[Chem. Pharm. Bull. 17(9)1854—1863(1969)] UDC 543.422.25 : 547.551.03

Nuclear Magnetic Resonance Spectra of *ortho*-Haloanilines—Analysis of Four-Spin Systems and Study of Solvent Effects on the Spectra

Mamoru Kamiya

Shizuoka College of Pharmacy[1]

(Received February 27, 1969)

The NMR spectra of *ortho* haloanilines measured in various solvents were analyzed as ABCD spin systems and the proton chemical shifts and spin–spin coupling constants were determined. Upon these data, solvent effects on the internal chemical shifts were investigated. The main feature in the solvent effects was the selective deshielding of the proton *ortho* to the amino substituent in polar solvents. The above shift in polar solvents was explained by a specific solute–solvent association involving a hydrogen-bonding formation which was competitive with the intramolecular interaction between the substituents and a polar mesomeric structure of the solute molecule was also considered for the explanation of the variation of the other internal chemical shifts. Furthermore, the solvent shifts in inert solvents and toluene were discussed. The proton chemical shifts of the isolated molecules were found to have large departures from those predicted by the additivity rule.

Introduction

Recently, vigorous studies have been made about the solvent effects on the nuclear magnetic resonance (NMR) spectra of substituted benzenes, and in certain derivatives the spectra of the ring protons were found to be strongly affected by the nature of solvents. In these cases, the proton shieldings alone, with little alteration of the spin–spin coupling constants, vary in specific ways dependent upon the positions relative to substituents, which gives rise to changes in the internal chemical shifts of the related protons and a remarkable variation in the over-all appearance of the NMR spectrum. As regards the main factors controlling this effect, the followings were pointed out previously;[2] 1) purely magnetic contributions due to solute-solvent interactions in the applied magnetic field, 2) polar interactions between solute and solvent molecules as influenced by changes in the dielectric constant of medium, 3) steric effects due to bulky substituent groups influencing solute-solvent interactions, 4) specific molecular interactions involving complex formations where solvent and solute molecules have preferred orientations with respect to each other.

Actual interactions in the present system, however, appear to complicatedly change according to the degree to which the above factors are combined together. Thus, case-by-case insights into the solvent effects are essential for better understandings of solute–solvent molecular interactions as well as some specific factors dominating the proton shieldings. This will be nicely illustrated by an earlier study[2a] of the solvent effects on a number of *para*-disubstituted benzenes where the authors have been led to a conclusion for the presence of a specific interaction through a preferential hydrogen-bonding formation between the ring protons and solvent molecules such as acetone or benzene. It seems, meanwhile, that the compounds employed in the previous works, including several attempts[3–5] to predict the

1) Location: *Oshika 160, Shizuoka.*
2) *a*) T. Schaefer and W.G. Schneider, *J. Chem. Phys.*, **32**, 1218 (1960); *b*) A.D. Buckinghum, T. Schaefer and W.G. Schneider, *ibid.*, **32**, 1227 (1960).
3) P. Diehl, *Helv. Chim. Acta*, **44**, 829 (1961).
4) P. Diehl, *Helv. Chim. Acta*, **45**, 568 (1962).
5) P. Diehl, *J. Chim. Phys.*, **61**, 199 (1964).

total solvent shifts generally upon the additivity of an absolute contribution allotted to each substituent using the data for various sorts of the derivatives, have been largely concentrated, though with extensive modifications of substituents, on such types of molecules as *mono*-substituted or *para*- and *meta*-disubstituted ones where (the analysis of the over-all spectrum for the extraction of the chemical shifts is simplified to a much extent by using molecular symmetry and somewhat puzzling perturbations arising from the solvent dependent interactions between the substituents can be well eliminated.

In the work described here, measurements and discussions on solvent effects have been selectively made about the NMR spectra of a series of *ortho*-haloanilines containing the mutually interacting two substituents, one of which is amino group, a typical hydrogen–donor, and the other chlorine, bromine or iodine atom as known to have considerable electronegativity and diamagnetic anisotropy. The variations in the relative chemical shifts between all the ring protons have been carefully checked under various solvent states by using the magnetic parameters derived from an iterative complete analysis for individual spectrum measured at a definite experimental condition.

Experimental

The solvents employed here were, for the most part, tetrachloromethane, deuterochloroform, deuterobromoform, acetone-d_6, dimethyl sulphoxide-d_6, methanol-d_4, pyridine-d_5, toluene-d_8. Deuterated solvents were obtained from Merk. Tetrachloromethane may be regarded as a relatively inert solvent, capable only of interacting by ordinary Van der Waals forces. Chloroform and bromoform are weak hydrogen–donors, acetone, dimethyl sulphoxide, methanol and pyridine being strong n-type donor solvents by virtue of the lone–pair electrons on the oxygen or nitrogen atom, while toluene is a weak π–electron donor. Methanol can act also as a hydrogen–donor and pyridine as a π–electron donor.

Dilute solutions of the compounds in each solvent were made up, for convenience, to a uniform concentration of 5 mole per cent. Each solution contained in a 5 mm o.d. sample tube was degassed thoroughly by the repetitions of freezing in liquid nitrogen, pumping and thawing and was sealed under a high vacuum.

The spectra were measured relative to TMS internal reference at 60 MHz using a high resolution JNM–C–60H spectrometer. Transition frequencies were determined by averaging several independent recordings.

Internal reference method was used because of the tediousness and errors of the bulk susceptibility corrections which are necessary with external reference method. Accordingly, caution was paid in the interpretations of the solvent shift data such that the relative chemical shifts between the ring protons were used as far as possible.

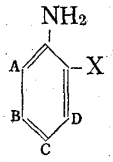
Analysis of Spectra

The analyses of the spectra for the determination of the chemical shifts and spin–spin coupling constants were performed with a refined iterative method developed by Swallen and Reilly,[6] of which details were introduced elsewhere. Actual numerical calculations were carried out with the Tokyo University HITAC 5020 computer. A more general method by Anderson and McConnell[7] involves the measurement of the moments of the spectrum from which the relations between the chemical shifts are derived. However, as this method depends on the precise measurements of the areas beneath the spectral lines, it was found to be difficult to accurately apply to the present spectrum, although it provides some information for the most intractable problem.

As the spin–spin coupling constants connecting benzene ring protons have known to be only slightly affected by substituents and solvents, the main problem, then, was to find the chemical shifts of the ring protons, and since the appearance of the spectrum depends on the relative magnitudes of the chemical shifts, only three parameters were involved in fact. At any rate, some preliminary informations of the magnetic parameters were required in order to obtain correct assignments of the spectral lines which are necessary for the determination of the energy levels of the spin state functions.

The resonance frequencies of the ring protons in the isolated solute molecule were assumed to be in an order of $\nu_A<\nu_C<\nu_B<\nu_D$ because the effects of a substituent on the proton shieldings were likely to act upon an *ortho*–proton more strongly than a *para*–proton and an amino group tends to increase the shielding of the ring protons while a halogen atom reduces the shielding (Here, the ring protons are designated as follows throughout the present work).

6) J.D. Swallen and C.A. Reilly, *J. Chem. Phys.*, **37**, 21 (1962).
7) W. Anderson and H.M. McConnell, *J. Chem. Phys.*, **26**, 1496 (1957).



According to this tentative relationship, the main features of the spectral changes illustrated in Figure 1 were attributed to the selective shift of the resonance frequency of the A proton. For example, in the spectra of the Cl deriv. A multiplet, *i.e.* those lines which in a first-order spectrum approximation correspond to the spin inversion of the A proton, can not be easily identified in inert solvents because of a slight difference between the resonance frequencies of the A and C protons while it becomes close to a first-order spectrum pattern in acetone and methanol which is composed of the two quartets of the 7, 8, 10, 11 lines and of the 13, 14, 15, 16 lines; the former is crossed with the lower-field doublet involved in the simultaneously simplified multiplet of the C proton. In pyridine and dimethyl sulphoxide, it shifts further towards a low field until all of the lines locate just between the B and C multiplets. In this case, using a first-order spectrum approximation, J_{AB}, J_{AC} and J_{AD} can be readily guessed from the A multiplet, J_{BC} and J_{CD} from the C multiplet, and J_{CD} from the D multiplet. These approximate coupling constants were used as fixed value in the trial-and-error simulative calculations of the spectra which were performed with the change of the resonance frequencies of the ring protons.

Results and Discussion

The internal chemical shifts between the ring protons in several typical solvents are summarized in Table I, the details of the observed and calculated spectra being listed in the appendix with the best fitting magnetic parameters.

Table I. The Internal Chemical Shifts (cps) between the Ring Protons and the Chemical Shifts of the Amino Protons relative to TMS in Polar and Non-Polar Solvents

Solvent	Solute	$\nu_A-\nu_C$	$\nu_D-\nu_A$	$\nu_B-\nu_A$	$\nu_B-\nu_C$	$\nu_D-\nu_B$	$\nu_D-\nu_C$	ν_{NH_2}
CCl_4	I	− 2.81	37.72	24.09	21.28	13.62	34.90	228.5
	II	− 0.42	46.33	28.24	27.82	18.09	45.91	229.3
	III	13.97	55.36	24.92	38.90	30.44	69.33	230.2
$CDBr_3$	I	− 4.62	40.72	26.14	21.52	14.58	36.10	238.5
	II	4.96	42.35	23.45	28.41	18.90	47.31	237.7
$CDCl_3$	I	− 0.81	35.19	22.59	21.78	12.60	34.38	231.2
	II	3.95	44.27	24.36	28.31	19.91	48.22	234.0
C_6D_5N	I	16.56	22.38	7.87	24.43	14.51	38.94	312.4
	II	22.50	32.82	14.47	36.97	18.35	55.32	313.5
$(CD_3)_2CO$	I	9.43	25.27	14.90	24.34	10.37	34.71	251.8
	II	20.48	32.56	10.37	30.85	22.19	53.04	264.2
	III	26.49	44.92	15.34	41.82	29.58	71.40	265.7
$(CD_3)_2SO$	I	16.59	19.52	9.50	26.09	10.03	36.12	250.3
CD_3OD	I	10.02	23.97	13.07	23.09	10.90	33.99	285.0
	II	14.08	33.96	15.74	29.82	18.23	48.04	262.5

I, II and III represent chloro-, bromo- and iododerivatives, respectively.

Fig. 1 illustrates a solvent dependent change of the NMR spectra quoted from the data for *ortho*-chloro and bromo-anilines which well represent the main features in the solvent dependent shifts of the spectra of all the compounds investigated here.

From this it can be implied that the changes of the spectra are so large as to make meaningless the determination of the relative chemical shifts unless solvent conditions (types of solvent and degree of dilution) are specified.

One of the profound solvent effects is that the proton *ortho* to the amino group is selectively deshielded in hydrogen-bonding polar solvents such as acetone, dimethyl sulphoxide, methanol and pyridine. An identical result has been suggested in the system of *ortho*-bromoaniline plus acetone.[8] From the pertinent data in Table I it can be known more definitely that in a

8) S. Clough, *Mol. Phys.*, **2**, 349 (1959).

fixed solute molecule the magnitude of an internal chemical shift $\nu_A - \nu_C$ of which sign is often minus in inert solvents but plus in polar solvents tends to increase in a sequence of acetone, methanol<pyridine. Such is also to be the case with the concurrent low-field shift of the signal of the amino protons (The result was somewhat exceptional in dimethyl sulphoxide).

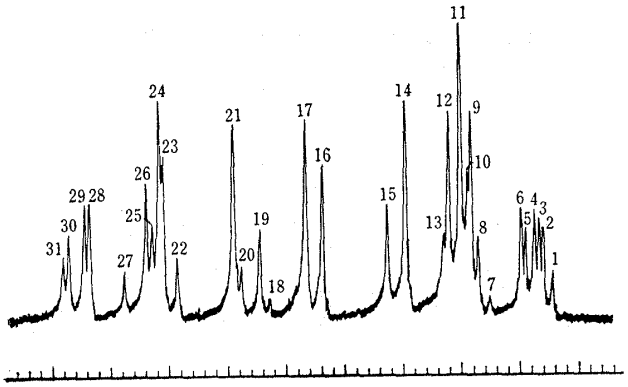


Fig. 1a. The Spectrum of *ortho*-Chloroaniline measured in Tetrachloromethane

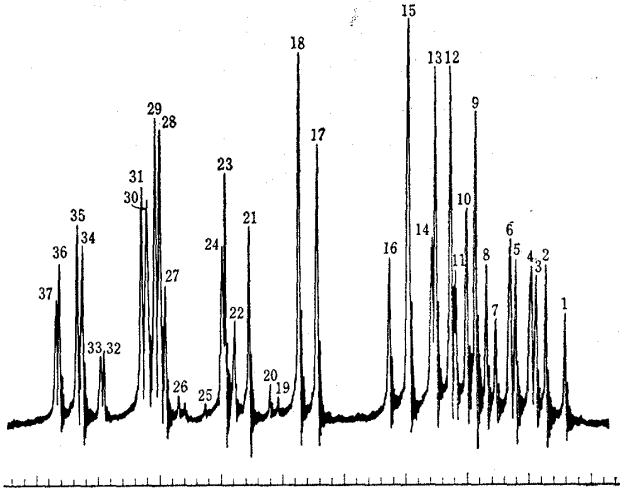


Fig. 1b. The Spectrum of *ortho*-Chloroaniline measured in Chloroform

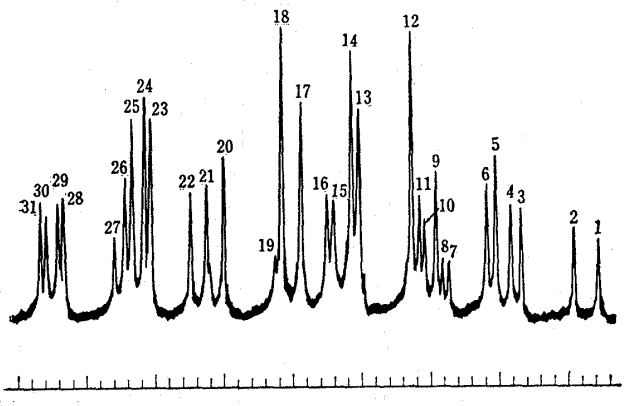


Fig. 1c. The Spectrum of *ortho*-Chloroaniline measured in Methanol-d_4

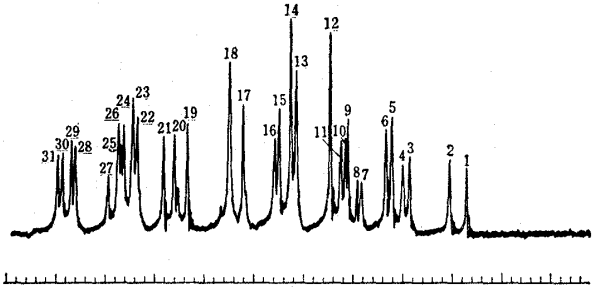


Fig. 1d. The Specturm of *othro*-Chloroaniline measured in Acetone-d_6

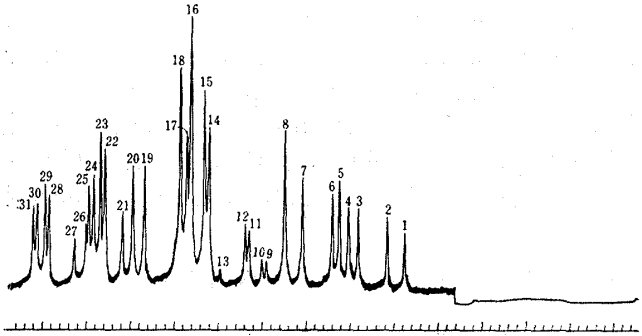


Fig. 1e. The Spectrum of *ortho*-Chloroaniline measured in Dimethyl Sulphoxide-d_6

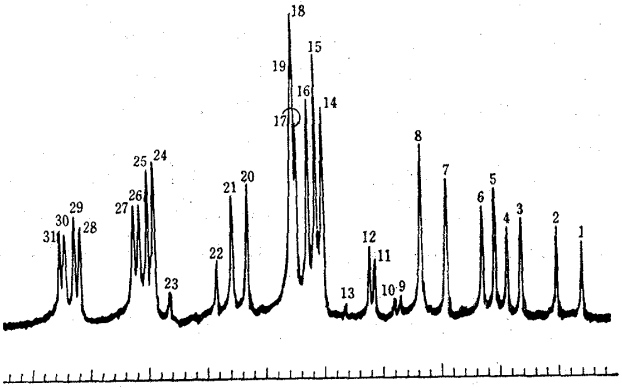


Fig. 1f. The Spectrum of *ortho*-Chloroaniline measured in Pyridine-d_5

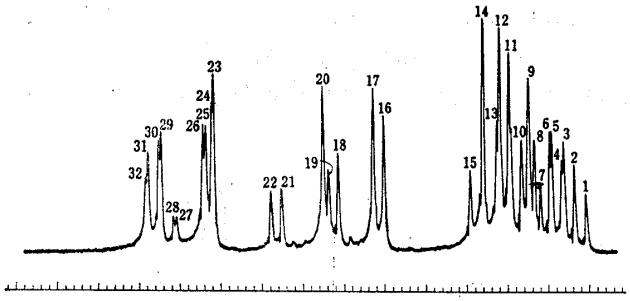


Fig. 1g. The Spectrum of *ortho*-Bromoaniline measured in Tetrachloromethane

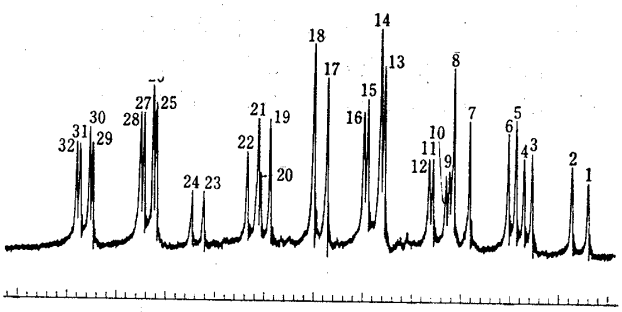


Fig. 1h. The Spectrum of *ortho*-Bromoaniline measured in Methanol-d_4

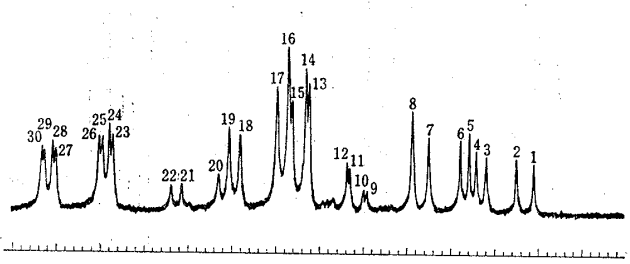


Fig. 1i. The Spectrum of *ortho*-Bromoaniline measured in Acetone-d_6

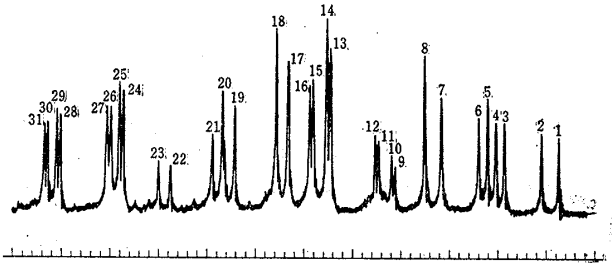


Fig. 1j. The Spectrum of *ortho*-Bromoaniline mehasured in Pyridine-d_5

It seems that the above-sequence is almost parallel with the accepted order of the hydrogen–bonding ability of these solvents estimated by IR and NMR studies.[9] Consequently, if one assumes an approximate proportionality between the hydrogen-bond strength and the magnitude of the deshielding of the related proton which can be explained theoretically[10] in terms of an asymmetric electric field caused by the polarization of the electrons in the vicinity of the hydrogen–bond, it will be concluded that the origins of the present effect should include, as a rather predominant factor, a specific solute–solvent association through the hydrogen–bonding formationn between the amino hydrogen of a solute molecule and the lone–pair electrons contained in the nitrogen or oxygen atoms of the polar solvent molecules. A preferential hydrogen–bonding interaction between the A ring proton of the solute molecule and the surrounding solvent molecules, such that has been pointed out[2a] as a cause of the solvent effect on the internal chemical shifts of the ring protons in *para*-disubstitued benzenes, will be of no importance here since a polarization of the C–H sigma bond which is favourable for this interaction is not expected at least from the electron-releasing effect of the neighbouring amino substituent.

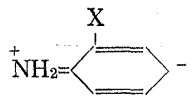
The problem is, then, to investigate how the formation of such a solute–solvent association is influenced by the steric or electronic effect of the *ortho*-halosubstituent which seems to be of much interest in comparison with the similar effects observed in *ortho*-halophenols[11] and *ortho*-methyl hindered phenols.[12] In the present case also, the existence of the intramolecular hydrogen–bond between the amino hydrogen and halogen atom can be supported by the facts that only a slight dilution shift is seen in the internal chemical shifts and that the chemical shift of the amino proton of *ortho*-chloroaniline is 0.3 ppm downfield from that of *meta*-chloroaniline. The strength of this bond is sure to be in an order of Cl>Br as have been evidenced

9) J.W. Emsley, J. Feeney, L.H. Sutcliffe, "Progress in N.M.R. Spectroscopy," Vol. 3, Pergamon Press, 1967.
10) W.G. Schneider, H.J. Bernstein and J.A. Pople, *J. Chem. Phys.*, **28**, 601 (1958).
11) C.M. Huggins, G.C. Pimentel and J.N. Shoolery, *J. Phys. Chem.*, **60**, 1311 (1956).
12) I. Yamaguchi, *Bull. Chem. Soc. Japan*, **34**, 744 (1961).

in similar hydrogen-bonds.[11] If the formation of the above solute-solvent association is competitive with this intramolecular hydrogen-bond in an isolated solute molecule, the magnitude of the solvent dependent perturbation of the internal cheical shift $\nu_A-\nu_C$ is expected to increase as the strength of the intramolecular hydrogen-bond is suppressed. Such holds true with the observed solvent dependent changes of the $\nu_A-\nu_C$ in the Br and Cl derivatives.

Meanwhile, it is probable that the polar solute molecules employed here suffer the influence of the reaction field arising in the polar or polarizable solvent in a way such that the internal chemical shifts of a solute molcule are altered in a linear correlation with the medium dielectric function $\varepsilon-1/2\varepsilon+2.5$ as theoretically derived.[13] This solvent effect will be also important in the pure liquid state of the solute molecules because of large dipole moments. In the present case, however, such an ideal relation does ont hold good, although the internal chemical shifts, $\nu_B-\nu_C$ and $\nu_D-\nu_C$ definitely tend to become larger along with the increase of the solvent dielectric constant. This discrepancy can not be explained simply in terms of a perturbation which is given by the above solute-solvent association because the local electric field or change-migration in the vicity of the hydrogen-bond is thought not to act so effectively as to cause a remarkable change in the shielding of the protons *meta* and *para* to the amino group.

An explanation covering all the experimental results will be given by adding a postulation that in polar solvents a mesomeric structure of the solute molecule, such a type as is induced and stabilized by the reaction field. This model is consistent with the change of the electronic structure of the solute molecule which corresponds to the cleavage of the NH_2–X intramolecuoar hydrogen-bond and the formation of the NH_2–solvent intermolecular hydrogen-bond. The negative π-charge of the C carbon will cause the polarization of the C–H sigma bond so as more shield the C proton in proportion to the increment of the negative π-charge and consequently give rise to the observed increase of the internal chemical shifts $\nu_B-\nu_C$ and $\nu_D-\nu_C$.



A concentration dependent shift of the proton signals has been examined in the system of *ortho*-chloroaniline plus acetone. When a proton of the solute molecule alternates rapidly between two environments, in a free state (A) and in interaction with solvent (B) and both of the states are independent of the solute concentration, the actual chemical shift ν may be expressed as $\nu=\nu_A\cdot(1-k)+\nu_B\cdot k$ (k: the fraction interacting with solvent). The consistency of the above equation was checked by examining whether or not a proportional relationship holds between the chemical shifts of the amino protons and the proton ortho to the amino group. The result was proved to be negative though a parallel relation was found. This may be correlated with the concentration dependent variation of the associated structure which is induced by a polarized state of the solute molecule.

In such solvents as tetrachloromethane, bromoform and chloroform without any specific interaction with the solute except a weak hydrogenbond formed between the ring π-electrons,[15] no drastic changes were observed in the relative chemical shifts of the ring protons. It should. be noted, however, that the deshieldings of all the ring protons are increasing, as is shown in Table II, in an order of tetrachloromethane<chloroform<bromoform. Furthermore, it was known that the magnitudes of the shifts were almost same with those of the amino protons. These facts show that the Van der Waals interactions between the solutes and solvents which are liekly to deshield all the protons of the solute molecule to an identical extent are increasing from solvent to solvent according to the previous sequence.

In toluene solvent, most of the chemical shifts of the ring protons relative to the TMS internal reference move toward a high field compared with those in inert tetrachloromethane solvent (Table II). This can be attributed to the diamagnetic ring current effect of the solvent

13) L. Onsager, *J. Amer. Chem. Soc.*, **58**, 1486 (1956); A.D. Buckingham, *Can. J. Chem.*, **38**, 300 (1960).
14) G. Fraenkel, R.E. Carter, A. McLachlan and J.H. Richards, *J. Amer. Chem. Soc.*, **82**, 5846 (1960).
15) G. Korinek and W.G. Schneider, *Can. J. Chem.*, **35**, 1157 (1957).

Table II. The Converged Values of the Magnetic Parameters

Solute	Solvent	ν_A	ν_B	ν_C	ν_D	J_{AB}	J_{AC}	J_{AD}	J_{BC}	J_{BD}	J_{CD}
I	CCl_4	388.996	413.091	391.809	426.712	7.99	1.45	0.29	7.33	1.49	7.98
	$CDCl_3$	395.589	418.177	396.396	430.799	8.15	1.38	0.49	7.26	1.45	7.98
	$CDBr_3$	393.013	419.154	397.635	433.737	8.11	1.46	0.17	7.37	1.39	7.86
	$C_6D_5CD_3$	391.955	405.898	382.509	418.069	7.95	1.52	0.30	7.31	1.47	7.95
	C_6D_5N	411.319	419.189	394.755	433.700	7.99	1.50	0.34	7.30	1.47	7.91
	$(CD_3)_2CO$	405.780	420.685	396.345	431.053	7.94	1.49	0.28	7.33	1.44	7.89
	CD_3OD	404.281	417.348	394.258	428.247	7.97	1.51	0.29	7.31	1.42	7.89
	$(CD_3)_2SO$	411.235	420.733	394.644	430.760	8.00	1.47	0.34	7.11	1.46	7.91
II	CCl_4	386.465	414.705	386.885	432.791	7.87	1.57	0.30	7.29	1.37	7.91
	$CDCl_3$	394.741	419.099	390.791	439.012	7.88	1.48	0.44	7.29	1.48	7.73
	$CDBr_3$	398.459	421.908	393.497	440.810	7.91	1.54	0.27	7.31	1.40	7.96
	$C_6D_5CD_3$	395.900	411.623	381.914	429.939	7.99	1.55	0.30	7.27	1.42	7.94
	C_6D_5N	411.082	421.449	390.602	443.644	7.99	1.52	0.22	7.27	1.51	8.01
	$(CD_3)_2CO$	406.997	421.471	384.500	439.820	8.05	1.58	0.29	7.14	1.46	7.96
	CD_3OD	405.332	421.070	391.252	439.297	8.02	1.54	0.31	7.28	1.46	7.97
III	CCl_4	397.151	422.074	383.178	452.510	7.92	1.52	0.29	7.20	1.44	7.84
	$(CD_3)_2CO$	408.626	423.962	382.138	453.542	7.94	1.57	0.20	7.24	1.52	7.78

toluene molecule. However, the unequal shifts at the different protons and especially the deshielding of the A proton are rather questionable since such a high field shift is also likely to occur with an almost same magnitude throughout the solute molecule. The deshielding of the A proton due to a preferential hydrogen-bonding interaction between this proton and the ring π-electrons of the solvent-molecule will not be a prominent factor because of the electron-releasing effect of the amino group causing the high π-electron density at the A carbon and consequently the increase of the negative change at the A hydrogen through σ-π interaction.

It is of much interest, hereupon, that the strength of this effect tends to diminish at the four ring protons in an order of C<D,B<A. This order is remarkably different from that predicted by the additivity rule[4] for such solvent effect. The fact that the D proton *ortho* to the halosubstituent is more affected by this effect than the C proton shows that the above result can not be interpreted simply by the steric hindrance of the substituents to the solute-solvent association with the parallel orientation of the benzene rings. Similar results have been reported on the benzene-induced shifts of the proton signals of the substituted pyridines.[16] Considering that such solute-solvent complex as stated above is formed as a result of the polarization of the π-electrons in the solvent molecule which is induced by the electron distribution in the polar solute molecule, the deshielding of the A proton attached to the π-electron rich carbon may be caused by the hindrance of a close approach of the solvent molecule due to an electronic repulsion.

A few remarks about the substituent effects on the chemical shifts of the ring protons in an isolated solute molecule can be drawn from the data in dilute solutions of tetrachloromethane (Table II).

When an approximate linear relationship[14] between the chemical shift of a benzene ring proton and the π-electron density of the adjacent carbon atom is assumed to be valid and the *ortho–para* orienting effects of the amino and halogen substituents are taken into account, then the fact that the protons *ortho* and *para* to the amino group are more shielded than the others can be explained by the stronger resonance effect of the amino group. The inversion of the shielding order between the two protons by replacing I with Br or Cl is consistent with the concurrent increase of the electron-withdrawing inductive effect of the substituent.

16) J.N. Murrell and V.M.S. Gil, *Trans. Faraday Soc.*, **61**, 402 (1965).

Table III. The Comparisons between Observed and Calculated Spectra

IA) The spectrum of *ortho*-chloroaniline measured in tetrachloromethane

Line	Transition		Obs. freq.	Calc. freq.	Calc. intensity
1	16	15	382.4	382.44	0.45
2	16	14	383.4	383.38	0.68
3	12	8	383.8	383.77	0.64
4	14	11	384.2	384.21	0.68
5	15	11	385.1	385.15	0.67
6	7	4	385.6	385.60	0.75
7	13	10	388.9	388.95	0.13
8	12	7	390.1	390.07	0.66
9	9	5	390.8	390.77	1.92
10	6	3	391.1	391.17	0.77
11	13	9	391.9	391.81	2.26
12	2	1	393.1	393.04	1.83
13	10	5	393.6	393.62	0.28
14	6	2	397.5	397.50	2.37
15	3	1	399.4	399.38	0.97
16	16	13	406.0	405.93	1.47
17	12	6	407.8	407.74	2.09
18	14	10	411.5	411.50	0.14
19	15	10	412.4	412.44	0.81
20	14	9	414.3	414.36	0.43
21	8	3	415.1	415.14	1.17
	7	2	415.1	415.18	0.68
22	11	5	420.9	420.92	0.51
23	16	12	422.4	422.32	1.39
24	4	1	422.7	422.62	0.49
	14	8	422.7	422.71	1.43
25	9	3	423.5	423.49	0.57
26	13	6	424.1	424.13	1.05
27	10	3	426.3	426.34	0.37
28	15	7	429.9	429.95	0.84
29	11	4	430.4	430.40	0.83
30	5	1	432.1	432.10	0.71
31	10	2	432.7	432.68	0.41

IB) The spectrum of *ortho*-chloroaniline measured in chloroform

Line	Transition		Obs. freq.	Calc. freq.	Calc. intensity
1	16	15	387.1	387.11	0.52
2	14	11	388.9	388.83	0.60
3	16	14	389.9	389.75	0.58
4	12	8	390.3	390.34	0.63
5	15	11	391.6	391.47	0.72
6	7	4	392.4	392.11	0.71
7	13	10	393.8	393.82	0.41
8	12	7	394.7	394.75	0.65
9	9	5	395.7	395.60	1.55
10	8	4	396.6	396.53	0.91
11	6	3	397.7	397.76	0.55
12	13	9	398.1	398.04	1.97
13	2	1	399.6	399.59	2.10
14	10	5	400.0	399.81	0.64
15	6	2	402.2	402.22	2.63
16	3	1	404.2	404.05	0.71
17	16	13	411.1	411.04	1.48
18	12	6	412.9	412.81	2.13
19	14	10	415.0	415.12	0.08
20	7	3	415.8	415.81	0.15
21	15	10	417.8	417.76	0.90
22	14	9	419.3	419.33	0.45
23	8	3	420.1	420.23	1.09
24	7	2	420.4	420.28	0.65
25	15	9	422.1	421.97	0.05
26	8	2	424.7	424.69	0.07
27	11	5	425.9	426.10	0.50
28	16	12	426.4	426.32	1.42
29	14	8	426.9	426.90	1.44
30	9	3	427.7	427.80	0.65
	4	1	427.7	427.75	0.48
31	13	6	428.2	428.08	1.05
32	10	3	432.0	432.02	0.26
33	9	2	432.2	432.26	0.26
34	15	7	434.0	433.96	0.84
35	11	4	434.5	434.60	0.82
36	5	1	436.2	436.25	0.71
37	10	2	436.5	436.48	0.49

IC) The spectrum of *ortho*-chloroaniline measured in methanol-d_1

Line	Transition		Obs. freq.	Calc. freq.	Calc. intensity
1	16	15	384.9	384.96	0.53
2	14	11	387.1	387.09	0.62
3	13	10	391.7	391.66	0.78
4	12	9	392.6	392.52	0.74
5	8	5	393.8	393.87	1.12
6	7	4	394.6	394.62	0.84
7	16	14	398.0	397.97	0.34
8	12	7	398.5	398.49	0.33
9	6	3	399.1	399.11	1.01
10	15	11	400.1	400.10	0.59
11	9	4	400.6	400.58	0.67
12	2	1	401.3	401.28	2.08
13	13	8	405.8	405.84	1.79
14	6	2	406.4	406.43	2.39
15	10	5	408.1	408.05	1.18
16	3	1	408.6	408.60	0.81
17	16	13	410.8	410.85	1.67
18	12	6	412.5	412.47	2.36
19	7	3	413.1	413.09	0.15
20	15	10	417.6	417.56	1.10
21	9	3	419.0	419.06	0.90
22	7	2	420.4	420.41	0.82
23	16	12	423.9	423.94	1.45
24	14	7	424.5	424.46	1.45
25	13	6	425.6	425.56	1.04
26	8	2	426.2	426.15	0.84
27	4	1	427.1	427.08	0.40
28	15	9	431.5	431.51	0.84
29	11	4	432.0	431.99	0.83
30	10	3	433.0	433.01	0.73
31	5	1	433.5	433.57	0.70

ID) The spectrum of *ortho*-chloroaniline measured in acetone-d_6

Line	Transition		Obs. freq.	Calc. freq.	Calc. intensity
1	16	15	387.1	387.08	0.54
2	14	11	389.0	389.08	0.63
3	13	10	393.9	393.91	0.78
4	12	9	394.6	394.66	0.75
5	8	5	396.0	396.00	1.11
6	7	4	396.7	396.62	0.86
7	16	14	399.7	399.69	0.41
8	12	7	400.2	400.18	0.40
9	6	3	401.4	401.35	0.98
10	15	11	401.7	401.69	0.62
11	9	4	402.2	402.14	0.66
12	2	1	403.4	403.39	2.08
13	13	8	407.5	407.52	1.73
14	6	2	408.1	408.11	2.32
15	10	5	409.6	409.62	1.15
16	3	1	410.1	410.15	0.77
17	16	13	414.0	413.98	1.59
18	12	6	415.6	415.61	2.28
19	15	10	420.7	420.80	1.07
20	9	3	422.3	422.30	0.87
21	7	2	423.6	423.54	0.92
22	16	12	426.8	426.74	1.45
23	14	7	427.2	427.24	1.48
24	13	6	428.4	428.38	1.03
25	11	5	428.8	428.73	0.41
26	8	2	429.0	428.96	0.78
27	4	1	430.3	430.32	0.44
28	15	9	434.3	434.33	0.84
29	11	4	434.8	434.77	0.84
30	10	3	435.8	435.82	0.73
31	5	1	436.3	436.36	0.70

IE) The spectrum of *ortho*-chloroaniline measured in dimethyl sulphoxide-d_6

Line	Transition		Obs. freq.	Calc. freq.	Calc. intensity
1	16	15	385.6	385.55	0.57
2	14	11	387.9	387.88	0.65
3	13	10	391.9	391.85	0.81
4	12	9	393.2	393.19	0.79
5	8	5	394.1	394.29	1.05
6	7	4	395.5	395.40	0.89
7	6	3	399.5	399.51	1.20
8	2	1	401.8	401.82	1.78
9	16	14	404.5	404.39	0.19
10	12	7	405.0	405.05	0.21
11	15	11	406.7	406.72	0.49
12	9	4	407.3	407.25	0.57
13	7	3	410.7	410.71	0.11
14	13	8	412.2	412.25	1.80
15	6	2	412.8	412.91	2.30
16	16	13	414.7	414.73	1.76
17	3	1	415.3	415.21	1.15
18	12	6	416.2	416.24	2.47
19	15	10	421.0	421.03	1.22
20	9	3	422.6	422.57	1.10
21	7	2	424.0	424.10	0.66
22	16	12	426.4	426.40	1.47
23	14	7	427.1	427.05	1.41
24	13	6	427.9	427.91	1.04
25	8	2	428.6	428.57	0.81
26	11	5	429.1	428.99	0.30
27	4	1	430.6	430.53	0.37
28	15	9	434.0	434.04	0.86
29	11	4	434.5	434.57	0.85
30	10	3	435.6	435.57	0.74
31	5	1	436.1	436.10	0.70

IF) The spectrum of *ortho*-chloroaniline measured in pyridine-d_5

Line	Transition		Obs. freq.	Calc. freq.	Calc. intensity
1	16	15	385.5	385.53	0.56
2	14	11	388.1	388.13	0.65
3	13	10	391.7	391.76	0.80
4	12	9	393.2	393.15	0.75
5	8	5	394.4	394.40	1.10
6	7	4	395.7	395.67	0.88
7	6	3	399.5	399.46	1.16
8	2	1	402.0	402.00	1.80
9	16	14	404.1	404.11	0.11
10	12	7	404.8	404.77	0.13
11	15	11	406.7	406.72	0.45
12	9	4	407.3	407.29	0.54
13	7	3	409.7	409.69	0.14
14	13	8	412.0	412.02	1.98
15	6	2	412.7	412.68	2.41
16	16	13	413.5	413.53	1.94
17	10	5	414.7	414.66	1.36
18	12	6	415.0	415.00	2.50
19	3	1	415.2	415.22	1.16
20	15	10	419.8	419.77	1.24
21	9	3	421.3	421.31	1.09
22	7	2	422.9	422.90	0.41
23	11	5	427.7	427.71	0.27
24	16	12	429.3	429.28	1.38
25	14	7	430.0	429.94	1.28
26	13	6	430.8	430.75	1.09
27	8	2	431.4	431.40	0.97
28	15	9	436.9	436.91	0.87
29	11	4	437.4	437.47	0.84
30	10	3	438.4	438.45	0.76
31	5	1	439.0	439.00	0.74

TABLE III. continued

IIA) The spectrum of *ortho*-bromoaniline measured in tetrachloromethane

Line	Transition	Obs. freq.	Calc. freq.	Calc. intensity
1	16 15	377.7	377.73	0.52
2	14 11	379.5	379.53	0.79
3	16 14	381.1	381.00	0.78
4	12 8	381.4	381.31	0.62
5	15 11	382.9	382.79	0.66
6	7 4	383.2	383.15	0.85
7	13 10	384.4	384.57	0.47
8	12 7	385.4	385.48	0.84
9	9 5	386.3	386.38	1.60
10	8 4	387.3	387.32	0.82
11	13 9	389.2	389.08	1.90
12	2 1	390.5	390.48	1.99
13	10 5	390.9	390.88	0.62
14	6 2	393.0	393.03	2.33
15	3 1	394.8	394.88	0.64
16	16 13	407.5	407.47	1.45
17	12 6	409.0	409.01	1.79
18	15 10	414.1	414.31	0.94
19	14 9	415.6	415.54	0.69
20	8 3	416.4	416.33	1.00
	7 2	416.4	416.56	0.78
21	11 5	422.6	422.39	0.57
22	4 1	423.9	423.89	0.57
23	16 12	432.4	432.33	1.25
24	14 8	432.6	432.64	1.23
25	9 3	433.5	433.42	0.75
26	13 6	433.8	433.87	1.07
27	10 3	437.7	437.93	0.27
28	9 2	438.1	437.82	0.27
29	15 7	440.0	440.08	0.87
30	11 4	440.4	440.43	0.88
31	5 1	442.0	441.92	0.80
32	10 2	442.3	442.33	0.55

IIB) The spectrum of *ortho*-bromoaniline measured in methanol-d_4

Line	Transition	Obs. freq.	Calc. freq.	Calc. intensity
1	16 15	382.1	382.13	0.62
2	14 11	384.1	384.12	0.70
3	13 10	388.9	388.96	0.87
4	12 8	390.0	389.92	0.79
5	9 5	391.0	390.97	1.13
6	7 4	391.9	391.91	0.93
7	6 3	396.7	396.70	1.12
8	2 1	398.7	398.70	1.73
9	16 14	399.2	399.21	0.44
10	12 7	399.7	399.63	0.46
11	15 11	401.2	401.20	0.62
12	8 4	401.6	401.62	0.66
13	13 9	407.2	407.20	1.69
14	6 2	407.6	407.65	1.97
15	10 5	409.2	409.21	1.20
16	3 1	409.7	409.66	1.01
17	16 13	414.2	414.25	1.65
18	12 6	415.8	415.81	2.03
19	15 10	421.1	421.08	1.10
20	14 9	422.3	422.24	0.45
21	8 3	422.6	422.59	1.03
22	7 2	423.8	423.83	0.75
23	11 5	429.1	429.08	0.45
24	4 1	430.6	430.62	0.48
25	16 12	434.8	434.78	1.29
26	14 7	435.2	435.20	1.27
27	13 6	436.4	436.34	1.06
28	9 2	436.8	436.79	1.00
29	15 8	442.5	442.57	0.89
30	11 4	443.0	442.99	0.88
31	10 3	444.1	444.08	0.80
32	5 1	444.5	444.53	0.78

IIC) The spectrum of *ortho*-bromoaniline measured in acetone-d_6

Line	Transition	Obs. freq.	Calc. freq.	Calc. intensity
1	16 15	381.5	381.51	0.64
2	14 11	383.8	383.82	0.72
3	13 10	388.0	388.02	0.88
4	12 8	389.3	389.35	0.81
5	9 5	390.3	390.33	1.11
6	7 4	391.6	391.59	0.93
7	6 3	396.0	395.92	1.18
8	2 1	398.2	398.16	1.59
9	16 14	404.4	404.40	0.23
10	12 7	404.9	404.84	0.26
11	15 11	406.7	406.70	0.51
12	8 4	407.1	407.08	0.56
13	13 9	412.3	412.36	1.88
14	6 2	412.8	412.80	2.07
15	10 5	414.7	414.67	1.34
16	16 13	415.2	415.24	1.87
17	12 6	416.7	416.71	2.18
18	15 10	421.7	421.74	1.23
19	14 9	423.3	423.20	0.25
	8 3	423.3	423.28	1.15
20	7 2	424.7	424.67	0.49
21	11 5	429.7	429.71	0.35
22	4 1	431.2	431.24	0.39
23	16 12	439.1	439.09	1.25
24	14 7	439.6	439.54	1.21
25	13 6	440.6	440.57	1.08
26	9 2	441.0	441.02	1.03
27	15 8	446.9	446.94	0.90
28	11 4	447.3	447.32	0.89
29	10 3	448.5	448.47	0.82
30	5 1	448.8	448.85	0.80

IID) The spectrum of *ortho*-bromoaniline measured in pyridine-d_5

Line	Transition	Obs. freq.	Calc. freq.	Calc. intensity
1	16 15	381.4	381.46	0.63
2	14 11	383.6	383.59	0.72
3	13 10	388.1	388.07	0.88
4	12 8	389.2	389.26	0.68
5	9 5	390.2	390.22	0.92
6	7 4	391.4	391.36	0.94
7	6 3	395.9	395.86	1.17
8	2 1	398.0	397.98	1.64
9	16 14	401.6	401.63	0.37
10	12 7	402.1	402.06	0.39
11	15 11	403.7	403.76	0.57
12	8 4	404.2	404.16	0.56
13	13 9	409.7	409.65	1.39
14	6 2	410.1	410.10	1.97
15	10 5	411.8	411.80	1.26
16	3 1	412.2	412.22	1.12
17	16 13	414.9	414.89	1.71
18	12 6	416.4	416.40	2.08
19	15 10	421.5	421.50	1.16
20	14 9	423.0	422.90	0.31
	8 3	423.0	422.99	0.96
21	7 2	424.4	424.43	0.66
22	11 5	429.5	429.53	0.41
23	4 1	431.0	431.05	0.45
24	16 12	435.3	435.31	1.28
25	14 7	435.7	435.74	1.25
26	13 6	436.9	436.82	1.07
27	9 2	437.3	437.27	0.87
28	15 8	443.1	443.11	0.74
29	11 4	443.5	443.51	0.88
30	10 3	444.6	444.61	0.80
31	5 1	445.0	445.03	0.78

Frequency (cps) are measured relative to TMS internal reference.

The most deshielding of the proton *ortho* to the halosubstituent can not be interpreted simply in terms of the resonance and inductive effects of the substituents and suggests the existence of the anisotropic effect of the halogen atoms which has been found[17] to appreciably influence the shift of the *ortho* proton, especially for the bromo- and iodo-derivatives where such effect is expected to be large. The departure of the present data from the results predicted upon the additivity rule[3,4] is considerably large; the predicted order of the proton deshieldings is A<B<D<C in Cl deriv., A<B<C<D in Br deriv., B<C<A<D in I deriv. These discrepancies would be attributed to the previously mentioned interaction between the two substituents.

The discussions presented here, though some of them speculative, are well consistent with the observed solvent effects and some other types of interactions may be introduced for more precise explanations. Advanced discussions will be given when the informations of the detailed electronic effects of the substituents and the way in which these effects alter the measured proton chemical shifts are obtained.

Acknowledgement The author wishes to thank Mr. S. Katayama for assistance in the NMR spectra measurements.

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