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NMR Spectral Parameters of Seven Di-substituted Anilines

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The 56 and 60 MHz spectra of seven di-substituted anilines have been recorded and analyzed. The compounds were studied as neat liquids and 10 mol% solutions in carbon tetrachloride and acetone. The 21 spectra, which are of the $ABCMX_3$ type, were analyzed in terms of chemical shifts and coupling constants, using a computer. Effects of substituents on the spectral parameters have been discussed in relation to the relevant mono-substituted benzenes. The proton chemical shifts and proton-proton coupling constants have been calculated empirically from the spectral data of the mono-substituted benzenes, assuming additivity of substituent effects. It is found that the additivity concept predicts the correct trends in the spectral parameters. Distinct medium effects on the spectral parameters have been observed and discussed.

In the last decade, the nuclear magnetic resonance (NMR) spectra for a large number of substituted benzenes have been the subject of considerable study.[1] The main emphasis has been on the chemical shifts, but over the past few years, considerable effort has also been devoted to the determination and interpretation of nuclear magnetic coupling constants.

It has been shown that the chemical shifts of aromatic protons in numerous substituted benzenes reflect changes in π-electron density of the aromatic ring upon substitution. Several factors other than changes in π-electron charge distribution also affect the chemical shifts of protons *ortho* (and possible *meta*) to a substituent. For a number of poly-substituted benzenes, additivity relationships of substituent effects have also been established.[1–4]

The proton-proton coupling constants are found to be fairly independent of the substituents in aromatic molecules. For various series of substituted benzenes, a linear correlation has, however, been observed between the coupling constants and the total electronegativity of the substituents attached to the ring.[1,5,6] Interactions giving rise to *ortho* and *meta* proton-proton couplings are thought to operate *via* the σ-electronic system.[1] The *para* proton-proton coupling constants and long-range coupling constants in aromatic systems are, however, mainly controlled by the π-electronic system.[1] It has also been found that the coupling constants in di-substituted benzenes can be

calculated empirically from data of the mono-substituted benzenes, by simple additivity relationships similar to those for the chemical shifts.[7–10]

This paper reports the results of a complete analysis of the proton magnetic resonance (PMR) spectra of eight di-substituted anilines. The parameters were obtained for the neat liquids and 10 mol% solutions in carbon tetrachloride and acetone. In interpreting the observed data, it is reasonably assumed that solute-solvent interactions are negligible in the relatively inert solvent CCl_4.

The PMR spectra of aniline,[11] toluene,[12] benzotrifluoride,[13] and fluorobenzene [14] have been analyzed, and the NMR parameters are available in the literature. The data obtained in this work appear particularly relevant to a test of additivity relationships in tri-substituted benzenes. Any deviations from additivity which occur can then, to a certain extent, be interpreted as a measure of interactions between the substituents on the same benzene ring.

EXPERIMENTAL

The seven di-substituted anilines studied in this paper, were all commercially available. The structural formulas are given in Table 1. All the anilines were examined as 10 mol% solutions in carbon tetrachloride and acetone, and as neat liquids, apart from the solid 2-methyl-5-fluoroaniline, which was studied in a saturated solution in acetonitrile. A small amount of tetramethylsilane (TMS) was added and used as an internal reference and lock signal source. A small quantity of hexafluorobenzene was used as an internal standard for the fluorine signals. All samples were thoroughly degassed and sealed under vacuum. No impurity peaks of any significance were observed.

The spectra were run on a JEOL 60 MHz spectrometer (JNMC-60H) at ambient temperature (27°C). All spectra were calibrated, using a JEOL frequency counter (JNM-SD-30). Line positions were obtained by averaging the results of 3 upfield and 3 downfield scans. Sweep widths of 54 Hz and 108 Hz were employed for the proton and fluorine spectra, respectively. Computations were carried out, using the IBM 360-50H computer at the University of Bergen. Graphical plots were obtained, using a Calcomp Plotter.

SPECTRAL ANALYSIS

All the 21 NMR spectra – 3 for each compound – were analyzed as 7-spin systems. According to standard NMR nomenclature, all the spectra are of the $ABCMX_3$ type. The labels A, B, and C refer to the 3 protons of the aromatic ring, and the labels M and X_3 designate, respectively, the "aromatic" fluorine nucleus and the 3 magnetically equivalent nuclei of the methyl or trifluoromethyl group. No couplings between ring nuclei and nuclei of the amino group were observed.

Spectra were analyzed in terms of chemical shifts and coupling constants, using the computer program [15] LAOCN3. A new Part I version of the computer program [16] LAOCOONII, having sub-routines for obtaining "stick" and line-shape plots on a Calcomp Plotter, were written.[17] The stick-plot routine made it easier to obtain the trial parameters needed for the iterative calculation.

The ring proton signals showed a distinct medium effect. The spectrum for each compound, that showed the highest number of resolved lines in the ABC part, was therefore analyzed first. The obtained coupling constants were then used as trial values for the remaining spectra of the same compound.

Trial parameters for the coupling constants between the ABC and M parts were found from first order analysis of the M part. The J_{F,CX_3} coupling constants were also obtained from first order analysis of the X_3 part in those cases where the splitting was resolved. Trial values for the remaining coupling constants were estimated from similar coupling constants of analogous compounds.

Reasonable trial values for the chemical shifts of the ring protons were assigned by looking at the intensity distribution of the ABC part, partly on the basis of splitting patterns and from long-range couplings, if observed, to the M and X_3 nuclei. Effects of the various substituents on the chemical shifts of the ring protons were also taken into account.

Some of the experimental PMR spectra showed little line structure, particularly in the neat liquids, due to nearly identical shifts. These spectra

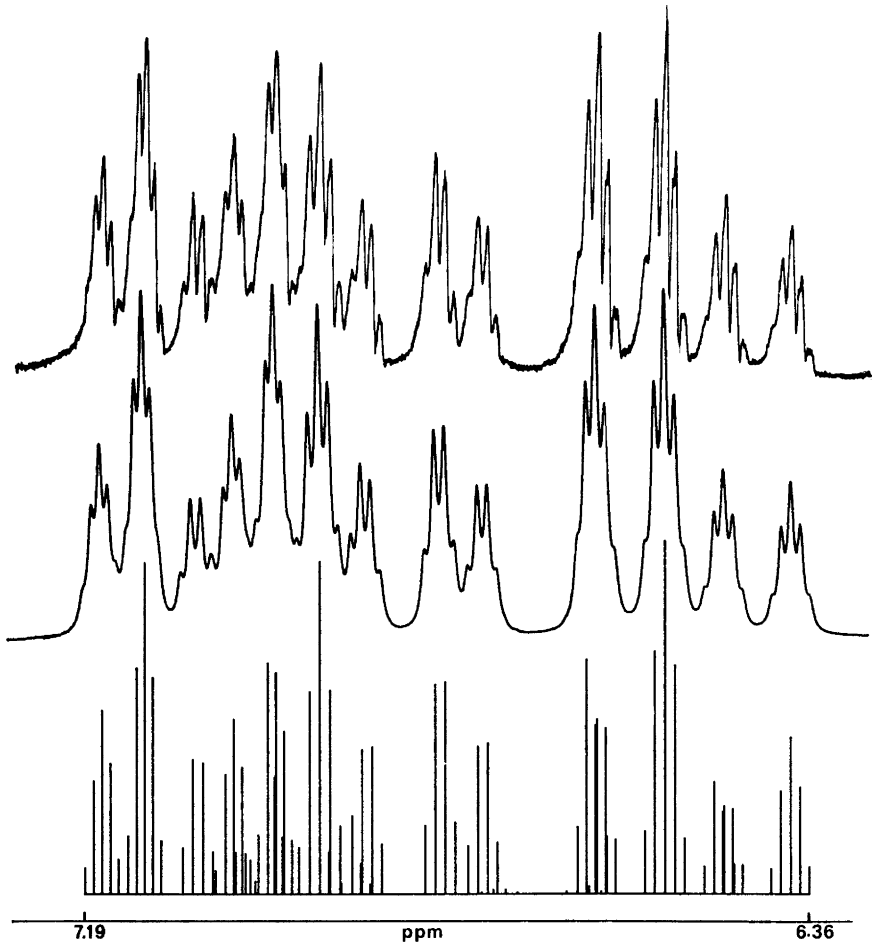


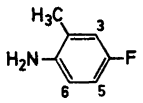
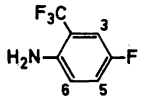
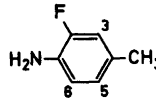
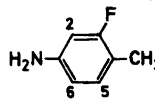
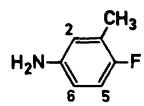
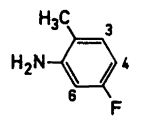
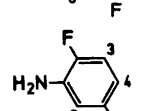
Fig. 1. Experimental (upper part) and theoretical (middle and lower part) proton spectra at 60 MHz of neat 2-trifluoromethyl-4-fluoroaniline.

were, however, improved in several cases by utilization of the induced solvent shift technique.

The final NMR parameters were obtained by iteration of all the resolved lines in the ABC part. The found parameters were also checked by comparing the computed spectra for the M and X_3 part with the corresponding experimental spectra. The root-mean-square deviations for the calculated and experimental lines were routinely 0.06 Hz or less. The calculated probable errors for the parameters were usually less than 0.04 Hz.

The experimental and calculated proton spectra for neat 2-trifluoromethyl-4-fluoroaniline are shown in Fig. 1, as an example of the quality of these analyses.

Table 1. Experimental and calculated proton chemical shifts (in ppm), for di-substituted anilines in 10 mol% carbon tetrachloride solution.

Structural formula[a]	Comp. No.	δ_{ortho}		δ_{meta}		δ_{para}		δ_{CH_3}	δ_{NH_2}
		exp.[b]	calc.	exp.[b]	calc.	exp.	calc.	exp.	
	I	6.41	6.37	6.65(3) 6.60(5)	6.51 6.53			2.06	3.29
	II	6.59	6.60	7.10(3) 6.96(5)	7.01 6.89				3.94
	III	6.50	6.37	6.68(3) 6.60(5)	6.51 6.57			2.19	3.41
	IV	6.20(2) 6.20(6)	6.12 6.16	6.81	6.78			2.10	3.63
	V	6.30(2) 6.26(6)	6.28 6.30	6.66	6.60			2.14	3.32
	VI	6.19	6.12	6.83	6.78	6.25	6.22	2.02	3.50
	VII	6.93	6.78	6.99	6.83	6.91	6.90		3.81

[a] Hydrogen atoms are designated *ortho*, *meta* and *para* with respect to the amino group.
[b] The figures in parentheses indicate the positions in the aromatic ring.

RESULTS AND DISCUSSION

The proton chemical shifts and coupling constants for the seven compounds (21 samples) studied are given in Tables 1, 2, 4, and 5. The chemical shifts are given in δ values (ppm) downfield from internal TMS. The interpretation of the NMR parameters is based on the results obtained for the 10 mol% solutions in carbon tetrachloride, because it is reasonable to assume that medium effects are negligible in those solutions.

Table 2. Experimental proton chemical shifts (in ppm) for di-substituted anilines.[a]

Comp. No.	δ_{ortho}	δ_{meta}	δ_{para}	δ_{CH_3}	δ_{NH_2}
I	6.33	6.62(3) 6.64(5)	–	1.86	3.42
	6.62	6.73(3) 6.66(5)	–	–	3.66
II	6.51	7.07(3) 6.89(5)	–	–	4.06
	6.93	7.14(3) 7.11(5)	–	–	4.55
III	6.48	6.64(3) 6.57(5)	–	2.07	3.62
	6.70	6.74(3) 6.68(5)	–	–	3.71
IV	6.19(2) 6.18(6)	6.77	–	2.07	3.61
	6.36(2) 6.36(6)	6.85	–	–	3.93
V	6.20(2) 6.24(6)	6.71	–	2.07	3.59
	6.48(2) 6.42(6)	6.69	–	–	3.71
VI[b]	6.35 6.41	6.87 6.89	6.28 6.23	2.01 –	4.06 4.15
VII	6.88 7.15	6.89 7.10	6.85 6.88	– –	3.92 4.77

[a] The first entry for each compound is for neat liquid, the second for 10 mol% acetone solution. The other symbols have the same meaning as in Table 1. [b] The first entry is for saturated solution in acetonitrile.

The 4 substituents dealt with in this study are of the inductive +I and −I types. If the mesomeric effect upon substitution to an unsaturated system is taken into account, a further sub-division is obtained, thus [18]

$-I^+$ type: F, NH_2
$-I^-$ type: CF_3
$+I^+$ type: CH_3

where the superscripts + and − designate the +M and −M mesomeric effects. It is noted that the substituents belonging to the $-I^+$ class have the most electronegative atom directly attached to the unsaturated system, while the $-I^-$ type has the electronegative atoms one position removed.[18]

The inductive and mesomeric charge displacements, occurring when the trifluoromethyl group is attached to an aromatic system, require some comments. The inductive effect of fluorine and trifluoromethyl is almost the same.[19] The strongly deactivating effect of the CF_3 group is, however, well recognized.[20] Sheppard argues, on the basis of pK_a measurements, substituent parameters, and ^{19}F chemical shift, that an interaction between the fluorine lone pairs on the CF_3 group with the π-system of the aromatic ring explains the −M effect.[20] Hyperconjugation of the CF_3 group with the aromatic ring has also been suggested as a possible mechanism.[21,22]

(a) *Chemical shifts of ring protons.* Several trends are apparent on comparison of the chemical shift data in Table 1. It appears that the amino group has a dominant effect on the shifts, in that the screening of protons increases in the order *meta*, *ortho*, and *para* to the amino group. Fluorine and trifluoromethyl have also a significant effect on the shifts. The proton shifts can be divided into several classes on this basis. The 5 compounds possessing a methyl substituent will be discussed first.

All shifts of protons *ortho* to the amino group appear in the range 6.19 to 6.50 ppm. Among these nuclei, protons *ortho* or *para* to fluorine produce a much narrower range of shifts (6.19 to 6.20 ppm), while protons *meta* to fluorine appear at lower field (6.26 to 6.50 ppm).

Protons *meta* to the amino group have shifts in the range 6.60 to 6.83 ppm. Within this group, chemical shifts of protons *ortho* or *para* to fluorine appear at 6.60 to 6.68 ppm, and protons being *meta* to fluorine produce the narrow range 6.81 to 6.83 ppm.

The only nucleus *para* to the amino group has a chemical shift of 6.26 ppm.

The two compounds possessing a CF_3 substituent produce chemical shifts in the wider range 6.59 to 7.10 ppm.

The chemical shifts of substituted benzenes are usually explained in terms of inductive and mesomeric effects, together with anisotropy and electric field effects resulting from substituent perturbation. π-Electron charge density is, however, a dominant factor in determining the *ortho* and *para* proton shifts, and perhaps the *meta* shifts too.[24–28] The small variation in the *meta* shift agrees well with predictions based on several molecular orbital (MO) calculations, in that substituent perturbation of the π-system should be smallest at the *meta* position.[1,26–28] MO calculations also predict that the π-charge densities at the *ortho* and *para* positions are similar.[1,26–28] A number of factors other than changes in π-electron density are likely to affect shifts of protons *ortho* to a substituent. The electric dipole field, magnetic anisotropy, and inductive mechanisms may have a significant effect at the *ortho* position.[1,23–31]

Before the chemical shifts of the 7 substituted anilines are discussed any further, it is appropriate to consider the shifts of the 4 mono-substituted benzenes: aniline,[11] toluene,[12] benzotrifluoride,[13] and fluorobenzene.[14] The numbers in Table 3 can be taken to represent the shifts of these compounds relative to benzene (*vide infra*).

Table 3. Substituent constants for mono- and poly-substituted benzenes, in ppm relative to benzene.[a]

Substituent X	$S_{o;X}$	$S_{m;X}$	$S_{p;X}$
NH_2	−0.75	−0.25	−0.63
CH_3	−0.21	−0.12	−0.19
F	−0.30	−0.03	−0.24
CF_3	+0.29	+0.11	+0.17

[a] δ (benzene) = 6.27 ppm.

The π-electron densities of aniline, fluorobenzene, and toluene have been calculated, using modified MO methods.[26–28] If the shifts of the ring protons reflect the change in π-electron density at the carbon atoms, the calculations predict that the *ortho* and *para* shifts should appear at successively higher field relative to benzene, in the series toluene, fluorobenzene, and aniline. The observed shifts agree with this prediction (Table 3). The increased π-electron density at the *ortho* and *para* carbons of toluene are expected to be caused by the hyperconjugative interaction of the methyl group with the π-electrons of the aromatic ring.[12] The *ortho* protons may also suffer a small shift due to electric field effects.[12]

In fluorobenzene,[14] the ring protons also experience a high-field shift (relative to benzene), as expected from π-electron density calculations.[26,27] Fluorine will, of all the halogens, most easily form a double bond with the ring carbon.[25] Fluorine donates electrons into the ring by resonance, thereby giving rise to high-field shifts of the *ortho* and *para* protons.[18,25,32]

The high-field shifts of the ring protons in aniline[11] again invoke the predominance of resonance effects. The anisotropy and electric field effects are probably too small to offset the resonance effect in fluorobenzene and aniline.[24,25,27]

The aromatic ring proton shifts in benzotrifluoride[14] appear at low field relative to benzene. This is as expected in view of the mesomeric effect of the CF_3 group. The dipole moment of benzotrifluoride is quite large (2.61 D), and would be expected to give rise to a sizable electric field effect at the *ortho* protons.

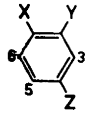
The chemical shifts of the *meta* protons are difficult to interpret. Current theories all seem to be inadequate in explaining the *meta* proton shifts in

substituted benzenes.[1,23,28] The hypothesis has, however, been put forward, that modifications of the ring-current intensity, occurring in the benzene ring upon substitution, may be one of the major contributions to the observed shifts.[28] This contribution has, however, been estimated to be no greater than 0.1 ppm. The validity of the ring current calculations seems open to doubt.[27]

Observed chemical shifts and π-electron density calculations of the mono-substituted benzenes discussed above, indicate that the amino group has the larger effect on the π-electron densities of the aromatic ring.

Some years ago, Diehl [2] showed that the effect of substituents on the ring proton shifts in *para* and *meta* di-substituted benzenes can be calculated empirically. He assumed the substituent effects on the shifts to be additively composed of partial *ortho*, *meta*, and *para* contributions. For *ortho*-di-substituted benzenes, the agreement was much poorer, predominantly due to the proximity of the two substituents. The additivity approach has since been found to give good agreement between calculated and observed chemical shifts in many poly-substituted benzenes.[1-4,24,25]

In a mono-substituted benzene C_6H_5X, the effect of the substituent X on the *ortho*, *meta*, and *para* positions are denoted,[1,2] $S_{o;X}$, $S_{m;X}$, and $S_{p;X}$, respectively, and similarly for substituents Y and Z. If these effects are additive, then for a 1,2,4-tri-substituted benzene, the chemical shift contributions become



$$\delta_{o;X} = S_{o;X} + S_{m;Y} + S_{m;Z}$$
$$\delta_{m;X}(3) = S_{m;X} + S_{o;Y} + S_{o;Z}$$
$$\delta_{m;X}(5) = S_{m;X} + S_{p;Y} + S_{o;Z}$$

Substituent constants for the amino and methyl groups, calculated for dilute solutions in carbon tetrachloride of di- and tri-substituted benzenes,[4] are given in Table 3. Substituent constants for fluorine and trifluoromethyl are not available. These constants can, however, be calculated from the ring proton shifts of fluorobenzene,[14] and benzotrifluoride [13] in dilute CCl_4 solutions (Table 3). Using these constants, fairly good agreement between calculated and observed shifts was obtained for the di-substituted anilines (Table 1). Relative chemical shifts agree in general to within 0.1 ppm with the observed shifts, except for compounds III and VII, where fluorine is *ortho* to the NH_2 group. It is obvious that the addition concept predicts the correct trends for the shifts. However, the calculated shifts appear on the high-field side of the corresponding observed shifts.

In the studied series of compounds, two of the substituents are always adjacent to each other. Deviations from the additivity rule is therefore expected, predominantly due to steric and mutually inductive effects. Van Meurs [4] has found that the *meta* and *para* substituent constants generally remain unchanged for substituted benzenes with isolated as well as adjacent substituents. At least two sets of *ortho* constants, however, appear to be needed.[4] Modified *ortho* substituent constants are not available for the substituents dealt with in this paper, apart from the methyl group.[4] All quoted modified constants, however, have smaller absolute values than the correspond-

ing constants for isolated substituents.[4] Therefore, if this effect were taken into account, it would presumably bring the experimental and calculated shifts into better agreement. The simultaneous presence of two groups of opposite mesomeric effect (*e.g.*, NH_2 and CF_3) might be expected to lead to rather large deviations from additivity. The chemical shift data, however, indicate that such effects are of minor importance in the series of compounds studied.

The above results indicate that the effects of the various substituents on the chemical shifts indeed are fairly independent of each other, but interactions mainly of steric and inductive origin, occurring between *ortho* substituents, cause deviations from additivity. Evidence for weak intramolecular hydrogen bonding has been found for 2-iodoaniline and 2-bromoaniline, but not for 2-fluoroaniline.[33]

It can also be concluded that the amino group has a dominant effect on the shifts by increasing the π-electron density in the aromatic ring. Fluorine and methyl appear to enhance this effect, by resonance, in near additive way.

The π-electron charge redistribution induced in the aromatic ring by the CH_3 and CF_3 groups is complementary. This can be seen by comparing the shifts of compound I and II. The effect is largest at protons *ortho* and *para* to the exchanged groups, and much smaller at the *meta* position. This confirms the results of MO calculations, that the effect on the π-electron density upon substitution is smallest at the *meta* position.

The extreme limits for the chemical shifts of aromatic protons in the two compounds, possessing a CF_3 group, occur in the same molecule at 7.10 and 6.59 ppm. This is at the low-field side of the aromatic proton shifts for the 5 compounds possessing a methyl instead of trifluoromethyl substituent (one exception). The extreme high-field shift (6.59 ppm) is found for the proton *ortho* to the NH_2 group and *meta* to the CF_3 group. The extreme low-field shift (7.10 ppm) is, on the contrary, suffered by the proton *meta* to the NH_2 group, and *ortho* to the CF_3 group. This is as expected, on basis of MO calculations, since these two groups have opposite resonance effects.

A distinct solvent effect is observed for the proton shifts on going from carbon tetrachloride to acetone solution. Relative to the observed shifts in carbon tetrachloride, the resonance signals of the aromatic protons and the amino protons are shifted to lower magnetic field in acetone solution. The *ortho* protons of the di-substituted anilines possessing both F and CH_3 substituents, experience a downfield shift of 0.16 to 0.22 ppm relative to the corresponding shifts in CCl_4 solutions. The *meta* and *para* protons also suffer a reduced shielding, but to a smaller extent (0.03 to 0.08 ppm). The benzotrifluorides show the same reduced screening of the aromatic protons, but the scattering in the shifts is greater.

These results agree with the observations that dilution in acetone generally causes low-field shifts relative to the corresponding shifts in an inert aliphatic solvent.[1,34,35] The magnitude of the solvent shifts varies in a regular manner with the position of the protons in the solute molecules. The down-field shift is greatest for the amino protons (*vide infra*), and then diminishes gradually for the aromatic protons on going from the *ortho* to the *para* position relative

to the amino group. This may imply that there is a certain preferred orientation between solute and solvent molecules. The solute molecules will probably orient themselves in planes roughly parallel to the heavy-atom skeleton of acetone,[35] with the NH_2 group situated closest to the acetone molecules. The amino hydrogens may also interact by weak hydrogen bonding with acetone. Hydrogen bonding could possibly explain the fairly large downfield shifts of the amino protons in acetone solution. Dyall[33] has examined the N–H stretching frequencies of a number of primary anilines in various solvents. The anilines were observed to form both 1 : 1 and 1 : 2 complexes with hydrogen bond acceptor molecules, such as acetone. Usually, *ortho* substituted anilines form only 1 : 1 complexes, in which the amino hydrogen involved in the association is the one remote from the *ortho* substituent.

The contribution of reaction field effects to the proton screening may become significant in a solvent of high dielectric constant, such as acetone. This contribution will, however, vary with the position in the solute molecules, and will not give rise to the observed regular solvent shifts.

The aromatic proton shifts in the neat liquids do not display the same regular medium effect. The chemical shift differences vary irregularly from 0.05 to −0.10 ppm, relative to the corresponding shifts in the CCl_4 solutions. Most of the aromatic protons, however, experience increased shielding. This high-field shift can be mainly attributed to the ring current effect of neighbouring molecules, because the aromatic solute molecules are further apart in solution than in neat liquids.

(b) Chemical shifts of amino protons. Yonemoto and co-workers[36] have observed the chemical shifts of the amino protons of *meta* and *para* substituted anilines, within a small range. This was interpreted in terms of small changes in the π-electron density on the nitrogen atom upon substitution. The much larger down-field shifts (relative to aniline) in the *ortho* substituted anilines were attributed to weak hydrogen bonding of the amino hydrogens with the substituent lone pair.

Amino proton shifts reported for mono-substituted anilines reveal that fluorine at *ortho* and *meta* positions causes deshielding (*ca.* 0.1 ppm) relative to aniline.[36] *para*-Substituted fluorine, on the contrary, gives rise to increased shielding (*ca.* 0.1 ppm).[36] Methyl substitution at all positions produce high-field shifts (*ca.* 0.1 ppm).[36,37] A relatively small resultant effect of the substituents methyl and fluorine is therefore expected on the shielding. The results of this investigation (Table 1) confirm this, in that the measured amino proton shifts in carbon tetrachloride solution are all fairly close to the corresponding shift of aniline[37] in the same solvent (3.31 ppm).

The trifluoromethyl group, however, causes a larger deshielding of the amino protons. In *ortho* and *meta* trifluoromethyl aniline, the amino proton shifts increase by 0.34 and 0.28 ppm, respectively, relative to aniline.[37] This observation is qualitatively confirmed by the results of this study. The amino proton shifts of the two compounds possessing a CF_3 substituent *ortho* or *meta*, respectively, to the amino group, appear fairly close to each other. This indicates that the deshielding is not primarily caused by intra-molecular hydrogen bonding between the amino hydrogens and the fluorine lone electron

pairs of the *ortho* substituent.[36] Reasonably, the substituent effect of the CF_3 group is transmitted *via* the π-electron system.

The amino protons suffer a low-field shift (0.30 to 0.98 ppm) in acetone solution relative to carbon tetrachloride solution. This acetone dilution shift has already been attributed to anisotropy effects. A similar deshielding is also observed for the neat liquids, apart from compound IV, where there is a small high-field shift. These displacements of the chemical shifts can again be attributed to differential anisotropic shielding exerted by the medium.

(c) *Chemical shifts of the methyl protons.* A linear relationship has been observed between methyl proton shifts of substituted toluenes and ring protons at the same position in the ring after replacing the relevant methyl group by hydrogen.[25,38,39] The effect of the substituents on the screening of the methyl protons was therefore attributed to the same origin as for the aromatic protons. The effect is, however, reduced for the methyl protons, as would be expected owing to larger distance from the aromatic ring.

The methyl proton shifts in carbon tetrachloride solution, measured in this investigation, display increased screening relative to toluene (2.37 ppm) in the same solvent.[38] These high-field shifts are expected in view of the substituent effects discussed before. Whether the small variation of the proton shifts argues for hyperconjugation of the methyl group with the ring, is questionable.

For the pure liquids, the methyl protons suffer increased shielding relative to the carbon tetrachloride solutions. This is contrary to the effect observed for the amino protons, in 6 of 7 compounds, and is again attributed to specific medium interactions.

(d) *H – H coupling constants of the aromatic ring.* The H – H coupling constants, J_{HH}, which have been obtained in this work, are all seen to fall within the characteristic range of values expected for *ortho*, *meta*, and *para* coupling constants [1] (Tables 4 and 5). Medium effects on ring proton coupling constants are usually small and, at any rate, difficult to interpret. Only the coupling constants obtained for the 10 mol% solutions in carbon tetrachloride will therefore be discussed.

Effects of substituents on the H – H coupling constants appear to be short-range. It is therefore believed that the variations of these parameters are primarily determined by inductive effects.[1,7,11,35,40,41] Further evidence for this is also the lack of correlation between chemical shifts (strongly influenced by mesomeric effects) and coupling constants.[7] The propagation of the spin-spin coupling (possible except the *para* coupling) therefore presumably involves the σ-electrons.[1,11–13] The *para* coupling has also been attributed to $\sigma - \pi$ interactions.[1,12,13] Williamson *et al.*,[12] however, argue that all the proton couplings of the aromatic ring are governed by the same mechanism.

At this stage, it is appropriate to discuss briefly the relevant coupling constants of aniline,[11] toluene,[12] fluorobenzene,[14] and benzotrifluoride.[13] If compared with the corresponding parameters of benzene (Table 6), the qualitative variations of the coupling constants between the ring protons are similar to those observed for numerous mono-substituted benzenes.[1,11–14] It is seen that the perturbation introduced by the substituents attenuates rapidly and

Table 4. Experimental and calculated coupling constants (in Hz) for di-substituted anilines in 10 mol% carbon tetrachloride solution.

Compound No.[a]	J^o_{HH}		J^m_{HH}		J^p_{HH}	J^o_{HF}	J^o_{HH}	J^m_{HF}	J^m_{HH}	J^p_{HF}	J_{H,CX_3}		
	exp.	calc.	exp.	calc.	exp.	exp.[b]	exp.	exp.[b]	exp.	exp.	*ortho*[b]	*meta*[b]	para
I	8.59	8.83	2.87	2.86	0.42	9.20(3,4) 8.20(4,5)	7.47 7.38	4.71	1.24	–	– 0.72	~ 0.0	– 0.55
II	8.92	8.85	2.98	2.84	0.23	8.65(3,4) 7.68(4,5)	7.78 7.40	4.42	1.03	–	– 0.54	0.75	– 0.70
III	7.94	8.03	1.83	1.79	0.48	11.99	8.12	9.48	2.66	– 1.28	– 0.62(3,4) – 0.67(4,5)	~ 0.0	–
IV	8.12	8.03	2.21	2.36	0.34	11.42	8.12	8.66	2.09	– 0.90	– 0.76	0.53(2,4) 0.40(2,6)	–
V	8.50	8.83	2.90	2.85	0.37	9.32	7.47	6.41(2,4) 3.96(4,6)	1.60 0.99	–	– 0.75	0.33	– 0.57
VI	8.21	8.31	2.64	2.61	0.29	10.15(5,6) 8.34(4,5)	8.01 7.38	6.38	1.34	–	– 0.74	0.43(2,6) 0.31(2,4)	–
VII	8.44	8.60	2.12	2.15	0.38	11.14	8.03	7.76(2,6) 3.84(2,4)	2.40 0.99	–	– 0.67(5,6) – 0.73(4,5)	0.85	–

[a] The number of the compound refers to Table 1. [b] The figures in parentheses designate the position of the coupled nuclei in the aromatic ring.

Table 5. Experimental coupling constants (in Hz) for di-substituted anilines.[a]

Comp. No.	J^o_{HH}	J^m_{HH}	J^p_{HH}	J^o_{HF}	J^m_{HF}	J^p_{HF}	J_{H,CX_3}		
							ortho	*meta*	*para*
I	8.53	2.99	0.49	9.54(3,4) 8.52(4,5)	5.05	–	−0.77	0.34	−0.57
	9.43	3.20	~0.0	9.56(3,4) 8.68(4,5)	4.92	–	−0.74	0.32	−0.44
II	8.93	3.01	0.34	9.06(3,4) 8.05(4,5)	4.56	–	−0.56	0.74	−0.74
	9.05	3.05	0.47	9.19(3,4) 8.00(4,5)	4.92	–	−0.45	0.68	−0.71
III	8.19	1.92	0.26	12.20	9.83	−1.36	−0.62(3,4) −0.65(4,5)	~0.0	–
	8.02	1.83	0.36	11.76	10.28	−1.80	−0.73(3,4) −0.58(4,5)	~0.0	–
IV	8.14	2.31	0.27	11.71	8.88	−0.60	−0.73	0.37(2,4) 0.29(4,6)	–
	8.13	2.28	0.30	12.13	8.99	−0.44	−0.71	0.36(2,4) 0.31(4,6)	–
V	8.54	2.85	0.46	9.63	5.89(2,4) 4.17(4,6)	–	−0.77	0.36	−0.57
	8.53	2.87	0.62	9.61	7.30(2.4) 4.26(4,6)	–	−0.71	0.38	−0.56
VI	8.25	2.59	0.26	11.20(5,6) 8.85(4,5)	6.74	–	−0.85	0.42(2,6) 0.30(2,4)	–
	8.24	2.66	0.26	11.20(5,6) 8.79(4,5)	6.60	–	−0.73	0.38(2,6) 0.34(2,4)	–
VII	8.63	2.16	0.43	10.30	8.73(2,6) 4.73(2,4)	–	−0.47(5,6) −0.68(4,5)	0.78	–
	8.48	2.34	0.30	10.99	8.29(2,6) 4.26(2,4)	–	−0.55(5,6) −0.74(4,5)	0.79	–

[a] Experimental conditions and meaning of symbols as in Table 2.

Table 6. Effects of substituents on the H – H coupling constants in mono-substituted benzenes.[10–14]

Substituent [a]	ΔJ^{o}_{23} [b]	ΔJ^{o}_{34}	ΔJ^{m}_{24}	ΔJ^{m}_{26}	ΔJ^{m}_{35}	ΔJ^{p}_{36}
NH_2	0.48	−0.15	−0.26	1.16	0.23	−0.22
CH_3 [c]	0.10	−0.01	−0.12	0.49	0.13	−0.08
F	0.82	−0.07	−0.30	1.37	0.45	−0.26
CF_3	0.39	0.01	−0.13	0.59	−0.08	−0.09

[a] Numbering begins with substituent.
[b] Defined as the difference (in Hz) between corresponding coupling constants in benzene and mono-substituted benzene in CCl_4 solution.
[c] Derived from data for neat toluene.

is not appreciable beyond the carbons *ortho* to the substituent, as expected for an inductive effect.

The variation in the coupling constants for the 7 compounds studied in this work is fairly small ($\lesssim 1.0$ Hz). This is as expected in view of the fact that the coupling constants of substituted benzenes are not affected appreciably by the nature of the substituents, except for small systematic variations. Another point is that the studied compounds all have about the same total electronegativity of the substituents, and this parameter has been shown to be linearly related to the coupling constants in substituted benzenes.[1,5,6] It is also believed that the σ-system becomes less susceptible to perturbation with increasing substitution.[10]

The additivity of substituent effects on aromatic coupling constants has been established for several poly-substituted benzenes.[7–10,43,44] The coupling constants have been calculated from data of the relevant mono-substituted benzenes by an additivity scheme, similar to the one applied for the chemical shifts. The agreement between predicted and observed coupling constants is usually fairly good, though small saturation effects have been observed when a coupled hydrogen has two *ortho* substituents.[10]

The substituent constants, ΔJ, applied in this work have been calculated, using the benzene values [45] $J^{o}_{HH} = 7.54$ Hz, $J^{m}_{HH} = 1.37$ Hz, and $J^{p}_{HH} = 0.69$ Hz, together with the corresponding parameters for the relevant mono-substituted benzenes.[10–14] The ΔJ values listed in Table 6 refer to dilute solutions in carbon tetrachloride, except for toluene, where only the spectral parameters for the neat liquid are available.[12] Castellano and co-workers [11] have, however, reported the dilution effect on these parameters to be smaller than the estimated experimental error (< 0.05 Hz), for a series of mono-substituted benzenes.

Using the ΔJ values summarized in Table 6, the *ortho* and *meta* coupling constants have been calculated for the present compounds (Table 4). The small magnitude and relatively large uncertainties of the *para* coupling constants did not make it worthwhile to predict those parameters. The agreement between experimental and additivity-calculated coupling constants is fair, considering that the error resulting when adding up various ΔJ contributions may be cumulative. The saturation effect observed by Schaefer and

co-workers [10] should mainly affect the *meta* coupling constants of the present work. This is not observed by the present authors. The *ortho* coupling constants have, on the contrary, larger deviations between experimental and predicted values than the *meta* coupling constants. The results of this study seem to verify that the substituent effects on the H – H coupling constants are indeed additive within the limits of accuracy of the experimental data.

(e) *Long-range coupling of methyl or trifluoromethyl to protons of the aromatic ring.* All the measured long-range H – X coupling constants, J_{H,CX_3}, in carbon tetrachloride solutions are given in Table 4. The relative signs of these parameters were obtained directly from the computer. It is seen that the *ortho* and *para* side-chain coupling constants both are negative and of approximately the same magnitude. The *meta* coupling constants are of opposite sign (positive) and much smaller, except for compounds II and VII, where the long-range coupling involves the CF_3 group. Both the magnitudes and signs of these coupling constants agree with earlier investigations on a series of benzene derivatives.[12,13,46–50] The sign sequence, negative, positive, and negative, for the *ortho*, *meta*, and *para* side-chain coupling constants, respectively, has been obtained by applying double resonance techniques on the PMR spectra of 2-bromo-5-chloro toluene [47] and 2,6-dinitro benzaldehyde,[49] and from spectral analysis of the toluene [12] PMR spectrum.

The long-range coupling constants, J_{H,CF_3}, have also been reported to have the same sign sequence, from spectral analysis and tickling experiments on the PMR spectra of benzotrifluoride [13] and 2-amino-5-bromo benzotrifluoride,[48] respectively. It is interesting to note that the methyl-methyl H – H coupling constants in xylene derivatives have been reported to have the same signs as the corresponding proton-methyl coupling constants.[51]

The relative signs and magnitudes of J_{H,CX_3}, in substituted toluenes, benzotrifluorides, and benzaldehydes, have been qualitatively interpreted in terms of $\sigma-\pi$ mechanisms, involving hyperconjugation of the CX_3 group with the aromatic ring. A substantial σ-electron contribution to J^m_{H,CH_3}, has, however, been proposed.[13,48,51] MO calculations of the $\sigma-\pi$ interactions [48] predict that J^o_{H,CH_3} and J^p_{H,CH_3} should be negative, and that J^m_{H,CH_3} should have a small positive value. In several fluorinated compounds,[13,48] however, J^m_{H,CF_3} has about the same absolute value as the corresponding *ortho* and *para* coupling constants. This observation has been rationalized by postulating a larger positive σ contribution [13,48] to J^m_{H,CF_3} than to J^m_{H,CH_3}. From comparison of the long-range coupling constants of toluene and benzotrifluoride, it has been suggested that the hyperconjugation of the CF_3 group with the ring is comparable to that of the CH_3 group.[13,48] The near identity of corresponding H – H and H – F coupling constants in compounds I and II also indicates that the CH_3 and CF_3 groups have similar effects on the coupling constants.

The long-range coupling constants reported in this paper support previous interpretations in the sense that the parameters have the same signs and similar magnitudes.

(f) *H – F coupling constants of the aromatic ring.* The measured H – F coupling constants, J_{HF}, are collected in Tables 4 and 5. It is seen that several of the H – F coupling constants are subject to significant solvent effects. In

order to minimize this source of error, the discussion will again be based on the parameters in the carbon tetrachloride solutions.

The H – F coupling constants fall within the usual ranges. These ranges are, however, larger and not as well-defined as the corresponding ranges for H – H coupling constants. It is seen that three J^m_{HF} values are larger than the minimum value of J^o_{HF}.

The relative signs of these H – F coupling constants were obtained from the complete analyses of the spectra. The *ortho* and *meta* H – F coupling constants are reported to have the same sign (positive) as the H – H coupling constants in substituted benzenes.[1,44,52–54] The *para* H – F coupling constants, unlike those of the protons, have, however, been observed to have either sign relative to the other H – F coupling constant.[1,44,52–54]

By comparing the H – F coupling constants listed in Table 4 with the corresponding fluorobenzene data [44] ($J^o_{HF} = 9.31$, $J^m_{HF} = 5.79$, and $J^p_{HF} = 0.34$ Hz), it is seen that these parameters are considerably influenced by the substituents. The largest values of both the *ortho* and *meta* H – F coupling constants occur in the compounds possessing NH_2 and CH_3 (or CF_3) substituents *para* to each other. The *para* H – F coupling constants measured in these compounds also have quite large values, and opposite sign, compared to fluorobenzene. This is reasonable, since *ortho* substituents have been found to have a relatively large effect on the *para* H – F coupling constants.[44] The smaller *ortho* and *meta* H – F coupling constants are, with a few exceptions, observed in compounds possessing the NH_2 and CH_3 (or CF_3) substituents *ortho* to each other.

The magnitude of the H – F coupling constants appears to depend on the positions of the substituents relative to the H – F fragment as a whole, rather than on the positions relative to the individual H and F atoms. This effect can, in particular, be observed by comparing the relevant *ortho* H – F coupling constants of compounds III and IV, and I and VI, respectively. The *meta* H – F coupling constants of compounds III and IV also have comparable values. Apart from this, it appears difficult to perceive any well-defined relations between the positions of the substituents and the corresponding variations in the coupling constants.

Additivity of substituent effects on H – F coupling constants has been established for some di- and tri-substituted benzenes.[52] A similar calculation cannot, however, be performed on the present compounds, because the data of the relevant mono-substituted fluorobenzenes are not available. It might also be of interest to investigate if a correlation exists between H – F and corresponding H – H coupling constants obtained on replacing fluorine by hydrogen in the present anilines. The relevant data are again lacking. The H – H coupling constants have, however, been estimated, using the established additivity relationship and the data of Table 6. These "expected" *ortho* and *meta* coupling constants are summarized in Table 4. By plotting experimental H – F coupling constants against "expected" H – H coupling constants (not shown here), rough linear correlations were obtained. It therefore seems that the substituents partially have the same effect on the H – H as on the H – F coupling constants, though the interpretation of the latter parameters presents, in general, a more difficult problem.

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