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NMR SPECTRA OF AROMATIC AMINES AND AMIDES—I

CORRELATIONS OF AMINO PROTON SHIFTS WITH HAMMETT SUBSTITUENT CONSTANTS AND WITH HÜCKEL ELECTRON DENSITIES*

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Abstract—The chemical shifts of the amino protons in sets of substituted anilines, carbocyclic aromatic amines, and heteroaromatic amines have been measured in DMSO solvent. For a series of 28 substituted anilines, including several compounds possessing *ortho*-substituents, an excellent linear correlation between appropriate Hammett substituent constants and chemical shift is observed. Substituted *ortho*-nitroanilines require a greatly enhanced substituent constant (ca. +2) if they are to be fitted to the regression line appropriate to the other anilines.

Hückel (HMO) calculations of the π-electron densities at the exocyclic atom have been made for a series of 8 carbocyclic aromatic amines, and for 15 heteroaromatic amines. The electron densities are linearly related to the chemical shifts observed for each series, although the slopes differ for the carbocyclic and heteroaromatic amines.

It is therefore possible to relate Hammett substituent constants linearly with HMO electron densities, although the parameters of such relationships will be a function of the assumptions made in the HMO calculations.

INTRODUCTION

PREVIOUS investigations[1,2] have revealed linear relationships between amino proton chemical shift and Hammett substituent constant (σ) for *meta*- and *para*-substituted anilines in acetonitrile,[1] carbon tetrachloride,[1] cyclohexane,[2] and deuteriochloroform[1] solutions. Schaefer *et al.*[2] found that the amino proton shifts of *ortho*-substituted anilines were linearly related to Taft's[3] σ_o values, but the intercept differed from that observed for the *meta* and *para* compounds; their definitive paper concludes that the amino proton shifts are primarily dependent upon the π-electron density at the amino nitrogen atom.

The present work explores this dependence in more detail. We have used DMSO (a powerful hydrogen-bond acceptor)[4,5] as solvent, and have sought relationships applicable to anilines carrying *ortho*, *meta*, and *para* substituents. Further, in the expectation of a relationship between proton shift and calculated π-electron density, we have calculated the π-electron density at the amino nitrogen in a series of carbocyclic aromatic amines using the simple Hückel (HMO) method.[6] This expectation is based upon Elliott and Mason's[7] observation of a relationship between pK_a for the cation of a polycyclic aromatic amine and the calculated π-electron density at the exocyclic atom in the isoelectronic carbanion, and observation[1,2] of a relationship between pK_a of an anilinium ion and the amino proton shift. We have also made

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HMO calculations of the π-electron density at the amino proton in a series of heteroaromatic amines for comparison with the observed chemical shifts.

RESULTS

The observed amino proton chemical shifts, rounded off to the nearest Hz, in 36 variously substituted anilines are listed in Table 1, together with appropriate σ constants from the compilation by Hine[8] or from Taft.[3] Table 2 lists similar chemical shift data for a series of 8 carbocyclic aromatic amines, together with appropriate

TABLE 1. HAMMETT SUBSTITUENT CONSTANT—CHEMICAL SHIFT RELATIONSHIPS FOR AMINO PROTONS IN SUBSTITUTED ANILINES

Substituent	Chemical shift (Hz from TMS)	Sigma value[a]	Substituent	Chemical shift (Hz from TMS)	Sigma value[a]
1. 2,6-Me_2	263	−0·34	19. 2-Me, 5-NO_2	331	+0·54
2. 4-OMe	270	−0·268	20. 3-NO_2	345	+0·71
3. 4-OEt	270	−0·24	21. 2-OMe, 4-NO_2	378	1·002 (0·88)
4. 2-OEt	274	−0·24 (−0·35)	22. 3-Me, 4-NO_2	383	1·201
5. 2-OMe	276	−0·268 (−0·39)	23. 4-NO_2	398	1·27[c]
6. 2-Me	278	−0·170	24. 2-F, 4-NO_2	400	1·335 (1·51)
7. 4-Me	282	−0·170	25. 2-OMe, 4,5-$(NO_2)_2$	401	1·59 (1·468)
8. 3-Me	287	−0·069	26. 2-Cl, 4-NO_2	407	1·497 (1·47)
9. H	288	—	27. 2-Br, 4-NO_2	406	1·502 (1·48)
10. 3-OMe	295	+0·115	28. 3-F, 4-NO_2	417	1·607
11. 3-OEt	296	+0·12	29. 4,5-Me_2, 2-NO_2	430	
12. 4-Ph	309	+0·16[b]	30. 2-NO_2	440	
13. 4-Cl	309	+0·227	31. 5-I, 2-NO_2	444	
14. 4-Br	309	+0·232	32. 4-OMe, 2-NO_2	447	
15. 2-Cl	312	+0·227 (+0·20)	33. 5-Cl, 2-NO_2	449	
16. 2-Br	312	+0·232 (+0·21)	34. 4-Cl, 2-NO_2	450	
17. 3-F	315	+0·337	35. 5-OMe, 2,4-$(NO_2)_2$	482	
18. 3-Cl	319	+0·373	36. 2,4-$(NO_2)_2$	497	

[a] Primary values equate sigma values for ortho and para substituents. Values in parentheses use Taft's special values for ortho substituents.

[b] From J. G. Traynham and G. A. Knesel, *J. Org. Chem.* **31**, 3350 (1966).

[c] σ^- is used for 4-NO_2 substituent.

HMO electron densities, and Table 3 lists chemical shifts and HMO amino-group electron densities for 15 heteroaromatic amines. Table 4 summarizes amino proton chemical shifts and appropriate σ constants for a series of substituted 2-aminopyridines and 2-aminopyrimidines.

Linear relationships exist between the tabulated quantities for each table, and Table 5 summarizes the appropriate parameters describing these linear relationships. Least-squares regression lines were established using a standard Fortran II program with an IBM 1620 computer, and correlation coefficients, $\bar{r}$, were also evaluated.

TABLE 2. ELECTRON DENSITY—CHEMICAL SHIFT RELATIONSHIPS FOR AMINO PROTONS IN CARBOCYCLIC AROMATIC AMINES

Compound	Chemical shift (Hz from TMS)	Electron density Carbanion[a]	Amine[b]
1. Aniline	288	1·572	$1·729_5$
2. 4-Aminobiphenyl	309	1·516	1·707
3. 2-Aminonaphthalene	315	1·529	1·714
4. 2-Aminoanthracene	328	1·471	1·698
5. 1-Aminonaphthalene	336·5	1·450	1·672
6. 1-Aminoanthracene	350·5	1·381	1·648
7. 1-Aminopyrene	376	1·364	1·636
8. 9-Aminoanthracene	392	1·286	1·583

[a] From Hückel calculation assuming all C atoms are of identical electronegativity.
[b] From Hückel calculation assigning $h = +\frac{1}{2}$ for the amino nitrogen.

DISCUSSION

(a) *Hammett substituent constants and amino proton chemical shifts*

As Tables 1 and 5 show, there is an excellent linear relationship between σ constant and amino proton chemical shift for the *meta*- and *para*-substituted anilines over a range of 147 Hz ($\bar{r}$, 0·997), where the chemical shift changes by 79·27 Hz per unit change in σ. If *ortho*-substituents are included and the Taft[3] σ_o values are employed, the correlation (over a range of 154 Hz) is still highly significant ($\bar{r}$, 0·992), and the regression line has a closely similar slope to that for the *meta* and *para* substituted

TABLE 3. ELECTRON DENSITY—CHEMICAL SHIFT RELATIONSHIP FOR AMINO PROTONS OF HETEROAROMATIC AMINES

Compound	Chemical shift (Hz from TMS)	Electron density at Amino Nitrogen[a]
1. 3-Aminopyridine	304	1·729
2. 4-(3-Aminophenyl)-pyrimidine	315	1·731
3. 6-Aminoquinoline	333	1·714
4. 3-Aminoquinoline	337·5	1·713
5. 2-Aminopyridine	348	1·698
6. 2-Aminopurine	355	1·697
7. 4-Aminopyridine	356	1·694
8. 2-Aminoquinoline	384·5	1·661
9. 2-Aminopyrimidine	385	1·676
10. 4-Aminopyrimidine	400	1·666
11. 2-Amino-1,8-naphthyridine	413	1·646
12. 2-Amino-1,5-naphthyridine	418	1·658
13. 2-Amino-1,6-naphthyridine	422	1·648
14. 6-Aminopurine	422	1·643
15. 4-Aminopyrazolo(3,4-d)pyrimidine	450	1·626

[a] From Hückel calculation assigning $h = +\frac{1}{2}$ to all N atoms.

TABLE 4. HAMMETT SUBSTITUENT CONSTANT—CHEMICAL SHIFT RELATIONSHIPS FOR AMINO PROTONS IN SUBSTITUTED PYRIDINES AND PYRIMIDINES

	Compound	Chemical shift (Hz from TMS)	Sigma
1.	2-NH_2 pyridine	348	0·00
2.	4-Me, 2-NH_2 pyridine	340	−0·069
3.	4,6-Me_2, 2-NH_2 pyridine	336	−0·138
4.	5-Cl, 2-NH_2 pyridine	363	+0·227
5.	5-Br-2-NH_2 pyridine	365	+0·232
6.	2-NH_2 pyrimidine	385	0·00
7.	4-Me, 2-NH_2 pyrimidine	382	−0·069
8.	4,6-Me_2-2-NH_2 pyrimidine	381	−0·138
9.	4-Cl-2-NH_2 pyrimidine	420	+0·373

TABLE 5. REGRESSION PARAMETERS OF CHEMICAL SHIFT RELATIONSHIPS

(1) CHEMICAL SHIFTS *vs.* HAMMETT SUBSTITUENT CONSTANTS

	Series	in	Parameters a and b $\nu = a + b\Sigma\sigma$ a	b	$\bar{r}$	Average deviation, Hz	No. of data points	Chemical shift range Hz
1.	*meta* and *para* substituted anilines		290·6	79·27	0·997	2·70	15	147
2.	All anilines[a]		291·6	77·25	0·996	3·30	28	154
3.	All anilines[b]		293·1	75·37	0·992	4·75	28	154
4.	Phenols[c]		556·9	78·88	0·988	3·90	16	134
5.	Substituted 2-aminopyridines		346·5	76·87	0·996	0·90	5	29
6.	Substituted 2-aminopyrimidines		388·6	81·10	0·987	2·32	4	39

(2) CHEMICAL SHIFTS *vs* π-ELECTRON DENSITIES

		Parameters in $\nu = a + b\,q_\pi$ a	b				
7.	Carbocyclic amines[d]	851·1	−355·6	0·984	4·50	8	104
8.	Carbocyclic amines[e]	1493·1	−690·9	0·972	6·00	8	104
9.	Heteroaromatic amines	2579·4	−1311·5	0·987	5·67	15	146

[a] Equating sigma values for *ortho* substituents with those for *para*.
[b] Using Taft's special "σ_o" values.
[c] Shifts from J. G. Traynham and G. A. Knesel, *J. Org. Chem.* **31**, 3350 (1966).
[d] Using carbanion electron density from HMO calculation.
[e] Using exocyclic nitrogen electron density from HMO calculation.

compounds (75·37 Hz/σ). Since the chemical shifts observed for *ortho*-substituted amines are closely similar to those for the *para* isomers (cf. Nos. 2 and 5, 3 and 4, 6 and 7, 13 and 15, 14 and 16), the chemical shift–σ relationship is further improved ($\bar{r}$ = 0·996) if we assign equal values to σ for both *ortho* and *para* substituents; the relationship is illustrated in Fig. 1. The average deviation is 3·30 Hz. It appears likely

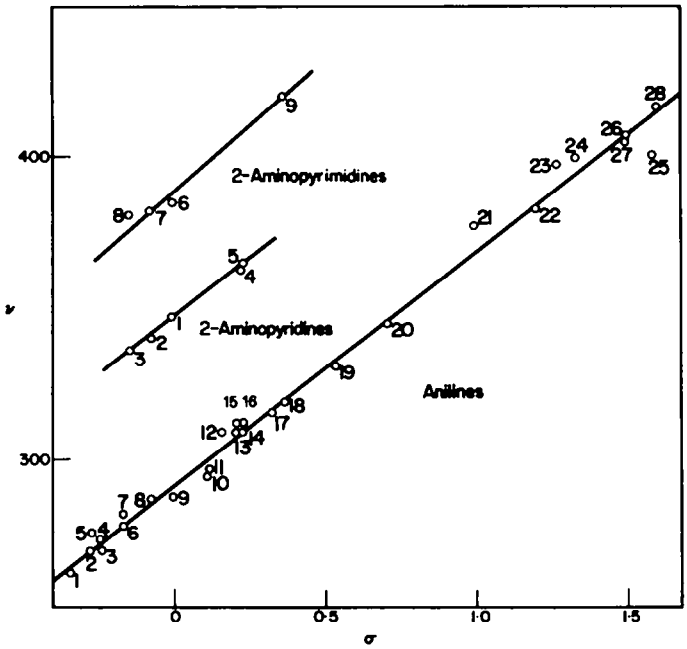


FIG. 1. (cf. Tables 1, 4, and 5)

that $\sigma_o = \sigma_p$ for many substituents in these ground-state correlations, and also that the amino proton chemical shift measurement for a substituted aniline offers a convenient, rapid method for assignment of new σ constants.

Similar suggestions have been made for substituted N,N-dimethylanilines[9] and for phenols.[5] In Traynham and Knesel's paper,[5] (which uses an identical solvent system to that of the present paper) it should be noted that their regression line is probably in error since there are arithmetical errors in their tabulations of σ values for 4-chloro-3-methylphenol and 3,4-dimethylphenol; a corrected regression line for their data is given in Table 5, where it is evident that the response of the OH proton (78·88 Hz/σ) is virtually the same as for the N—H group in the anilines. In particular, the NMR method offers a very simple route to σ values appropriate to heteroatom replacement in an aromatic ring (e.g. with pyridines and pyrimidines) (see section (d) for discussion of this point) (cf. Katritzky and Swinbourne[10]).

(b) *Amino proton shifts in* ortho-*nitroanilines*

The excellent linear relationships noted above break down when an *ortho*-nitro substituent is present in the molecule (Table 1, compounds 29–36). In these examples,

it appears likely that the N—H bonds are appreciably acidic, and hydrogen bonding to the acceptor DMSO is strongly favored. The electron distribution implied by II rather than I is regarded as a good representation for substituted *ortho*-nitroanilines and would require an enhanced σ value for the *ortho*-nitro substituent. If a value of +1·93 is selected, this would allow the compounds 29, 30, 31, 32, 36 of Table 1 to be fitted to regression Eq. (3) of Table 5 with an average deviation of 10 Hz. This value seems too large for the other three compounds, but a value appreciably greater than σ^- for the *para*-nitro substituent (1·27) seems appropriate. The enhanced nitro-group effect would be expected to be critically dependent upon the coplanarity of aromatic ring, amino, and nitro group, and in 6-chloro-2-nitroaniline, where the vicinal trisubstitution might be expected to twist the amino and nitro groups away from the conformation implied by II, the amino proton chemical shift is 372 Hz.

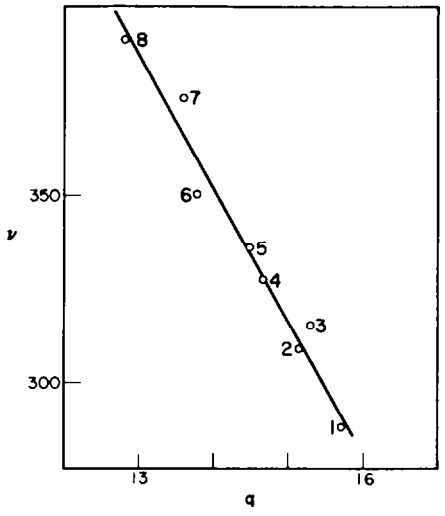


FIG. 2. (cf. Tables 2 and 5)

For this compound, use of σ_p ($=\sigma_o$) for the chloro substituent, and −0·778 for the nitro group (σ_p appropriate for the nitro group when isolated from conjugation) gives $\Sigma\sigma = 1{\cdot}005$; the chemical shift calculated from application of regression Eq. (3) of Table 5 is (291·6 + 77·25 (1·005)) = 369·3 Hz.

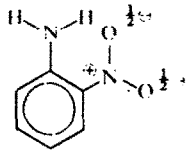
Rae[11] has examined solvent effects on the ring proton chemical shifts of substituted *ortho*-nitroanilines. In contrast to the argument for strong amino-nitro interaction proposed above, he argues that the increased *shielding* of the proton *ortho* to the nitro group on change of solvent from deuteriochloroform to DMSO results from *rotation* of the nitro group away from coplanarity with the ring protons, as a consequence of the change in hydrogen bonding of the amino protons from an intramolecular (to the oxygen of the nitro group) to an intermolecular type (to the oxygen of DMSO). If such a phenomenon occurred, the nitro group would become a less effective electron-attracting group, and the electron density at the amino nitrogen would be greater than in a situation where the nitro group was exerting its full

conjugation effect. Also, any rotation of the amino group would increase the electron density at amino nitrogen through loss of conjugation with the ring.

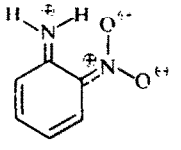
The amino proton shifts summarized in the latter part of Table 1 are not consistent with Rae's suggestion. The *ortho*-nitro substituent is more effective in *deshielding* the amino protons than any other substituent studied, implying that structure II is a good representation for *ortho*-nitroanilines in DMSO solvent. The solvent effect noted by Rae[11] is readily explained in terms of the increased electron density at the nitro oxygens in II as compared with I, thus shielding the neighboring ring protons.

The enhanced electron donation by the amino group, reflected by deshielding of the amino protons and by the increased electron density at the nitro oxygens, is ascribed to the effect of DMSO ($Me_2SO...H—N—$) in enhancing the electron-donating effect of the amino group (tending towards an $—NH^-$ substituent).

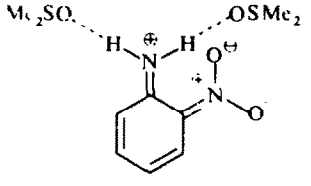
Rae's argument is based on the assumption that breaking of the intramolecular N—H...O bond of *ortho*-nitroanilines is sufficient to lead to mutual rotation of substituents and decreased interaction between substituents, but both intermolecular hydrogen bonding (as in III) *and* enhanced substituent interactions are probable.



I



II



III

(c) *Amino proton shifts and calculated electron densities*

As noted above, Elliott and Mason[7] found a fair linear correlation ($\bar{r} = 0{\cdot}935$) between the pK_a of the cations derived from carbocyclic aromatic amines and the carbanion HMO electron densities for the isoelectronic carbocyclic systems; the electron densities are readily deducible using the Longuet-Higgins procedure.[12] A significantly better correlation ($\bar{r} = 0{\cdot}984$) is obtained (Tables 3 and 5, and Fig. 2) when the amino proton chemical shifts are plotted against the π-electron density at the exocyclic C atom, and the slope of the regression line (355 Hz/electron, or 6 ppm/electron) is similar to that observed for ring protons in aromatic and heteroaromatic systems.[13,14] It seems probable, therefore, that in these systems, the π-electron density at the exocyclic atom is the dominant factor in determining the chemical shift, with ring-current and anisotropy effects being of minor importance.

Modification of the HMO calculation by incorporation of a heteroatom' parameter for the amino nitrogen ($h = +\frac{1}{2}$) decreases the range of electron densities

observed, and the linear correlation becomes slightly worse ($\bar{r}$ = 0·972) (Fig. 3). The choice of the electronegativity parameter merits comment, since the usually accepted value for amino nitrogen is +2 (cf. Streitwieser[21]); the enhanced electron-donating capacity of the amino group in the presence of the DMSO solvent is postulated in explanation. (Obviously, the slope in Hz/electron or ppm/electron will be critically dependent upon the range of electron density for the various compounds; choice of

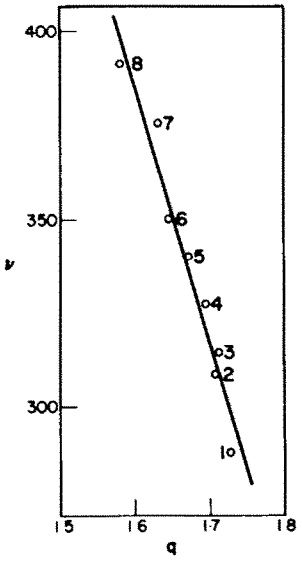


FIG. 3. (cf. Tables 2 and 5)

+2 as electronegativity parameter would give an absurdly high response value (ca. 40 ppm/electron)).

The approach relating electron densities to chemical shifts was extended to a series of heteroaromatic amines (Tables 3 and 5). A relationship as noted by Elliott and Mason between pK_a and π-electron density is not evident in these examples, since the *cyclic* N atoms are generally the basic centers in these molecules, but there is a good linear relationship (r = 0·987) (Fig. 4) between the observed amino proton shifts and the π-electron densities calculated by the HMO method, again assigning the N atom in the amino group (and the cyclic nitrogens) an electronegativity parameter of +½. The slope of the regression line (1311 Hz/electron, or 21·9 ppm/electron) is much higher than noted with the carbocyclic amines (691 Hz/electron, 11·5 ppm/electron). This suggests that amino nitrogen is less electronegative (i.e. has a greater tendency to donate electrons to the aromatic C atoms) when electron-attracting pyridine-type nitrogens are present in the aromatic rings. In other words, a more appropriate electronegativity parameter for the heteroaromatic amino nitrogen would be between zero and +½. This seems qualitatively reasonable and corresponds to the situation previously commented on with respect to *ortho*-nitroaniline.

Again, with the heteroaromatic amines, it appears that the π-electron density at the amino nitrogen is the dominant term controlling chemical shift, with ring-current and nitrogen anisotropic effects being unimportant. Simple HMO calculations are an excellent correlative tool for these chemical shifts, and could obviously be used to predict chemical shifts for newly synthesized heteroaromatic amines.

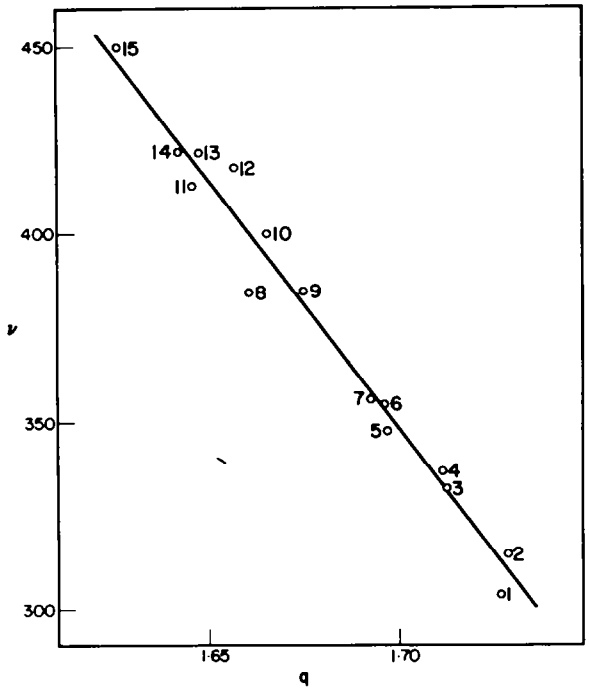


FIG. 4. (cf. Tables 3 and 5)

Although electron density–chemical shift relationships have been observed for the ring protons of carbocyclic[13] and heterocyclic[14] aromatic compounds, they are largely restricted to comparisons of different positions in the same molecule,[14] or to aromatic anions and cations.[13] *Our results with the carbocyclic and heterocyclic aromatic amines are the first examples where sufficient distinct sets of chemical shifts and electron densities are available to establish statistically significant linear relationships.*

It is remarkable that the simplest MO calculations give such a good account of the order and magnitudes of the chemical shifts. Although our computing facilities are not adequate for advanced SCF calculations on the heteroaromatic amines, we carried out ω-type calculations[22] using the output of the HMO calculations on 3-aminopyridine and 4-aminopyrazolo (3,4-d)pyrimidine as starting points. The amino nitrogen electron densities were 1·513 and 1·453, indicating a slope of 2433 Hz/electron, or 40·5 ppm/electron. Thus, attempts at self-consistent treatments lead to unacceptably high chemical shift responses to the calculated changes in electron density.

(d) *Correlation of Hammett substituent constants and electron densities*

The relationships discussed in sections (a) and (c) indicate that it should be possible to correlate the electron densities derived from HMO calculations with Hammett σ quantities. A good test for this possibility is to choose a heteroaromatic amine whose amino proton chemical shift and electron density are related by the regression equation No. 9 of Table 5, and determine the effect of an exocyclic substituent on the chemical shift. This effect should be closely similar to that observed for an aniline carrying an identical exocyclic substituent.

Table 4 shows that this is the case for substituted 2-aminopyridines and 2-aminopyrimidines; excellent chemical shift—σ relationships are evident (Table 5, entries 5 and 6, also Fig. 1) and the slopes of the regression lines are closely similar to those for substituted anilines.

The correlation will allow a set of heteroatom MO parameters to be assigned to substituents such as the halogens, hydroxy and methoxy, and nitro, with the test for self-consistency of the parameters with those for carbon and nitrogen involving agreement between calculated amino nitrogen π-electron density and that deduced from the simultaneous application of chemical shift—electron density and chemical shift—Hammett σ relationships. We are commencing a detailed set of calculations seeking to evaluate these parameters for the above-mentioned substituents (for an approach to this problem before the advent of NMR techniques, see Jaffe[15]).

Alternatively, Hammett σ values may be derived for heteroatom substituents. Direct application of Eq. 2 of Table 5 to the chemical shift for 2-aminopyridine would lead to a σ for α—N: of +0·73, intermediate between the recently suggested values of +1·0[10] and +0·56,[16] and application of this equation to the chemical shift of 2-aminopyrimidine would give a σ for two α—N: of +1·25 (cf. +1·12[16]).

EXPERIMENTAL

Materials. The amines were obtained from commercial sources with the exception of the aminonaphthyridines (donated by Dr. W. W. Paudler), and the various substituted nitroanilines (prepared by Mrs. Y. Wigfield and Miss C. Chen of this laboratory[17,18]). The NMR spectra of the samples gave satisfactory signal integrations, with no evidence for contamination by isomeric amines. The ring proton shifts and coupling patterns were consistent with the expected structures in all cases.

DMSO (Fisher Scientific Co. "Certified" Grade) was dried over CaH_2; DMSO-d_6 was supplied by Merck, Sharp, and Dohme of Canada.

Spectra. The NMR spectra were recorded using a Varian A-60A spectrometer (probe temp, 37°), for 2–5% w/w solns. Amino proton signal positions (typical half-height width: 4 Hz) were reproducible to 0·3 Hz, and showed no dependence on amine concentration; they are expressed in Hz downfield from TMS, present as internal reference, or alternatively with reference to the 221 Hz low field C_{13}—H satellite of DMSO. Sweep width calibration was effected using standard solns.

MO calculations. π-Electron densities, bond orders, and orbital energies were evaluated on an IBM 1620 computer, with a Fortran II program.[19,20] The input parameters were those of the simple Hückel (HMO) method,[21] and the electronegativity parameter h for all N atoms was assigned a value of $+\frac{1}{2}$. ω-Technique HMO calculations were programmed using the output from the HMO results by the averaging method suggested by Ettinger.[22] Results other than the electron densities summarized in the Table are available from the authors on request, as is the program listing for the ω-technique calculations.

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REFERENCES

[1] L. K. Dyall, *Austral. J. Chem.* **17**, 419 (1964).
[2] T. Yonemoto, W. F. Reynolds, H. M. Hutton and T. Schaefer, *Canad. J. Chem.* **43**, 2668 (1965).
[3] R. W. Taft, *Steric Effects in Organic Chemistry* (Edited by M. S. Newman) p. 618. Wiley, New York (1956).
[4] R. J. Ouellette, *Canad. J. Chem.* **43**, 707 (1965).
[5] J. G. Traynham and G. A. Knesel, *J. Org. Chem.* **31**, 3350 (1966).
[6] A. Streitwieser, *Molecular Orbital Theory for Organic Chemists* p. 33. Wiley, New York (1962).
[7] J. J. Elliott and S. F. Mason, *J. Chem. Soc.* 2352 (1959).
[8] J. Hine, *Physical Organic Chemistry* (2nd Edition) pp. 87–90. McGraw-Hill, New York (1962).
[9] I. D. Rae and L. K. Dyall, *Austral. J. Chem.* **19**, 835 (1966).
[10] A. R. Katritzky and F. J. Swinbourne, *J. Chem. Soc.* 6707 (1965).
[11] I. D. Rae, *Austral. J. Chem.* **20**, 1173 (1967).
[12] H. C. Longuet-Higgins, *J. Chem. Phys.* **18**, 275 (1950).
[13] T. Schaefer and W. G. Schneider, *Canad. J. Chem.* **41**, 966 (1963).
[14] B. M. Lynch and H. J. M. Dou, *Tetrahedron Letters* 2627 (1966).
[15] H. H. Jaffe, *J. Chem. Phys.* **20**, 279 (1952).
[16] D. D. Perrin, *J. Chem. Soc.* 5590 (1965).
[17] Y. Hung (Mrs. Y. Wigfield), *Selective Nitrations of Weakly Basic Aromatic Compounds.* M.A. Thesis, St. Francis Xavier University, 1964.
[18] B. M. Lynch, H. S. Chang, Y. Hung and J. G. Webb, *9th Ann. Report*, p. 32. Petroleum Research Fund, American Chemical Society, Washington (1965).
[19] C. L. Wilkins and C. E. Klopfenstein, *J. Chem. Educ.* **43**, 10 (1966).
[20] B. M. Lynch and L. Poon, *Canad. J. Chem.* **45**, 1431 (1967).
[21] Ref. 6, p. 117.
[22] R. Ettinger, *Tetrahedron* **20**, 1579 (1964).