid.*, **1**, 311 (1958).

[10] G. G. Hall and A. Hardisson, *Proc. Roy. Soc.* (London), **A268**, 328 (1962).

[11] J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. 1, Pergamon Press Ltd., London, 1965, p 142.

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TABLE I

METHYL CHEMICAL SHIFTS OF METHYLARENES

No.	Aryl group	Chemical shift, Hz^{a}	ΣR^{-3} ^{b}	ΣIR^{-3}
1	Phenyl	142.2	0.02913	0.02913
2	1-Naphthyl	161.0	0.04364	0.04770
3	2-Naphthyl	151.0	0.03514	0.03840
4	1-Anthryl	168.0	0.04847	0.05542
5	2-Anthryl	153.0	0.03724	0.04158
6	9-Anthryl	183.5	0.05815	0.06877
7	1-Phenanthryl	163.7	0.04720	
8	2-Phenanthryl	153.5 (153)^{g}	0.03760	0.04165
9	3-Phenanthryl	156.2 (156)^{h}	0.03878	0.04298
10	4-Phenanthryl	184.2 (187)^{g}	0.06118	0.06700
11	9-Phenanthryl	163.2^{c} (161)^{g}	0.04965	0.05165
12	1′-1,2-Benzanthryl	192.2	0.06945	0.07713
13	2′-1,2-Benzanthryl	158.8	0.04073	0.04353
14	3′-1,2-Benzanthryl	154.0	0.03872	0.04114
15	4′-1,2-Benzanthryl	164.2	0.04923	0.05080
16	3-1,2-Benzanthryl	163.2^{d} (163)^{g}	0.05175	0.05061
17	4-1,2-Benzanthryl	167.5^{d} (169)^{g}	0.05448	0.05635
18	5-1,2-Benzanthryl	170.6	0.04995	0.05812
19	6-1,2-Benzanthryl	155.8	0.03836	0.04310
20	7-1,2-Benzanthryl	155.0	0.03836	0.04312
21	8-1,2-Benzanthryl	175.8	0.05222	0.06011
22	9-1,2-Benzanthryl	203.2	0.07567	0.08770
23	10-1,2-Benzanthryl	185.5 (186)^{g}	0.06190	0.07272
24	1-Benzo[*c*]phenanthryl	142.6		
25	2-Benzo[*c*]phenanthryl	156.2		
26	3-Benzo[*c*]phenanthryl	154.7		
27	4-Benzo[*c*]phenanthryl	166.8		
28	5-Benzo[*c*]phenanthryl	167.8^{e}		
29	6-Benzo[*c*]phenanthryl	169.2^{f}		

[a] Downfield from TMS on 60-MHz instrument. Literature values are in parentheses. [b] Å^{-3}. [c] Doublet, $J = 0.9$ Hz. [d] Doublet, $J = 1.2$ Hz. [e] Doublet, $J = 0.8$ Hz. [f] Doublet, $J = 1.0$ Hz. [g] P. Durand, J. Parello, and N. P. Buu-Hoi, *Bull. Soc. Chim. Fr.*, 2438 (1963). [h] See ref 12.

mercial sample of solvent. There is no significant concentration dependence of the chemical shifts for the concentration range employed. Literature values in other solvents are listed in Table I in parentheses. The substituent positions of the arenes are given in Figure 1.

The compounds exhibit sharp singlet methyl proton resonances except for 9-methylphenanthrene, 3-methyl-1,2-benzanthracene, 4-methyl-1,2-benzanthracene, 5-methylbenzo[*c*]phenanthrene, and 6-methylbenzo[*c*]-phenanthrene, all of which are doublets. This phenomenon has been noted previously in similar compounds and attributed to allylic coupling due to a high degree of double-bond character adjacent to the methyl group.[13] Similar splittings of the ring protons have been examined.[14-16]

Discussion

The methyl proton chemical shifts determined in CCl_4 and CS_2 as solvents by other workers are in general agreement with our values in dimethyl sulfoxide-d_6. Apparently the highly polar solvent does not complex with the aromatic rings or, if it does, there is no significant solvent contribution to the shielding of the methyl group.

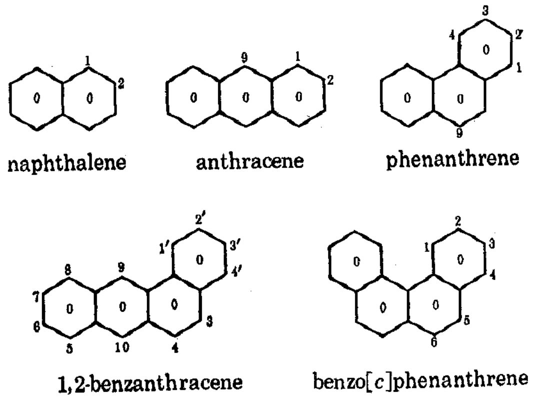

Figure 1.—Substituent positions of aromatic hydrocarbons.

The point dipole model was used to correlate the observed chemical shifts and the distance separating the methyl protons and the center of each aromatic ring. A single point at a distance 0.4 Å beyond the center of the methyl carbon nucleus on a line extension of the carbon–carbon bond was used, since the observed chemical shift is a weighted time average of the three methyl protons. All distances used in this work were determined by projections of Drieding models on paper and are estimated to be accurate to ±0.02 Å.

The reference point was chosen on the basis of a projection on the carbon–carbon bond line extension of the locus of points describing the position of the methyl protons. As shall be seen from the correlations obtained in this work there is little reason to undertake a more complex analysis involving specifically located protons in hypothetically preferred conformers. Indeed, consideration of specific conformers in compounds of symmetry different than toluene, 4-methylpyrene, or 1-methylcoronene reveals that for any decrease in the distance separating one methyl proton from a distant ring there is a corresponding increase in the distance separating the remaining methyl protons from the same ring. We feel, therefore, that the reference point chosen is proportionally representative of the methyl group regardless of conformational considerations. However, this approximation clearly will not be valid for substituents of a different symmetry.

The chemical shifts of all the methylarenes, excluding the methylbenzo[*c*]phenanthrenes, are compared with ΣR^{-3} in Figure 2. If only the compounds containing three or fewer rings (excluding 4-methylphenanthrene) are considered, the correlation line[17] is given by eq 2 with a correlation coefficient[18] $r = 0.986$. When 4-

$$\delta = 1288.8\Sigma R^{-3} + 104.4 \qquad (2)$$

methylphenanthrene and the methyl-1,2-benzanthracenes are included with the data, the correlation line is given by eq 3 with a correlation coefficient $r = 0.980$.

$$\delta = 1247.3\Sigma R^{-3} + 106.3 \qquad (3)$$

The decrease in the correlation coefficient indicates that the implicit assumption of equal ring currents in each hexagon of a polynuclear aromatic hydrocarbon is a poor one and that the assumption becomes less

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(13) E. Clar, B. A. McAndrew, and M. Zander, *Tetrahedron*, **23**, 985 (1967).

(14) K. Bartle and J. Smith, *Spectrochim. Acta*, **23A**, 1689 (1967).

(15) P. Nair and G. Gopakumar, *Tetrahedron Lett.*, 709 (1964).

(16) H. Rottenforf and S. Sternhell, *Aust. J. Chem.*, **17**, 1315 (1964).

(17) W. J. Youden, "Statistical Methods for Chemists," John Wiley & Sons, Inc., New York, N. Y., 1951, p 40.

(18) C. A. Bennett and N. L. Franklin, "Statistical Analysis in Chemistry and The Chemical Industry, John Wiley & Sons, Inc., New York, N. Y., 1954, p 37.

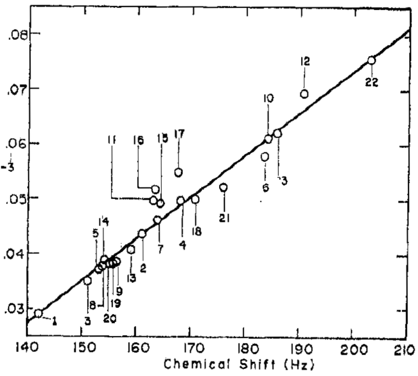

Figure 2.—Correlation of chemical shifts of methylarenes with ΣR^{-3}.

valid as the number of rings increases. In addition, the deviations of 9-methylanthracene, 9-methylphenanthrene, and 3- and 4-methyl-1,2-benzanthracene from the correlation line are substantial and further indicate that ring current intensities must be considered.

The methylbenzo[*c*]phenanthrenes are not included in the simple point dipole model since the ring system is nonplanar. 4-Methylphenanthrene is also nonplanar and the proximity of this datum point to the correlation line should be noted. However, the apparent agreement is an artifact as will be illustrated in the subsequent discussion of the ring current intensity model.

Pople[8] has calculated the current intensities in each ring of low molecular weight compounds and some multiring compounds of high molecular symmetry. Jonathan, Gordon, and Daily[7] calculated ring current intensities for unsubstituted polycyclic aromatic hydrocarbons and utilized Johnson and Bovey's[6] tables to obtain chemical shifts of ring protons. The absolute agreement between experimental and calculated chemical shifts is not high. However, the order of chemical shifts within respective compounds is somewhat better.

In our treatment of methylarenes the Johnson and Bovey tables were not used and no attempt was made to calculate absolute chemical shifts. Only the ΣIR^{-3} term, where I is the ring current intensity, was evaluated for each compound and compared with the experimental chemical shift as shown in Figure 3. The ring current intensities reported by Jonathan for one- to three-ring cyclic compounds were used. The ΣIR^{-3} terms are listed in Table I. The relative ring current intensities are given in Figure 4 along with those calculated in this work for the planar 1,2-benzanthracene and the nonplanar benzo[*c*]phenanthrene.

The correlation line for the compounds containing three or fewer rings, excluding 4-methylphenanthrene, is given by eq 4 with $r = 0.997$. Therefore, ΣIR^{-3} provides a better fit of the data than ΣR^{-3}. It is

$$\delta = 1038.5\Sigma IR^{-3} + 110.9 \tag{4}$$

significant that the data points for 9-methylanthracene and 9-methylphenanthrene are moved to the correlation line for ΣIR^{-3}. The deviations of these compounds from the ΣR^{-3} correlation line are in opposite directions. These directional deviations are a reflection of the major contribution to the chemical shift for the ring to which the methyl group is directly attached. The ring current intensities of the center rings of phenanthrene and anthracene are less than and greater than benzene, respectively.

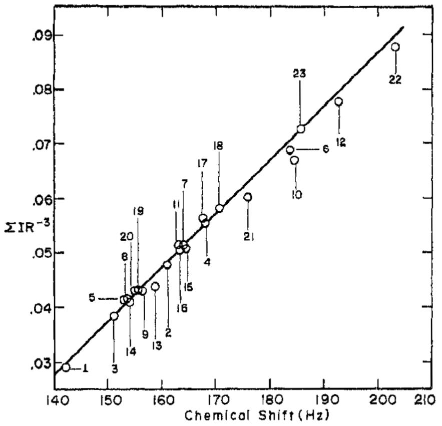

Figure 3.—Correlation of chemical shifts of methylarenes with ΣIR^{-3}.

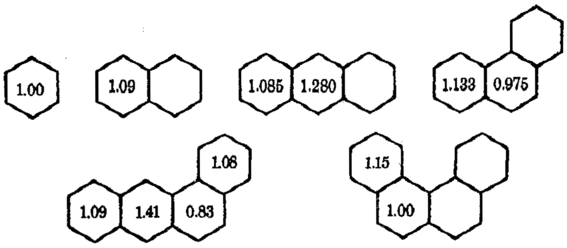

Figure 4.—Relative ring current intensities of aromatic compounds.

4-Methylphenanthrene is the only compound of those containing three or fewer rings which deviates substantially from the ΣIR^{-3} correlation line. The aromatic rings are nonplanar and the ring current intensities would not be expected to be valid. In addition, there may be a chemical-shift contribution due to steric compression of one or two of the methyl protons. The combination of both factors operating in a single compound, without suitable models for either contribution, makes a discussion of the direction of the deviation of little value. Similar deshielding effects upon the 5 proton by the 4-methyl group have been previously noted.[19]

The intercept of the correlation line using ΣIR^{-3} (110.9 Hz) is close to the chemical shift of the methyl protons in propene which resonate at 103 Hz.[20] Propene is the most structurally similar molecule in which there are no aromatic ring anisotropic contributions to the chemical shift of the methyl group. The correlation line appears to represent more than a fortuitous empirical relationship.

Ring current intensities of pyrene, triphenylene, perylene, and coronene have been calculated,[11] enabling predictions of the chemical shifts of the related methylarenes. The calculated chemical shift of methylcoronene on the basis of reported ring current intensities of 1.038 for the center ring and 1.460 for the outer ring is 204 Hz. This value compares favorably with the reported value, 195 Hz, which was obtained at an unspecified concentration in chloroform.[13] The agreement between calculated and experimental chem-

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[19] R. Martin, N. Defay, F. Geerts-Evrard, and H. Figeys, *Bull. Soc. Chim. Belges*, **73**, 199 (1964).

[20] A. A. Bothner-By and C. Naar-Colin, *J. Amer. Chem. Soc.*, **83**, 231 (1961).

ical shifts is satisfying and actually may be closer. Chloroform causes upfield shifts of approximately 5 Hz relative to carbon tetrachloride for simple compounds,[21] and the shift may be even larger for methylcoronene.

The observed correlation between the chemical shift and ΣIR^{-3} is quite remarkable and is substantially better than previously reported calculated ring proton correlations. Many calculated ring proton positions cannot be compared with experimental values as these are unavailable. Benzo[*c*]phenanthrene and 1,2-benzanthracene are examples of the numerous and complex positioning and coupling of aromatic ring protons for which a complete analysis has not been achieved.[11] The absence of reported ring current intensities for the 1,2-benzanthracene nucleus provides an opportunity to calculate them from the experimental chemical shifts and the known correlation line established for lower molecular weight substances. Excluding the 9- and 1′-methyl compounds, which would be expected to exhibit anomalous behavior due to the presence of a sterically hindered group which should force the rings to be nonplanar, the remaining isomers provide sufficient data with which to determine the necessary four-ring current terms.

In order to calculate accurately the ring current intensities, it is necessary to select compounds where the chemical-shift differences are significant and where the major contribution to the methyl proton chemical shift is from different rings. Accordingly, the 3-, 4-, 10- and 3′-methyl-1,2-benzanthracenes were chosen. Equations were set up relating the measured R terms to the ΣIR^{-3} term evaluated from the experimental chemical shift and the correlation line. The calculated ring current intensity terms are given in Figure 4. These values are intuitively acceptable and consistent with those directly calculated for other compounds.

The ΣIR^{-3} functions are listed in Table I. The correlation line including the sterically hindered 4-methylphenanthrene and 1′- and 9-methylbenzanthracene is given by eq 5 with $r = 0.996$. The inclusion of the 1,2-benzanthracenes with those compounds containing fewer rings decreases the correlation coefficient very slightly. This small change is indicative of the degree of fit predicted by the calculated ring current intensities for 1,2-benzanthracene.

$$\delta = 1049.4\Sigma IR^{-3} + 110.6 \qquad (5)$$

The 1′- and 9-methyl-1,2-benzanthracene points deviate from the correlation line in the same direction as the structurally similar 4-methylphenanthrene. Part of the decrease in the correlation coefficient when the 1,2-benzanthracenes are included with the other compounds is due to the deviations of the two sterically hindered isomers. Neglecting all three 4-phenanthryl type molecules the correlation line is given by eq 6 with $r = 0.997$.

$$\delta = 1002.4\Sigma IR^{-3} + 112.8 \qquad (6)$$

Benzo[*c*]phenanthrene is known to be nonplanar in the solid state.[22] Assignments of ring current intensities utilizing the observed methyl resonance for the six isomeric methylbenzo[*c*]phenanthrenes constitutes a greater challenge than the planar methyl-1,2-benzanthracenes. In order to achieve a consistent fit of the data it is necessary to utilize a $\cos^2 \theta$ term where θ is the angle between a line drawn from the center of the ring to the affected proton and the plane of the ring. The expression chosen to relate the chemical shift to θ, I, and R is given by eq 7. The correlation line for the planar molecules incorporates a $-2/3$ in the slope. Therefore, the ΣIR^{-3} terms for the nonplanar benzo[*c*]phenanthrene must be multiplied by $(3 \cos^2 \theta - 1)/2$ in order to evaluate the ring current intensities from the experimental chemical shifts.

$$\delta = {}^1/_3(1 - 3\cos^2\theta)(1002.4)\Sigma IR^{-3} + 112.8 \qquad (7)$$

All of the distances and angles were calculated using a molecular representation of the aromatic system constructed on the basis of X-ray data.[22] For the calculation of the unknown ring current intensities the experimental chemical shifts of the 4- and 5-methyl derivatives were employed. The calculated ring current intensities and the expected chemical shifts for the 2-, 3-, 4-, 5- and 6-methyl derivative compared with experimental values are shown in Table II. The average deviation is 1 Hz if the 1-methyl compound is excluded.

TABLE II

CHEMICAL SHIFTS OF METHYLBENZO[*c*]PHENANTHRENES

Ring position	Chemical shift, Hz Calcd	 Exptl
1	165.0	142.6
2	155.7	156.2
3	156.5	154.7
4	166.7	166.8
5	168.0	167.8
6	167.5	169.2

The relatively high field chemical shift of the 1-methyl compound deserves comment. If the molecule were planar the chemical shift would be approximately 250 Hz as a result of the cumulative deshielding contribution of the four proximate rings. The twisting of the aromatic rings, however, increases the distance separating them and the methyl group and the angular contribution of $(3 \cos^2 \theta - 1)/2$ leads to a further diminuation of the deshielding contribution of the rings. The degree of twisting in benzo[*c*]phenanthrene is such as to lead to a net change from a deshielding to a shielding effect of the other terminal ring acting upon the 1-methyl substituent. Our calculation leads to a chemical shift for 1-methylbenzo[*c*]phenanthrene which is still 22 Hz at lower field than the experimental value. This calculation is based on molecular dimensions for benzo[*c*]phenanthrene whereas the methyl group should lead to further ring distortions. Therefore the change from 250 Hz calculated for a planar molecule to 165 Hz for a nonplanar molecule suggests that further distortions of relatively small magnitude would be sufficient to bring the calculated chemical shift to 143 Hz.

Registry No.—**1**, 108-88-3; **2**, 90-12-0; **3**, 91-57-6; **4**, 610-48-0; **5**, 613-12-7; **6**, 779-02-2; **7**, 832-69-9; **8**, 2531-84-2; **9**, 832-71-3; **10**, 832-64-4; **11**, 883-20-5;

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[21] Reference 11, Vol. 2, p 846.

[22] F. H. Herbstein and G. M. J. Schmidt, *J. Chem. Soc.*, 3302 (1954).

12, 2498-77-3; **13**, 2498-76-2; **14**, 2498-75-1; **15**, 316-49-4; **16**, 2319-96-2; **17**, 316-14-3; **18**, 2381-31-9; **19**, 2381-16-0; **20**, 2381-15-9; **21**, 6111-78-0; **22**, 2422-79-9; **23**, 2541-69-7; **24**, 4076-39-5; **25**, 2606-85-1; **26**, 2381-19-3; **27**, 4076-40-8; **28**, 652-04-0; **29**, 2381-34-2.

Acknowledgment.—The authors are grateful to Professor M. S. Newman of this department for his contribution of the isomeric methyl-1,2-benzanthracenes and methylbenzo[*c*]phenanthrenes used in this study.

The Equilibrium between N-Benzyl-N-methylpiperidinium Ion and N-Benzylpyridinium Ion. The Carbon Basicity of Nitrogen[1]

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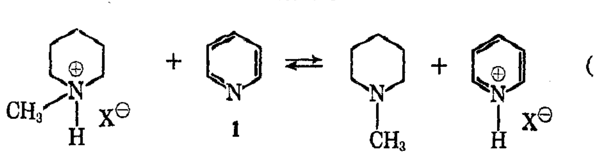
The equilibrium constants for the reaction between N-benzyl-N-methylpiperidinium halides and pyridine to form N-benzylpyridinium salts and N-methylpiperidine (eq 2) have been measured in organic solvents, principally benzyl alcohol and nitrobenzene, at temperatures from 140 to 195°. The temperature coefficient of the equilibrium has been determined from the linear plot of log K *vs.* $1/T$, and the equilibrium constant at 25° in benzyl alcohol has been obtained. Similar measurements have been made on the equilibrium between N,N-dimethylpiperidinium bromide and pyridine. Measurements of equilibrium concentrations have been made by two independent methods—electrometric titration of N-methylpiperidine in nonaqueous solution with perchloric acid in dioxane and comparisons of nmr absorptions of the product mixture. The relative pK_a values for N-methylpiperidine and pyridine in benzyl alcohol at 25° have been determined; combination of these data and the equilibrium constants shows that, under the conditions specified, N-methylpiperidine is a stronger base than pyridine toward the proton by a factor of 2.5×10^6. The ratio of carbon basicities of N-methylpiperidine compared with pyridine is much smaller, however; for the N-benzyl-N-methylpiperidinium reaction, the corresponding ratio is 1.7×10^2, and, for the N,N-dimethylpiperidinium case, the ratio is 1.4×10^3.

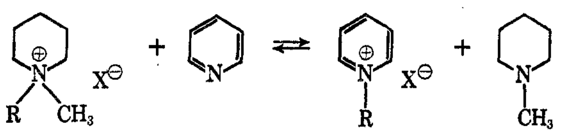
It is well known that pyridine (1) is a much weaker base than a saturated amine, such as N-methylpiperidine (2), the dissociation constants differing by a factor of about 10^5 in water at 25°;[2] in other words, the equilibrium constant for reaction 1 is about 10^{-5}. We wished to know whether the equilibrium constant would be of the same order of magnitude for reaction 2, in which a carbon group instead of a proton is transferred. In other terminology, we wished to determine the carbon basicity[3] of the nitrogen in the aromatic heterocycle compared to that of the nitrogen in the saturated heterocycle. This is an *equilibrium* and not a *rate* measurement.



(1)

1 **2**

A_1 B_1 C_1 D_1



3a, R = $CH_2C_6H_5$; X = Cl
b, R = CH_3; X = Br

4a, R = $CH_2C_6H_5$; X = Cl
b, R = $CH_2C_6H_5$; X = Br

5

(2)

It is well known that quaternary ammonium salts are attacked by nucleophiles, with transfer of a carbon group from nitrogen to the nucleophile.[4] However, there appears to be little equilibrium data, as opposed to kinetic data, dealing with reactions like 2. Some qualitative studies of equilibrations of N-benzyl-N-methyl quaternary iodides, diastereoisomeric around nitrogen, have been reported; attempts to equilibrate N,N-dialkyl quaternary ammonium salts from saturated nitrogen heterocycles were unsuccessful.[5] With analogous compounds, House[6] found that lithium iodide in decalol required a 200° temperature to form methyl iodide from N,N-dimethyl quaternary salts.

The fundamental studies of Brown on the reactions of pyridines with protons and Lewis acids[7] do not include information about equilibria of the type of eq 2. Kosower[8] has determined equilibrium constants for the formation of charge-transfer complexes from pyridinium iodides.

The present paper reports determination of the equilibrium constants (by two independent analytical methods) for reaction 2 (R = $CH_2C_6H_5$ and R = CH_3) in organic solvents at 140–195°; the change of the equilibrium with temperature has been determined,

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[1] Aided by Grant 2252-C from the Petroleum Research Fund of the American Chemical Society. Grateful acknowledgment is expressed to the donors of this fund.

[2] D. D. Perrin ["Dissociation Constants of Organic Bases in Aqueous Solution," Butterworth and Co. Ltd., London, 1965, pp 138, 141] gives pK_a of pyridine as 5.2 and of N-methylpiperidine as 10.1.

[3] (a) J. F. Bunnett, C. F. Hauser, and K. V. Nahabedian, *Proc. Chem. Soc.*, 305 (1961); (b) A. J. Parker, *ibid.*, 371 (1961); (c) J. Hine and R. D. Weimar, Jr., *J. Amer. Chem. Soc.*, **87**, 3387 (1965); (d) W. P. Jencks, *Progr. Phys. Org. Chem.*, **3**, 104 (1964); (e) J. F. Bunnett, *Ann. Rev. Phys. Chem.*, **14**, 271 (1963).

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[5] J. McKenna, J. M. McKenna, and J. White, *ibid.*, 1733 (1965).

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[7] For leading references, see H. C. Brown and B. Kanner, *J. Amer. Chem. Soc.*, **75**, 3865 (1953); **88**, 986 (1966); H. C. Brown, D. Gintis, and L. Domash, *ibid.*, **78**, 5387 (1956); H. C. Brown, D. H. McDaniel, and O. Häfliger in "Determination of Organic Structures by Physical Methods," Vol. I, E. A. Braude and F. C. Nachod, Ed., Academic Press, New York, N. Y., 1955, pp 597 ff, 634 ff.

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