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Cumulative Influence of Dimethylamino Groups on the π -System Properties of Aromatic Hydrocarbons¹

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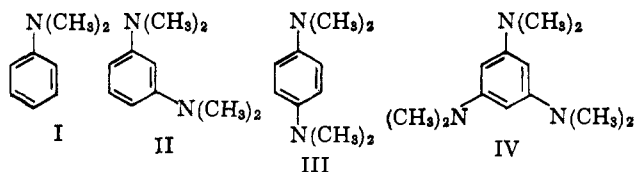
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Charge-transfer absorption maxima, polarographic oxidation potentials, and proton magnetic resonance spectral data are reported for *N,N*-dimethylamino- and methoxy-substituted *N,N*-dimethylanilines. The parameters $\alpha_N = \alpha_C + \beta_{CC}$, $\alpha_O = \alpha_C + 2\beta_{CC}$, and $\beta_{CO} = \beta_{CN} = 0.8\beta_{CC}$ used in the Hückel molecular orbital approximation appear capable of describing with reasonable accuracy those properties which are primarily characteristic of either electronic energy levels or electron distributions in sterically unhindered dimethylamino and methoxy aromatics. A moderate reduction in the hindered bond resonance integral can qualitatively account for the properties of sterically hindered dimethylamino-substituted aromatics.

Introduction

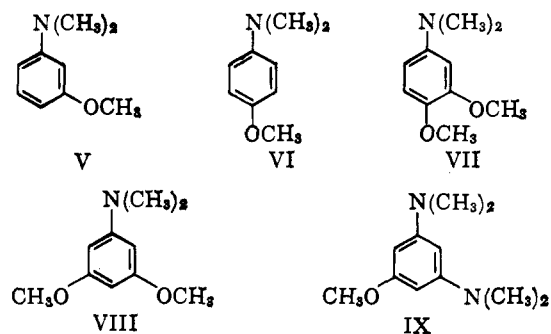
In previous work,²⁻⁶ we have shown that sterically unhindered multiple methoxy substitution on a benzene nucleus leads to π -electron properties which can be predicted with considerable accuracy by Hückel molecular orbital calculations. These properties include the polarographic half-wave oxidation potentials,² the charge-transfer spectra with various acceptors,^{3,4} aspects of the ultraviolet spectrum⁴ and the n.m.r. spectrum,⁵ and the e.s.r. spectrum of the derived cation radicals.² The correlation of these physical properties with Hückel molecular orbital calculations is observed even though the nonrigidity of the substituent removes the σ - π orthogonality condition and thus removes the justification for the usual neglect of the electrons in the σ -skeleton when examining delocalized electron systems.⁶

To determine if such simple molecular orbital relationships could be extended to other substituents on an aromatic ring with continued neglect of the σ -bonds, we considered the dimethylamino-substituted benzenes. This series of compounds is more limiting than the methoxy series, since the dimethylamino group has a larger steric requirement for coplanarity with the aromatic nucleus. For this reason, only four compounds (I-IV) could be expected to fit a simple molecular orbital scheme without resorting to variable resonance integrals. One of these compounds, *s*-tris(*N,N*-dimethylamino)benzene (IV), is presently unknown.

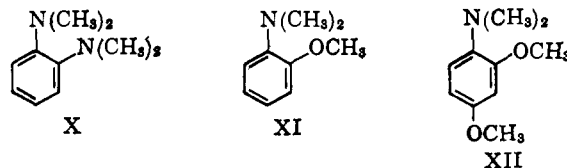


It was also of interest to see if heteroatom parameters within the Hückel framework could be selected for two types of substituents which would reflect the physical

properties of molecules containing both substituents. For this purpose five sterically unhindered benzene derivatives containing both dimethylamino and methoxy groups (V-IX) could also be considered. Two of these compounds, *N,N*-dimethyl-3,5-dimethoxy-



aniline (VIII) and 5-methoxy-*N,N,N',N'*-tetramethyl-*m*-phenylenediamine (IX), are not in the literature. Of the above nine compounds, seven (I-III and V-VIII) were obtained or prepared in this investigation (*cf.* Experimental). Also examined were three sterically hindered *ortho*-substituted *N,N*-dimethylanilines (X-XII). Although one can treat this type of steric hindrance in simple molecular orbital terms by reducing the value of the resonance integral for the bond from the ring to the hindered exocyclic heteroatom, introduction of additional empirical parameters reduces the value of the method. We thus treated the data for these last three compounds independently of the first seven.



Results

Charge-Transfer Complexes.—The positions of the first charge-transfer maxima of the *N,N*-dimethylanilines studied with the π -electron acceptor, *p*-chloranil, are reported in Table I. Charge-transfer maxima were also observed when tetracyanoethylene or 2,3-dichloro-5,6-dicyano-*p*-benzoquinone were employed as the acceptor component, but complex instability (*cf.* Discussion) hampered effective use of these systems.

(1) Cumulative Influence of Substituents on the π -Electron Properties of Aromatic Systems. VIII. Part VII, ref. 2.

(2) A. Zweig, W. G. Hodgson, and W. H. Jura, *J. Am. Chem. Soc.*, **86**, 4124 (1964).

(3) A. Zweig, *J. Phys. Chem.*, **67**, 506 (1963).

(4) A. Zweig, J. E. Lehnsen, and M. A. Murray, *J. Am. Chem. Soc.*, **85**, 3933 (1963).

(5) A. Zweig, J. E. Lehnsen, J. E. Lancaster, and M. T. Neglia, *ibid.*, **85**, 3940 (1963).

(6) A Hückel m.o. scheme which includes all interactions including those of the σ -electrons has recently been proposed: R. Hoffmann, *J. Chem. Phys.*, **39**, 1937 (1963).

TABLE I
CHARGE-TRANSFER MAXIMA WITH *p*-CHLORANIL AND
POLAROGRAPHIC OXIDATION POTENTIALS OF SOME SUBSTITUTED
N,N-DIMETHYLANILINES

Compound	$\epsilon_{1/2}$ (CH ₃ CN) vs. Ag ⁺ /0.01 M Ag ⁺	$\bar{\nu} \times 10^3$ cm. ⁻¹ (CH ₂ Cl ₂)
N,N-Dimethylaniline (I)	+0.53	15.3
N,N,N',N'-Tetramethyl- <i>m</i> -phenylenediamine (II)	+ .32	16.4
N,N,N',N'-Tetramethyl- <i>p</i> -phenylenediamine (III)	- .10	10.5
N,N-Dimethyl- <i>m</i> -anisidine (V)	+ .49	14.8
N,N-Dimethyl- <i>p</i> -anisidine (VI)	+ .33	13.7
3,4-Dimethoxy-N,N-dimethylaniline (VII)	+ .20	12.9
3,5-Dimethoxy-N,N-dimethylaniline (VIII)	+ .50	14.7
N,N,N',N'-Tetramethyl- <i>o</i> -phenylenediamine (X)	+ .28	12.8
N,N-Dimethyl- <i>o</i> -anisidine (XI)	+ .48	15.5
2,4-Dimethoxy-N,N-dimethylaniline (XII)	+ .27	14.8

Polarographic Oxidation Potentials.—Also described in Table I are the polarographic half-wave oxidation potentials of this series of compounds obtained in acetonitrile at a rotating platinum electrode. These compounds all gave well-defined first oxidation waves. The diffusion currents for the first wave were of the order of 18–20 μ a./mmole, and as oxidation of one of these compounds, N,N,N',N'-tetramethyl-*p*-phenylenediamine, is known to result first in a one-electron oxidation product (Wurster's Blue), it is probable that the first waves in all instances in this series are those of one-electron oxidations.

Nuclear Magnetic Resonance Spectra.—In Table II are reported the proton chemical shifts, in p.p.m. rela-

TABLE II
PROTON CHEMICAL SHIFTS FOR SOME SUBSTITUTED
N,N-DIMETHYLANILINES

Compound	Ring position	Chemical shifts (τ -units)		
		Aromatic protons	O-CH ₃	N-CH ₃
N,N-Dimethylaniline (I)	2,6	3.42 ^a		7.14
	3,5	2.91 ^a		
	4	3.42 ^a		
N,N,N',N'-Tetramethyl- <i>m</i> -phenylenediamine (II)	2	4.06		7.13
	4,6	3.99		
	5	3.10		
N,N,N',N'-Tetramethyl- <i>p</i> -phenylenediamine (III)	2,3,5,6	3.39		7.23
N,N-Dimethyl- <i>m</i> -anisidine (V)	2	3.90		7.11
	4,6	3.83 ^b	6.28	
	5	3.03		
N,N-Dimethyl- <i>p</i> -anisidine (VI)	2,3,5,6	3.36 ^b	6.32	
3,4-Dimethoxy-N,N-dimethylaniline (VII)	2	3.75	6.31	7.18
	5	3.35	6.23	
	6	3.90		
3,5-Dimethoxy-N,N-dimethylaniline (VIII)	2,4,6	4.26 ^b	6.31	7.14
N,N,N',N'-Tetramethyl- <i>o</i> -phenylenediamine (X)	3,4,5,6	3.23 ^b		7.24
N,N-Dimethyl- <i>o</i> -anisidine (XI)	3,4,5,6	3.23 ^b	6.20	7.28
2,4-Dimethoxy-N,N-dimethylaniline (XII)	3	3.68	6.32	7.37
	5	3.76	6.22	
	6	3.28		

^a Accuracy not better than ± 0.05 p.p.m. ^b No difference in chemical shifts for these protons could be detected, although they are not chemically equivalent.

tive to tetramethylsilane (τ -units), of the dimethylanilines studied in this investigation. The compounds were measured as 5 *M* solutions in carbon tetrachloride. The method of measuring was such (*cf.* Experimental) that the error in the assignment of the shifts is believed to be ± 0.01 p.p.m.

Experimental⁷

Materials. N,N-Dimethylaniline.—Commercial (Eastman Kodak Co.) material was distilled before use.

N,N,N',N'-Tetramethyl-*o*-phenylenediamine and N,N,N',N'-tetramethyl-*m*-phenylenediamine were prepared by methylation of the corresponding phenylenediamine according to a literature procedure.⁸ The tetramethylated *ortho* isomer was distilled at 60–63° (1 mm.) and did not discolor when stored in a stoppered vial. The tetramethylated *meta* isomer was distilled at 65–70° (1 mm.) and rapidly discolored soon after exposure to air.

N,N,N',N'-Tetramethyl-*p*-phenylenediamine was liberated from its dihydrochloride (Eastman Kodak Co.) by aqueous sodium hydroxide, extracted into ether which was then dried over sodium sulfate and concentrated. Distillation *in vacuo* gave white solid, m.p. 43–46°.

N,N-Dimethyl-*o*-anisidine, N,N-dimethyl-*m*-anisidine, and N,N-dimethyl-*p*-anisidine were prepared from the corresponding methoxyaniline (Eastman Kodak Co.) and trimethyl phosphate (Aldrich Chemical Co.) by a published procedure.⁹ The yields of these three tertiary amines obtained by this method were 40–50%. The physical constants (*ortho* isomer, b.p. 55–57° (0.6 mm.); *meta* isomer, b.p. 75° (0.75 mm.); *para* isomer, m.p. 45–47°), were in good agreement with literature values.⁹

N,N-Dimethyl-2,4-dimethoxyaniline, a new compound, was prepared from 10.0 g. (0.055 mole) of 2,4-dimethoxyaniline (Aldrich Chemical Co.) and a slight excess of trimethyl phosphate.⁹ A fraction of the distillate, 5.6 g. (48%), was collected at 105–106° and 2 mm.

Anal. Calcd. for C₁₀H₁₂NO₂: C, 66.27; H, 8.34; N, 7.73. Found: C, 66.66; H, 8.22; N, 7.95.

N,N-Dimethyl-3,4-dimethoxyaniline.—3,4-Dimethoxynitrobenzene (Aldrich) was reduced with sodium sulfide to give 3,4-dimethoxyaniline. Reaction of the latter with an equimolar amount of trimethyl phosphate gave N,N-dimethyl-3,4-dimethoxyaniline, m.p. 43–44°, reported¹⁰ 41.5°.

N,N-Dimethyl-3,5-dimethoxyaniline, a new compound, was prepared by methylation of 25.0 g. (0.163 mole) of 3,5-dimethoxyaniline (Aldrich Chemical Co.) with 22.8 g. (0.163 mole) of trimethyl phosphate in the same manner used to prepare N,N-dimethyl-3,4-dimethoxyaniline.¹⁰ The product weighed 17.2 g. (58%), m.p. 73–74° (ethanol).

Anal. Calcd. for C₁₀H₁₂NO₂: C, 66.27; H, 8.34; N, 7.73. Found: C, 66.34; H, 8.50; N, 7.75.

Measurements. Charge-transfer maxima were obtained by mixing concentrated methylene chloride (spectral grade) solutions of the substituted dimethylaminobenzenes and the various acceptors in equimolar proportions, then diluting if necessary. All spectral measurements were made on a Cary 14 spectrophotometer at 22°. Since only charge-transfer maxima were relevant to this investigation, no attempt was made to measure equilibria and extinction coefficients for the complexes.

Polarographic Oxidation Potentials.—The data were obtained at room temperature on a Leeds and Northrup Electrochemograph, Type E. Oxidations in anhydrous (0.02% H₂O) acetonitrile were carried out at a rotating platinum electrode with 0.1 *M* tetra-*n*-propylammonium perchlorate as supporting electrolyte. The electrochemical cell used to carry out controlled potential electrolyses in the e.s.r. cavity was essentially the same as that described in the literature.^{11,12}

Nuclear Magnetic Resonance Spectra.—The proton magnetic resonance spectra were obtained on a standard Varian Model

(7) All m.p.'s are uncorrected. The purity of liquid products was established by v.p.c. For spectral studies detectable impurities were removed by preparative v.p.c. We wish to thank Dr. R. Feinland and Mr. E. S. Everett of these laboratories for conducting many of these purifications.

(8) S. F. Torf and N. V. Khromov-Borisov, *Zh. Obshch. Khim.*, **30**, 1798 (1960).

(9) D. G. Thomas, J. H. Billman, and C. E. Davis, *J. Am. Chem. Soc.*, **68**, 895 (1946).

(10) H. P. Crocker and B. Jones, *J. Chem. Soc.*, 1808 (1959).

(11) D. H. Geski and A. H. Maki, *J. Am. Chem. Soc.*, **82**, 2671 (1960).

(12) M. T. Melchoir and A. H. Maki, *J. Chem. Phys.*, **34**, 471 (1961).

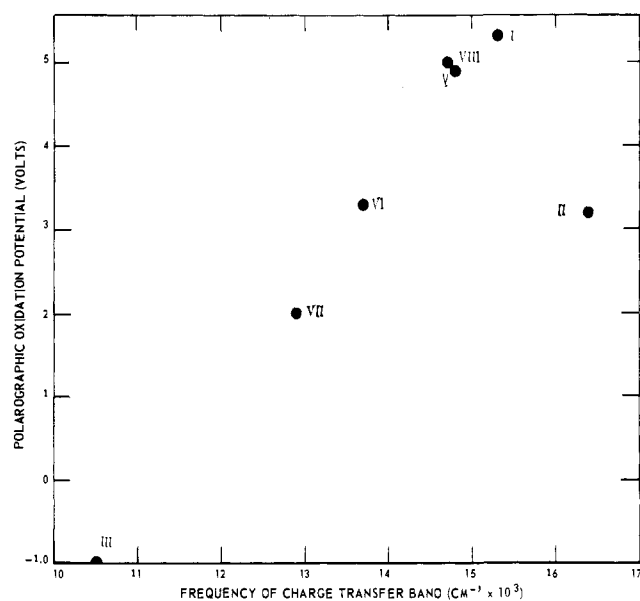


Fig. 1.—Polarographic oxidation potential (vs. $\text{Ag}^0/0.01 \text{ M Ag}^+$) in acetonitrile vs. frequency of absorption maximum with *p*-chloranil in methylene chloride for some *N,N*-dimethylanilines.

DP60 spectrophotometer at 56.4 Mc./sec. The compounds were measured at a concentration of 5 moles/l. in carbon tetrachloride containing a small amount of tetramethylsilane as an internal standard.

The chemical shifts relative to TMS were measured by the method of audiosideband modulation using a Hewlett-Packard frequency counter. Actual oscilloscope observation of a zero beat from the sideband peak and the peak being measured was used when feasible. For the complex aromatic patterns, interpolations using several sweeps were made with the sideband position set just above and below the pattern. The chemical shifts are thus believed to be accurate to better than 0.01 p.p.m. The aromatic coupling patterns, where reported, were evaluated by standard treatment. The assignments were made on the basis of the known values of *ortho*, *meta*, and *para* proton coupling constants in aromatic molecules.¹³

Molecular orbital calculations were made on a Burroughs Model 205 computer using programs especially written for this machine.

Discussion

Charge-Transfer Complexes.—The positions of the longest wave length charge-transfer maxima of a series of similar π -electron donor molecules with a single acceptor is, to a first approximation, a measurement of the relative ionization potentials of the members of the series.^{3,5} As did the methoxybenzenes,^{3,4} the substituted *N,N*-dimethylanilines used in this investigation gave deeply colored solutions with 2,3-dichloro-5,6-dicyano-*p*-benzoquinone, tetracyanoethylene, and *p*-chloranil in methylene chloride solution. The mixtures with 2,3-dichloro-5,6-dicyano-*p*-benzoquinone all showed several new maxima many of which varied considerably with time. It soon became evident in most cases being examined that chemical reaction was occurring.^{14,15} The ultraviolet-visible spectrum of these substituted *N,N*-dimethylanilines in methylene chloride solution with tetracyanoethylene also proved to be quite complex. It is known^{16,17}

(13) 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.

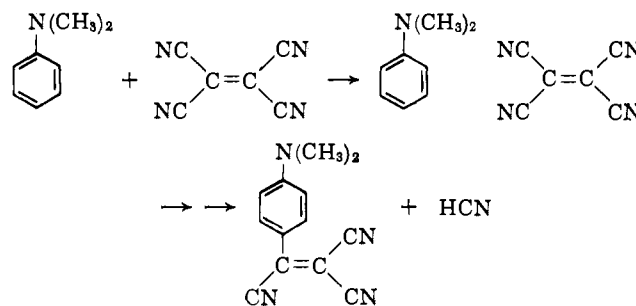
(14) R. Foster and T. J. Thomson, *Trans. Faraday Soc.*, **58**, 860 (1962).

(15) W. Brachmann, *Rec. trav. chim.*, **68**, 147 (1949), pointed out that reversible formation of a resonance complex, by reducing the activation barrier, may be a preliminary step in an irreversible chemical reaction.

(16) B. C. McKusick, R. E. Heckert, T. L. Cairns, D. D. Coffman, and H. F. Mower, *J. Am. Chem. Soc.*, **80**, 2806 (1958).

(17) Z. Rappoport, *J. Chem. Soc.*, 4498 (1963).

that although a transitory colored species is observed when *N,N*-dimethylaniline and tetracyanoethylene are mixed in an inert solvent, subsequent reaction soon occurs which results in the elimination of HCN and the formation of the highly colored *N,N*-dimethyl-4-tricyanovinylaniline. Thus the visible and near-in-



frared absorption bands which can be observed in solutions of substituted *N,N*-dimethylanilines (especially those with an unsubstituted position *para* to a dimethylamino group) and tetracyanoethylene could be due to chemical reaction products rather than charge-transfer complexes. The formation of ion radicals in solutions of very strong electron donors and acceptors is another cause of strong absorption in the visible and near-infrared regions.^{18,19} Both ion radicals and chemical reactions have been reported in the study of charge transfer in aromatic amines.¹⁸ The considerable complexity of the resulting spectra and the ensuing difficulty in assigning the charge-transfer maxima in such cases limits the usefulness of this spectroscopic technique as a facile method of obtaining relative values for molecular ionization potentials.

Despite these limitations, *p*-chloranil was found to be a useful acceptor for study of charge transfer from these substituted *N,N*-dimethylanilines. Most of the compounds examined with *p*-chloranil in methylene chloride gave ultraviolet-visible absorption spectra with reasonably stable, typically broad, featureless absorption maxima characteristic of charge-transfer complexes. Although *p*-chloranil is reported²⁰ to react rapidly with *N,N*-dimethylaniline in acetonitrile to give the *p*-chloranil semiquinone salt of crystal violet, in methylene chloride as in carbon tetrachloride²¹ ionization does not occur. Some of the substituted *N,N*-dimethylanilines, in particular *N,N,N',N'*-tetramethyl-*m*-phenylenediamine (II) and 3,5-dimethoxy-*N,N*-dimethylaniline (VIII), were more reactive. In order to obtain the charge-transfer maxima for these compounds with *p*-chloranil, low temperature and a rapid scan of the spectrum immediately after mixing of the donor and acceptor was required. Even so, the maximum observed for the *N,N,N',N'*-tetramethyl-*m*-phenylenediamine-*p*-chloranil mixture was probably not that of the complex (*cf.* Fig. 1).

Polarographic Oxidation Potentials.—Series of similar compounds where solvation effects may be expected to be slight give reversible electrochemical oxidation and reduction potentials which correlate well with

(18) R. Foster and T. J. Thomson, *Trans. Faraday Soc.*, **59**, 1059 (1963); P. G. Farrell and J. Newton, *Tetrahedron Letters*, 189 (1964).

(19) D. Bilj, H. Kainer, and A. C. Rose-Innes, *J. Chem. Phys.*, **30**, 765 (1959).

(20) J. W. Eastman, G. Engelsma, and M. Calvin, *J. Am. Chem. Soc.*, **84**, 1339 (1962).

(21) G. Breigleb and J. Czekalla, *Z. Elektrochem.*, **58**, 249 (1954).

charge-transfer absorption bands.^{2,4,22} As both methods also allow relative assignments of ionization potentials or electron affinities of such series of molecules, they may act as a check on one another. In Fig. 1 are plotted the first charge-transfer maxima with *p*-chloranil and the polarographic oxidation potentials of the sterically unhindered substituted N,N-dimethylanilines used in this study. The points fit a straight line, except for that representing N,N,N',N'-tetramethyl-*m*-phenylenediamine (II). Because of the reactivity of the latter (evidenced by its rapid air oxidation), it is unlikely that the maximum observed on mixing this amine with *p*-chloranil in methylene chloride was due to a charge-transfer complex.

Eigenvalues of Hückel Molecular Orbitals.—Koopmans' theorem states that the first ionization potential is equal to minus the energy of the highest filled orbital.²³ If the highest filled orbital is a delocalized π -orbital, then the Hückel molecular orbital method may be used to calculate its value,²⁴ although it is not certain that Koopmans' theorem will be valid when the effect of electron repulsion is neglected. The Hückel molecular orbital method when used with π -orbital systems containing heteroatoms requires selection of heteroatom-bond and core parameters relative to the carbon bond and core parameters in benzene. These parameters can take the form $\alpha_X = \alpha_C + h\beta_{CC}$ and $\beta_{CX} = k\beta_{CC}$, where α_X is the heteroatom core or coulomb integral, β_{CX} is the heteroatom to ring carbon bond integral, α_C and β_{CC} are the corresponding core and bond integrals in benzene, and h and k are characteristic constants. In the Hückel method, the core and bond integrals need not be given explicit values in order to obtain relative energy levels in series of similar molecules. Selection of values for the heteroatom parameters is usually empirical.

Streitwieser²⁴ recommends $\alpha_O = \alpha_C + 2\beta_{CC}$ and $\beta_{CO} = 0.8\beta_{CC}$ for ethereal oxygen, and in our previous work²⁻⁵ excellent correlations were achieved in the methoxybenzene series using these parameters. These correlations may have established an absolute relationship between the ethereal oxygen and benzene ring carbon parameters within the Hückel method framework.²⁵

For nitrogen contributing two electrons to a π -system, Streitwieser²⁴ recommended $h_N = 1.5$ and $k_{CN} = 0.8$. Pullman²⁶ has found that $h_N = 1.0$ and $k_{CN} = 0.9$ accounts satisfactorily for properties of a series of aromatic amines. Although the effect of changing k_{CN} from 0.8 to 0.9 on the calculated molecular properties is minor, a 0.5β alteration in the value of h_N produces large changes in the predicted properties of the molecules under investigation.

(22) E. S. Pysh and N. C. Yang, *J. Am. Chem. Soc.*, **85**, 2124 (1963).

(23) T. Koopmans, *Physica*, **1**, 104 (1933).

(24) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961.

(25) The value of β calculated from the h.f.m.o.'s and charge-transfer absorption maxima of a series of polycyclic aromatic hydrocarbons and the value of β obtained from charge-transfer complexes of methoxybenzenes and their h.f.m.o.'s using $h_O = 2.0$ and $k_{CO} = 0.8$ were in very good agreement. Similarly, the proportionality constant of aromatic proton chemical shifts in the $C_6H_5^-$, C_6H_6 , $C_6H_7^+$ series to charge density was the same as that observed in the methoxybenzene series using the m.o. parameters described above. The above oxygen heteroatom parameters thus appear to not only describe the relative changes in properties of methoxy-substituted aromatics, but are able to relate directly the numerical values of these properties to numerical values obtained for hydrocarbons.

(26) B. Pullman and A. Pullman, "Quantum Biochemistry," Interscience Publishers, Inc., New York, N. Y., 1963, p. 106.

No interaction of the π -system with the N-methyl group is normally considered, although the effect of the alkyl group on the nitrogen coulomb integral is implicitly included in the selection of the latter.

In this investigation, the effect of the selection of the nitrogen coulomb integral in the sterically unhindered N,N-dimethylanilines and methoxy-substituted N,N-dimethylanilines on their calculated highest filled molecular orbital (h.f.m.o.) energies has been studied. In Table III are reported the calculated

TABLE III
H.F.M.O.'S OF SOME N,N-DIMETHYLANILINES AS CALCULATED BY THE HÜCKEL M.O. METHOD AND AS MEASURED FROM POLAROGRAPHIC OXIDATION POTENTIALS

Compound	Calcd. by Hückel method ($ \beta $)		
	$\alpha_N = \alpha_C + 1.5\beta_{CC}^a$	$\alpha_N = \alpha_C + 1.0\beta_{CC}^a$	$\epsilon_{1/2(\text{oxid})}^{\chi_{\text{hfmo}}}$
N,N-Dimethylaniline (I)	-0.744	-0.586	-0.558
N,N,N',N'-Tetramethyl- <i>m</i> -phenylenediamine (II)	-0.682	-0.529	-0.499
N,N,N',N'-Tetramethyl- <i>p</i> -phenylenediamine (III)	-0.576	-0.390	-0.379
s-Tris(N,N-dimethylamino)-benzene (IV)	-0.682	-0.529
N,N-Dimethyl- <i>m</i> -anisidine (V)	-0.715	-0.576	-0.547
N,N-Dimethyl- <i>p</i> -anisidine (VI)	-0.629	-0.504	-0.501
3,4-Dimethoxy-N,N-dimethylaniline (VII)	-0.589	-0.484	-0.465
3,5-Dimethoxy-N,N-dimethylaniline (VIII)	-0.707	-0.570	-0.550
5-Methoxy-N,N,N',N'-tetramethyl- <i>m</i> -phenylenediamine (IX)	-0.682	-0.529

^a Other parameters used were $\alpha_O = \alpha_C + 2.0\beta_{CC}$, $\beta_{CN} = \beta_{CO} = 0.8\beta_{CC}$.

h.f.m.o.'s for these nine compounds using two different values for the nitrogen coulomb integral, $\alpha_N = \alpha_C + 1.5\beta_{CC}$ and $\alpha_N = \alpha_C + 1.0\beta_{CC}$.

In a previous study² we found that a linear relationship exists between the Hückel h.f.m.o. energies (χ_{hfmo}) of sterically unhindered methoxybenzenes and their reversible polarographic oxidation potentials. The relationship obtained is described in eq. 1 where the

$$\chi_{\text{hfmo}} = 0.282\epsilon_{1/2(\text{oxid})} \text{ v.} - 0.324 \quad (1)$$

polarographic oxidation potential ($\epsilon_{1/2(\text{oxid})}$) is measured relative to a standard calomel electrode.

If a 0.30-v. correction²² is made for the potential which in this study was made relative to an $\text{Ag}^\circ/0.01 M \text{Ag}^+$ electrode, the experimental values for χ_{hfmo} reported in the last column of Table III are obtained. The results compare quite favorably with the values calculated for all seven sterically unhindered compounds used in this study when the nitrogen coulomb integral is taken as $\alpha_C + 1.0\beta_{CC}$. A considerably greater error is obtained with $\alpha_N = \alpha_C + 1.5\beta_{CC}$, and, although the ordering in the series is not changed, the mean deviation from linearity is increased. To illustrate this further, in Fig. 2 the polarographic oxidation potentials of the planar methoxybenzenes and N,N-dimethylanilines are plotted against the Hückel h.f.m.o.'s, using the two values for h_N . Since the h.f.m.o. energies obtained from the calculations when $h_N = 1.0$ were consistently lower than the energies suggested by the polarographic oxidation potentials relative to the methoxyben-

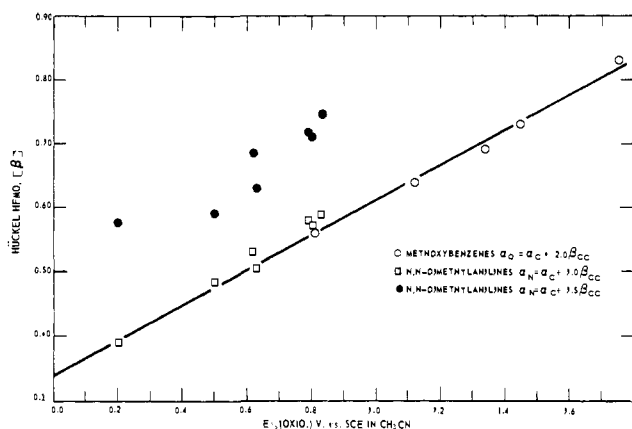


Fig. 2.—Plot of Hückel h.f.m.o. parameter vs. half-wave oxidation potentials of planar methoxy and dimethylamino-substituted benzenes.

zenes, a more exact fit could be obtained by further refinement of the heteroatom parameter, h_N . Calculations were made on N,N,N',N'-tetramethyl-*p*-phenylenediamine (III) using $\alpha_N = \alpha_C + 0.9\beta_{CC}$, keeping $\beta_{CC} = 0.8\beta_{CC}$. The value of $\chi_{\text{h.f.m.o.}}$ was increased to -0.342β , a higher energy than suggested by eq. 1. A value of h_N between 0.9 and unity is thus indicated for a still more exact fit. Statistical studies have been made correlating Hückel carbonyl oxygen heteroatom parameters with e.s.r. data.²⁷ Such a correlation could be made with the polarographic information here, but the number of compounds seemed insufficient, and little, if any, further understanding would be gained by such an *ad hoc* procedure. We also wished to learn if these parameter sets could be used to describe with reasonable accuracy electronic distribution as well as energy levels.

Nuclear Magnetic Resonance Spectra.—The relative chemical shifts in the magnetic resonance spectra of aromatic ring protons is a measure of their electronic environment, and particularly of the charge density accumulated on the contiguous ring carbon position. A direct proportionality between aromatic proton chemical shifts (δ_H) with the charge density on the contiguous ring carbon positions (ρ_C) as expressed by eq. 2 has frequently been used, where Q_H is a constant

$$\delta_H = Q_H \rho_C \quad (2)$$

found experimentally to have a value of ~ 10 p.p.m./electron.

Many other factors affect the ring proton chemical shifts. These include the intramolecular ring current,¹³ intermolecular ring current,²⁸ charge density on neighboring but not directly bonding atoms,²⁹ magnetic anisotropy,³⁰ and electric dipole³¹ effects. The magnetic anisotropy effect of substituents on the ring proton chemical shifts at present cannot be estimated so as to allow a satisfactory correction. It is known that electronegative groups such as $-\text{NO}_2$, $-\text{C}(=\text{O})\text{R}$, and $-\text{SO}_3\text{H}$, give rise to appreciable magnetic anisotropy; however, in a study of the n.m.r. spectra of trimethylamine and dimethyl ether no significant magnetic anisotropy effect on the proton shifts were found for the dimethyl-

amino and methoxy groups.³⁰ Since the magnetic anisotropy effect has a $1/r^3$ dependence, the effect on the protons *ortho* to the dimethylamino group in a dimethylaniline should be negligible. Intramolecular ring current variations in a series of substituted benzenes should be very small. Intermolecular ring current variations can be minimized by using equimolar solutions in a common solvent. The effect of charge densities of neighboring but not bonding atoms and the electric dipole effect may be calculated if necessary. Our experience in the methoxybenzene series indicated that these effects did not appear to be large in such a series. The aromatic proton chemical shift is then reasonably well described by the relationship of eq. 2.

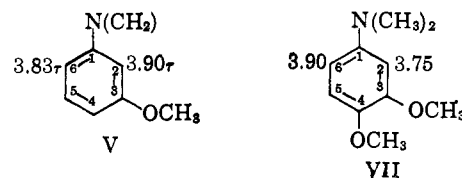
Most of the different proton chemical shifts for the substituted dimethylanilines used in this investigation were measurable, although the aromatic proton patterns were frequently complex. The charge density distributions in these compounds were calculated from the eigenvectors of the solutions to the Hückel determinants. Two sets of these calculated charge densities using the two previously discussed heteroatom parameters for the nitrogen coulomb integral are reported in Table IV.

The least-squares relationship of the aromatic proton chemical shifts of these molecules with the calculated charge densities on the contiguous ring position using $\alpha_N = \alpha_C + 1.5\beta_{CC}$ was chemical shift (τ) = $9.03 \times$ charge density $- 6.03$.

Using $\alpha_N = \alpha_C + 1.0\beta_{CC}$, the least-squares equation became chemical shift (τ) = $10.48 \times$ charge density $- 7.47$.

For all the methoxybenzenes, using $h_O = 2$ and $k_{CO} = 0.8$, the relationship found was chemical shift (τ) = $9.95 \times$ charge density $- 7.02$. Thus $h_N = 1.0$ is a choice more consistent with $h_O = 2.0$ in the Hückel approximation than is $h_N = 1.5$ for this approximate charge distribution relationship, as well as for the energy levels.

The same type of anomalous proton chemical shifts observed in 1,2,4-trimethoxybenzene⁵ were found in the sterically unhindered 1,2,4-trisubstituted benzene (VII) studied here. Both calculations and chemical reasoning argue that the ring proton at the 2-position should be at higher field than the ring proton at the 6-position³² in VII. In this case, as in 1,2,4-trimethoxybenzene,



the spectral analysis unequivocally assigns the chemical shift so that the addition of a methoxy group to the 4-position of N,N-dimethyl-*m*-anisidine (V) properly has a downfield effect on the ring proton at position 2 with two *ortho* substituents but does seemingly exert an anomalous upfield effect on the ring proton at position 6 which has only one *ortho* substituent.

(27) G. Vincow and G. K. Fraenkel, *J. Chem. Phys.*, **34**, 1333 (1961).
 (28) A. A. Bothner-by and R. E. Glick, *ibid.*, **26**, 1647 (1957).
 (29) J. C. Schug and J. C. Deck, *ibid.*, **37**, 2618 (1962).
 (30) H. Spiesscke and W. G. Schneider, *ibid.*, **35**, 722 (1961).
 (31) A. D. Buckingham, T. Schaefer, and W. G. Schneider, *ibid.*, **32**, 1227 (1960).

(32) Addition of a methoxy group to the 4-position of N,N-dimethyl-*m*-anisidine (V) would be expected to lower the charge densities at the 2- and 6-positions equally. As expected, a small downfield shift is noted at the 2-position in going from V to VII, but an unexplained upfield shift is noted at the 6-position.

TABLE IV
 CALCULATED CHARGE DENSITIES IN SOME STERICALLY UNHINDERED N,N-DIMETHYLANILINES

Compound	Position	Heteroatom parameters ^a					
		$\alpha_N = \alpha_C + 1.0\beta_{CC}; \beta_{CN} = 0.8\beta_{CC}$		$\alpha_N = \alpha_C + 1.5\beta_{CC}; \beta_{CN} = 0.8\beta_{CC}$			
		C	N	O	C	N	O
N,N-Dimethylaniline	1	0.956	1.879	0.954	1.917	...
	2,6	1.061	1.048
	3,5	0.998	0.998
	4	1.048	1.037
N,N,N',N'-Tetramethyl- <i>m</i> -phenylenediamine	1,3	0.954	1.880	0.952	1.917	...
	2	1.125	1.099
	4,6	1.106	1.083
	5	0.995	0.995
N,N,N',N'-Tetramethyl- <i>p</i> -phenylenediamine	1,4	0.997	1.8903	0.897	1.923	...
	2,3,5,6	1.057	1.045
	1	0.955	1.8795	0.952	1.917	...
N,N-Dimethyl- <i>m</i> -anisidine	2	1.103	1.090
	3	0.953	...	1.9401	0.953	...	1.940
	4	1.090	1.075
	5	0.996	0.996
	6	1.088	1.076
	1	0.981	1.886	0.980	1.922	...
N,N-Dimethyl- <i>p</i> -anisidine	2,6	1.058	1.046
	3,5	1.057	1.037
	4	0.999	...	1.9447	0.989	...	1.944
	1	0.9787	1.8863	0.978	1.922	...
3,4-Dimethoxy-N,N-dimethylaniline	2	1.100	1.088
	3	0.988	...	1.9428	0.988	...	1.943
	4	1.034	...	1.9476	1.024	...	1.947
	5	1.036	1.037
	6	1.086	1.074
	1	0.953	1.880	0.950	1.917	...
3,5-Dimethoxy-N,N-dimethylaniline	2,6	1.129	1.117
	3,5	0.951	...	1.940	0.951	...	1.940
	4	1.126	1.115
	1,3,5	0.953	1.880	0.950	1.917	...
<i>s</i> -Tris(dimethylamino)benzene	2,4,6	1.167	1.132
	1,3	0.953	1.880	0.950	1.917	...
5-Methoxy-N,N,N',N'-tetramethyl- <i>m</i> -phenylenediamine	2	1.151	1.126
	4,6	1.146	1.124
	5	0.951	...	1.940	0.951	...	1.940
	1	0.951	...	1.940	0.951	...	1.940

^a Other parameters used were $\alpha_O = \alpha_C + 2.0\beta_{CC}$ and $\beta_{CO} = 0.8\beta_{CC}$.

The n.m.r. pattern of the aromatic protons in N,N-dimethylaniline itself proved complex, as expected for an A₂B₂C pattern. The *meta* proton pattern was sufficiently removed from the *ortho* and *para* patterns so that the *meta* proton shift could be assigned. We have interpreted this pattern in terms of identical or near identical *ortho* and *para* proton chemical shifts. Similar results have been reported for this compound by others.^{33,34} Because of the greater difficulty in analysis of A₂B₂C spectra than most of the others encountered in the substituted benzenes, the accuracy for the measured *ortho* and *para* chemical shifts in N,N-dimethylaniline is probably no better than ± 0.05 p.p.m.

Interestingly, the *para* proton chemical shift in dimethylaniline has been reported to be at slightly higher field than the *ortho* protons.^{33,34} This has been ascribed to interaction of the *ortho* protons with the N-methyl groups,³³ since in the C¹³ spectrum³⁵ the *ortho* shift is at higher field. The m.o. calculations suggest that a slightly higher charge density is to be found at the *ortho* positions than at the *para*. The difference is quite small, however, and other factors may well reverse the indicated order in the chemical shifts.

(33) W. F. Reynolds and T. Schaefer, *Can. J. Chem.*, **41**, 2339 (1963).

(34) H. Spiesscke and W. G. Schneider, *J. Chem. Phys.*, **35**, 731 (1961).

(35) P. C. Lauterbur, *ibid.*, **38**, 1415 (1963), and references therein.

Sterically Hindered Dimethylamino-Substituted Benzenes.—Included in Tables I and II are charge-transfer absorption maxima, polarographic oxidation potential, and proton magnetic shifts for three sterically hindered dimethylamino-substituted benzenes. In these compounds, IX, X, and XI, coplanarity of the dimethylamino groups (but not the methoxy groups) with the benzene ring is prevented by steric hindrance due to a single *ortho* substituent. This noncoplanarity was taken into account in this investigation, by reduction of the nitrogen-ring bond integral (k_{CN}).

In Table V are reported the h.f.m.o.'s of these three compounds using $\alpha_O = \alpha_C + 2.0\beta_{CC}$, $\alpha_N = \alpha_C + 1.0\beta_{CC}$,

 TABLE V
 HIGHEST FILLED M.O.'S OF HINDERED N,N-DIMETHYLANILINES

	$\alpha_N = \alpha_C + 1.0\beta_{CC}; \beta_{CN} =$			Polarog. $\chi_{hfm.o.}$
	0.8	0.7	0.5	
N,N,N',N'-Tetramethyl- <i>o</i> -phenylenediamine	-0.4047	-0.478	-0.6284	-0.488
N,N-Dimethyl- <i>o</i> -anisidine	-.5207	-.566	-.6633	-.594
2,4-Dimethoxy-N,N-dimethylaniline	-.4541	-.500	-.5954	-.485

$\beta_{CO} = 0.8\beta_{CC}$, and three different values for β_{CN} : $0.8\beta_{CC}$ (as in unhindered dimethylamino compounds), $0.7\beta_{CC}$, and $0.5\beta_{CC}$. Also reported are the energies of the h.f. m.o.'s of these compounds as determined from eq. 1 and from their polarographic oxidation potentials.

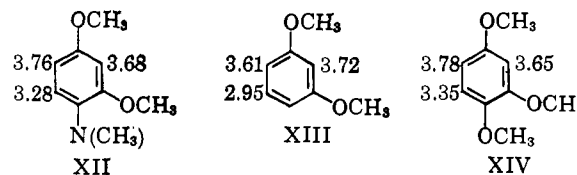
A 12.5% reduction of $k\beta_{CN}$ (from $0.8\beta_{CC}$ to $0.7\beta_{CC}$) is found to give quite good agreement with the polarographic data. This reduction corresponds to an average out-of-plane angle of $\sim 30^\circ$ for the sterically hindered dimethylamino group, assuming a cosine dependence of resonance integral on angle of interaction of atomic orbitals.²⁴

To complete this examination of the choice of k_{CN} in hindered dimethylamino-substituted aromatics, a comparison of the aromatic proton chemical shifts and the calculated charge densities is indicated. Unfortunately, these are too few aromatic proton chemical shifts to use effectively a least-mean-squares treatment. All the aromatic protons of both X and XI were found to exhibit the same chemical shift (3.23τ) under our standard conditions.

The average of the *calculated* charge densities (c.d.) at the ring positions contiguous to the ring proton positions in X and XI as a function of k_{CN} is: $k_{CN} = 0.8$, c.d. = 1.046; $k_{CN} = 0.7$, c.d. = 1.039; $k_{CN} = 0.5$, c.d. = 1.024. Using the relationship of chemical shift and charge density obtained for the sterically unhindered dimethylamines, with $\alpha_N = \alpha_C + 1.0\beta_{CC}$, a charge density of 1.022

is indicated for 3.23τ . These data indicate that the hindered bond integral, k_{CN} , should be close to 0.5, although the limited number of experimental values does not permit too much significance to be attached to this figure.

We did not try to use XII in the n.m.r. correlation with charge density because the chemical shifts of other 1,2,4-trisubstituted benzenes had been irregular. The results for XII, however, throw some light on the situation. The diagram below shows what happens to the proton chemical shifts in 1,3-dimethoxybenzene⁵ when



either a methoxy- or a dimethylamino group is added to the 4-position. The almost negligible differences in chemical shifts for the aromatic protons in XII and in XIV suggests that the alterations in the shifts in going from XIII are due at least in part to the restriction in rotation of the methoxy group in the 3-position. Further investigations of this effect are in progress.

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[CONTRIBUTION OF THE CHEMISTRY DEPARTMENT, TEXAS CHRISTIAN UNIVERSITY, FORT WORTH, TEXAS]

A Radiochemical Study of the Acetolysis of 3-Phenyl-2-butyl Tosylate

BY WILLIAM B. SMITH AND MAXINE SHOWALTER

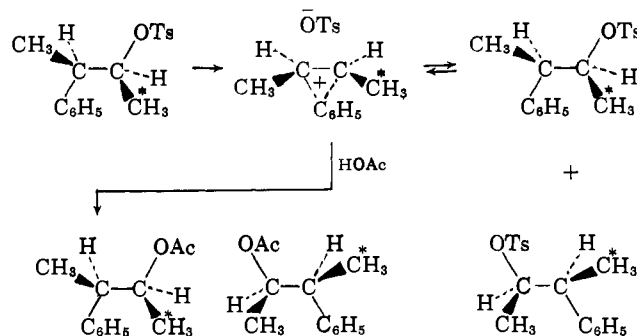
RECEIVED MAY 13, 1964

The acetolysis of (+)-*threo*-3-phenyl-2-butyl tosylate-1-C¹⁴ at 75° produced racemic *threo*-3-phenyl-2-butyl acetate which, upon reduction and resolution, gave (+)-*threo*-3-phenyl-2-butanol showing no isotope position rearrangement and (–)-*threo*-3-phenyl-2-butanol with all of the label at C-4. These results are in accord with the postulated phenonium ion intermediate and provide a tool for measuring the ratio of internal return to product formation in the *erythro* system. By studying the rate of scrambling in recovered tosylate this ratio has been obtained for the acetolysis of both the *threo*- and *erythro*-tosylates. Data on the former system agreed reasonably well with the kinetic and polarimetric data in the literature. Comparisons between the two systems indicate that steric effects are of little importance in the rate of formation of phenonium ion–tosylate ion pairs in either system and may even slightly favor the *erythro* system, a result in conflict with the expected methyl eclipsing effects.

Introduction

As the result of an extensive series of studies on the solvolysis and elimination reactions of the stereoisomers of 3-phenyl-2-butyl *p*-toluenesulfonate (tosylate) and related compounds, Cram and co-workers¹ postulated the formation of a symmetrically bridged phenonium ion–tosylate ion pair intermediate as a rationalization of the observed stereochemical consequences of the reaction. Support for the ion pair concept and a measure of the extent of internal return in the 3-phenyl-2-butyl tosylate system was provided by Winstein and Schreiber² who measured the polarimetric and titrimetric rates of solvolysis of (+)-*threo*-3-phenyl-2-butyl tosylate and who reported that for acetolysis the former exceeded the latter. Similar measurements on the

erythro system, of course, were not possible since collapse of the *erythro* ion pair to starting tosylate leads to material of retained configuration. The mechanistic scheme resulting from these studies may be summarized as



The postulation of the phenonium ion as an intermediate in the acetolysis of 3-phenyl-2-butyl tosylate

(1) (a) D. J. Cram, *J. Am. Chem. Soc.*, **71**, 3863 (1949); **71**, 3883 (1949); **74**, 2129 (1952); **74**, 2137 (1952); **74**, 2149 (1952); (b) D. J. Cram and F. A. Abd Elhafez, *ibid.*, **75**, 3189 (1953); (c) D. J. Cram, H. L. Nyquist, and F. A. Abd Elhafez, *ibid.*, **79**, 2876 (1957).

(2) S. Winstein and K. Schreiber, *ibid.*, **74**, 2165 (1952).