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## The Internal Chemical Shift. A Key To Bonding In Aromatic Molecules. I. Internal Shift Correlations

Donald W. Beistel  
*Missouri University of Science and Technology*

Holger E. Chen

P. J. Fryatt

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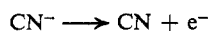
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In the second pair of reactions, 25% of the charge transferred from  $\text{CN}^-$  to  $\text{Li}^+$  comes from the carbon in producing  $\text{LiCN}$  and 66% in producing  $\text{LiNC}$ . Again, the latter is very considerably closer to the figure for



All of these numbers are only estimates, of course, and are computed from wave functions of differing degrees of accuracy. But the qualitative conclusion is clear; whether one views the formation of the molecule in terms of the interaction of  $\text{Li}$  with  $\text{CN}$  or  $\text{Li}^+$  with  $\text{CN}^-$ , the nature of the charge transfer in forming  $\text{LiNC}$  is very much the more consistent with what has been found to be the charge-transfer behavior in the  $\text{CN}$ ,  $\text{CN}^-$  pair. On this basis, therefore, one would predict, in agreement with Bak, *et al.*, that  $\text{LiNC}$  is the correct structure. Happily, a very recent study of isotopic infrared frequency shifts led to the same conclusion.<sup>30,31</sup>

(e) **OF, OF<sub>2</sub>, and HOF.** The molecules **OF** and **OF<sub>2</sub>** are examples of the infrequently encountered situation in which an oxygen atom has a positive charge. This is consistent with the common assertion that oxygen is in a positive oxidation state in **OF<sub>2</sub>**. The addition of a hydrogen to **OF** is sufficient to give the oxygen its usual negative charge.

(30) Z. K. Ismail, R. H. Hauge, and J. L. Margrave, *J. Chem. Phys.*, **57**, 5137 (1972).

(31) Clementi, *et al.*, have carried out another self-consistent-field calculation for this system, using a basis set even larger than that of ref 28.  $\text{LiNC}$  was again found to be the more stable form: E. Clementi, H. Kistenmacher, and H. Popkie, *J. Chem. Phys.*, **58**, 2460 (1973).

## Summary

The results and discussion presented in this paper indicate that the relationship which has been developed between atomic charges and  $1s$  orbital energies can be used to obtain meaningful estimates of the charges on atoms in molecules. The requirements are an all-electron *ab initio* molecular orbital wave function for the molecule and the appropriate charge *vs.* energy equations for the individual atoms; the actual calculations are simply the solving of a set of simultaneous linear equations. As with other calculated properties, the results will be better and more consistent as the quality of the wave function improves.<sup>32</sup> Charge *vs.* energy equations have now been developed for five widely occurring atoms; additional atoms, such as phosphorus, sulfur, etc., will be included as more *ab initio* molecular orbital wave functions for molecules containing these atoms become available.<sup>33</sup>

**Acknowledgment.** We greatly appreciate the computational assistance of Dr. Bella Wang.

(32) The charge-energy relationships in Table IV were obtained using atomic charges computed with molecular wave functions of near-Hartree-Fock accuracy.<sup>3,4</sup>

(33) Two procedures for estimating atomic charges from experimentally determined, rather than calculated, inner shell energies have recently been proposed.<sup>34,35</sup> The charges obtained are based upon other definitions of atomic charge than that used in the present work, which has as its basis the molecular electronic density function.

(34) D. W. Davis, D. A. Shirley, and T. D. Thomas, *J. Amer. Chem. Soc.*, **94**, 6565 (1972).

(35) G. D. Stucky, D. A. Matthews, J. Hedman, M. Klasson, and C. Nordling, *J. Amer. Chem. Soc.*, **94**, 8009 (1972).

## The Internal Chemical Shift. A Key to Bonding in Aromatic Molecules. I. Internal Shift Correlations

D. W. Beistel,\*<sup>1a</sup> Holger E. Chen,<sup>1a,b</sup> and P. J. Fryatt<sup>1c</sup>

*Contribution from the Department of Chemistry, University of Missouri—Rolla, Rolla, Missouri 65401, and the Department of Chemistry, Marshall University, Huntington, West Virginia 25701. Received March 23, 1973*

**Abstract:** The study of proton shift behavior in nine families of disubstituted benzenes has provided quantitative correlations of internal and meta shifts among all families. The equations of correlation are useful in the prediction of shifts to an error of 0.015 ppm. The studies demonstrate shift additivity for the 4-substituted halobenzenes and suggest a chain rule relationship for substituent effects in those compounds. For that reason previous theories of substituent interactions involving inductive and resonance contributors appear incorrect when applied to proton shift data. In decreasing order of upfield shift at the ortho protons the substituents studied include  $\text{N}(\text{CH}_3)_2$ ,  $\text{NH}_2$ ,  $\text{OCH}_3$ ,  $\text{OH}$ ,  $\text{F}$ ,  $\text{CH}_3$ ,  $\text{CH}_2\text{CH}_3$ ,  $\text{H}$ ,  $\text{Cl}$ ,  $\text{C}(\text{CH}_3)_3$ ,  $\text{Br}$ ,  $\text{CN}$ ,  $\text{COOCH}_3$ ,  $\text{COOH}$ ,  $\text{COCl}$ ,  $\text{NO}_2$ .

**I**nitial high-resolution proton magnetic resonance studies of substituted benzenes by Dailey<sup>2</sup> gave evidence that substituent effects on the chemical shifts of ring protons were predictable although not well behaved. Subsequent reports by Diehl,<sup>3</sup> Dailey,<sup>4</sup>

(1) (a) University of Missouri—Rolla. (b) Taken in part from a thesis submitted in partial fulfillment of requirements for the degree, Doctor of Philosophy, University of Missouri—Rolla, June 1972. (c) Taken in part from a thesis submitted in partial fulfillment of requirements for the degree, Master of Science, Marshall University, May 1967.

(2) R. L. Corio and B. P. Dailey, *J. Amer. Chem. Soc.*, **78**, 3043 (1956).

(3) P. Diehl, *Helv. Chim. Acta*, **44**, 829 (1961).

(4) S. Martin and B. P. Dailey, *J. Chem. Phys.*, **39**, 1722 (1963).

Smith,<sup>5</sup> Beachell and Beistel,<sup>6</sup> Reed,<sup>7</sup> and others suggested that trends in the shifts of aromatic protons (relative to benzene) paralleled trends in Hammett  $\sigma$  constants<sup>8</sup> and electronegativities.<sup>9</sup> But in no case were the confidence limits high for correlations with those parameters. Because no apparent relationships existed

(5) G. W. Smith, *J. Mol. Spectrosc.*, **12**, 146 (1964).

(6) H. C. Beachell and D. W. Beistel, *Inorg. Chem.*, **3**, 1028 (1964).

(7) J. J. R. Reed, *Anal. Chem.*, **39**, 1586 (1967).

(8) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill, New York, N. Y., 1940.

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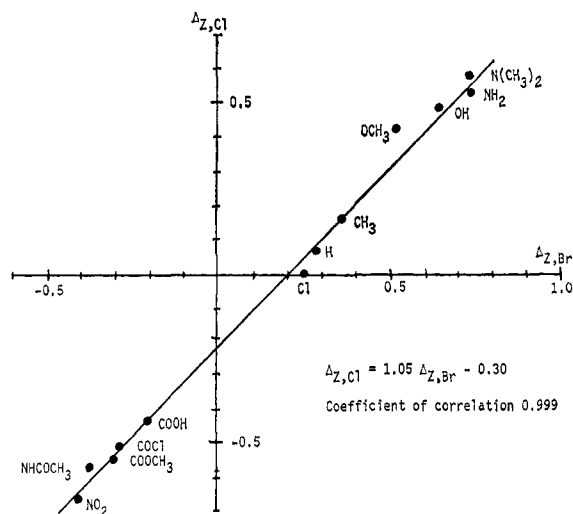


Figure 1. Internal shift correlation, chloro- vs. bromobenzenes.

between proton shift data and substituent parameters available at the time, attention was focussed on the development of empirical equations useful for shift prediction.

Diehl<sup>3</sup> was first to recognize the relative influences of a ring substituent at the ortho, meta, and para positions. He used shift data obtained from a number of mono-substituted benzenes to generate shift factors for each substituent. Then to estimate a proton shift in a disubstituted benzene the factors were added. If substituent  $R_1$  exerted a shift at the ortho position,  $d_o(R_1)$ , in the compound  $C_6H_5R_1$ , and substituent  $R_4$  exerted a shift  $d_m(R_4)$  at the meta position in the compound  $C_6H_5R_4$ , then the shift at the ortho position,  $\delta_2$ , in  $R_1C_6H_4R_4$  would be

$$\delta_2 = d_o(R_1) + d_m(R_4) \quad (1)$$

Dailey<sup>4</sup> perceived limitations in this approach and refined the meta shift parameter after studying additional disubstituted benzenes. The Dailey equation became

$$\delta_2 = d_o(R_1) + \gamma(R_1)d_m(R_4) \quad (2)$$

where  $\gamma(R_1)$  is an empirical constant. In both methods the shifts were relative to benzene.

## Results and Discussion

While the Dailey method gives rather poor estimates of shifts in many cases, it was an improvement of the approach of Diehl. Table I lists the possible shift

Table I. Predicted Chemical Shifts for Para-Disubstituted Benzenes for Which Contrasting Information Is Available<sup>a</sup>

X	Y	$\Delta_{XY}$ Obsd	Calcd $\Delta_{XY}$		Martin and Dailey
			Beistel- Chen	Diehl	
NO <sub>2</sub>	F	1.00	1.04	-1.10	
NO <sub>2</sub>	CH <sub>3</sub>	0.78	0.78	-0.83	-0.87
NO <sub>2</sub>	I	0	-0.03	-0.14	-0.11
NO <sub>2</sub>	NH <sub>2</sub>	1.44	1.43		-1.29
NO <sub>2</sub>	OCH <sub>3</sub>	1.21	1.18		-1.20
NO <sub>2</sub>	Cl	0.66	0.61		0.72
NO <sub>2</sub>	Br	0.41	0.40		0.48

<sup>a</sup> No  $\gamma(R_1)$  values are available for  $C\equiv N$ , COCl, and  $CO_2CH_3$ .<sup>4</sup>

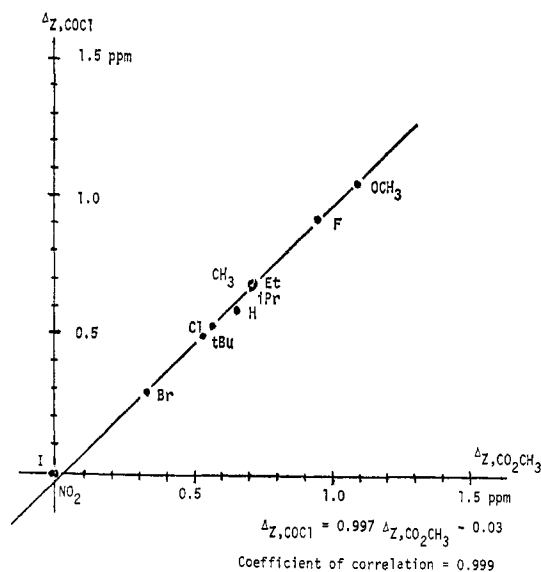


Figure 2. Internal shift correlation, benzoyl chlorides vs. methyl benzoates.

estimates one can generate to compare the two theories and it is seen that one cannot depend on the accuracy of either method. In addition the range of substituents limits application to only a few compounds, most of which have been analyzed in data files.

We first reported an alternative<sup>10</sup> to the Diehl method in 1967, showing that the halogens were well-behaved substituents when the data were examined in terms of the internal chemical shift. The internal chemical shift is

$$\Delta_{z,x} = \frac{\nu_x - \nu_z}{60 \text{ MHz}} \times 10^6 \quad (3)$$

where  $\nu_x$  is the shift of the protons ortho to substituent X, and  $\nu_z$  is the shift of protons ortho to substituent Z in a 4-substituted halobenzene,  $ZC_6H_4X$ . It was found that exact, linear correlations existed between families of halobenzenes<sup>11</sup> and that no competing inductive and resonance effects<sup>12</sup> appeared in the data. The quality of the correlations is illustrated in Figure 1.

The data were useful in predicting internal shifts for the halobenzenes using the shift relationships

$$\Delta_{z,x} = m\Delta_{z,y} + b \quad (4)$$

but had no broad application without extensive expansion to additional substituents. For that reason an investigation was undertaken to include additional halobenzenes and other families as well.<sup>13</sup> Figure 2 illustrates that the internal shift correlations extend to other families as well as the halobenzenes. The equations of correlation between all nine families are summarized in Table II and the shift data<sup>13</sup> are given in Table III.

Using the equations of correlation one can predict internal shifts to an average error of 0.015 ppm once the

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(11) P. J. Fryatt, M. S. Thesis, Marshall University, May 1967.

(12) J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. 2, Pergamon Press, New York, N. Y., 1966, pp 758-760.

(13) H. E. Chen, Ph.D. Thesis, University of Missouri-Rolla, June 1972.

**Table II.** Equations of Correlation for Internal and Meta Shifts in Parts per Million<sup>a</sup>

Y	X	m	b	Coefficient of correlation
$\Delta_{Z,F}$	$\Delta_{Z,Cl}$	1.11	-0.30	0.996
$\Delta_{Z,F}$	$\Delta_{Z,Br}$	1.17	-0.56	0.997
$\Delta_{Z,F}$	$\Delta_{Z,I}$	1.25	-0.98	0.991
$\Delta_{Z,Cl}$	$\Delta_{Z,Br}$	1.05	-0.23	0.999
$\Delta_{Z,Cl}$	$\Delta_{Z,I}$	1.11	-0.59	0.996
$\Delta_{Z,Br}$	$\Delta_{Z,I}$	1.07	-0.35	0.996
$\Delta_{Z,NO_2}$	$\Delta_{Z,F}$	1.19	1.01	0.994
$\Delta_{Z,NO_2}$	$\Delta_{Z,Cl}$	1.34	0.65	0.977
$\Delta_{Z,NO_2}$	$\Delta_{Z,Br}$	1.71	0.15	0.988
$\Delta_{Z,NO_2}$	$\Delta_{Z,I}$	2.10	-0.66	0.994
$\Delta_{Z,COOCH_3}$	$\Delta_{Z,F}$	0.97	0.86	0.993
$\Delta_{Z,COOCH_3}$	$\Delta_{Z,Cl}$	1.09	0.56	0.992
$\Delta_{Z,COOCH_3}$	$\Delta_{Z,Br}$	1.24	0.24	0.991
$\Delta_{Z,COOCH_3}$	$\Delta_{Z,I}$	1.40	-0.24	0.994
$\Delta_{Z,NO_2}$	$\Delta_{Z,CN}$	1.22	0.51	0.922
$\Delta_{Z,COCl}$	$\Delta_{Z,CN}$	1.09	0.44	0.992
$\Delta_{Z,COOCH_3}$	$\Delta_{Z,CN}$	1.03	0.45	0.995
$\Delta_{Z,COOH}$	$\Delta_{Z,CN}$	0.90	0.38	0.991
$\Delta_{Z,COOH}$	$\Delta_{Z,COOCH_3}$	0.80	0.04	0.978
$\Delta_{Z,COOH}$	$\Delta_{Z,NO_2}$	0.69	0.05	0.973
$\Delta_{Z,COOH}$	$\Delta_{Z,COCl}$	0.76	0.06	0.986
$\Delta_{Z,NO_2}$	$\Delta_{Z,COCl}$	1.16	0.05	0.994
$\Delta_{Z,COCl}$	$\Delta_{Z,COOCH_3}$	0.99	0.01	0.999
$\Delta_{Z,NO_2}$	$\Delta_{Z,COOCH_3}$	1.11	0.02	0.996

Y'	X'	m'	b'	
$M_{Z,CN}$	$M_{Z,COCl}$	1.02	-0.16	0.994
$M_{Z,COOH}$	$M_{Z,COOCH_3}$	1.02	-0.06	0.934
$M_{Z,COCl}$	$M_{Z,COOCH_3}$	1.05	-0.28	1.000
$M_{Z,NO_2}$	$M_{Z,COCl}$	1.04	-0.30	0.998
$M_{Z,NO_2}$	$M_{Z,COOH}$	1.03	-0.20	0.921
$M_{Z,CN}$	$M_{Z,COOCH_3}$	1.07	-0.44	0.994
$M_{Z,CN}$	$M_{Z,NO_2}$	0.93	0.47	0.991
$M_{Z,CN}$	$M_{Z,COOH}$	1.02	-0.19	0.977
$M_{Z,COOH}$	$M_{Z,COCl}$	0.97	0.26	1.000
$M_{Z,NO_2}$	$M_{Z,COOCH_3}$	1.09	-0.06	0.983
$M_{Z,F}$	$M_{Z,Cl}$	1.00	-0.25	1.000
$M_{Z,F}$	$M_{Z,Br}$	0.59	2.60	0.591
$M_{Z,F}$	$M_{Z,I}$	0.70	1.72	0.623
$M_{Z,I}$	$M_{Z,CN}$	0.25	5.64	0.410

<sup>a</sup> The slope is  $m$  and the intercept is  $b$  in the equation  $Y = mX + b$ .  $\Delta_{Z,F}$  is the internal shift in the Z-substituted fluorobenzene.  $M_{Z,F}$  is the shift of the meta protons in the Z-substituted fluorobenzene.

internal shift of the counterpart in one family is known. For example, if one required the internal shift of 4-nitroanisole he might determine the corresponding shift for 4-methoxybenzoyl chloride, which is 1.05 ppm (Table III). The equation of correlation for nitrobenzenes *vs.* benzoyl chlorides is  $\Delta_{Z,NO_2} = 1.10\Delta_{Z,COCl} + 0.017$  (Table II). Substituting  $\Delta_{Z,COCl} = 1.05$  ppm we find that  $\Delta_{Z,COCl}$  is 1.17 ppm compared with an observed value of 1.21 ppm, an error of only 3% in the estimate. If the internal shift for methyl 4-methoxybenzoate had been determined instead ( $\Delta_{OCH_3,COOCH_3} = 1.04$  ppm), the equation relating the nitrobenzenes and the methyl benzoates would be  $\Delta_{Z,NO_2} = 1.093\Delta_{Z,COOMe} - 0.059$ . Substitution gives a predicted  $\Delta_{OCH_3,NO_2}$  of 1.20 ppm, an error of less than 1%.

A comparison of predicted chemical shifts by this and previous methods is presented in Table I. It is seen that the accurate prediction of internal shifts is possible when the relations between families of compounds are known.

If one requires the shift of an equivalent pair of protons, such as the 2,2' protons of 4-nitrotoluene, first

he would calculate the shift of the 3,3' protons from a correlation of the meta shifts in nitrobenzenes with those of the benzoyl chlorides. The equations of correlation for meta shifts are listed in Table II. Knowing that the 3,3' shift in 4-methylbenzoyl chloride is 7.91 ppm, substitution into  $M_{Z,NO_2} = 1.043M_{Z,COCl} - 0.295$  gives 7.96 ppm (observed  $M_{OCH_3,NO_2} = 7.97$  ppm). Then knowing that the internal shift for 4-nitrotoluene is 0.78 ppm, subtraction gives 7.19 ppm (compared with the observed shift of 7.20 ppm).

Correlation coefficients for the meta shifts are not as high as those found for internal chemical shifts. However, the combined use of both sets of correlations provides accurate estimates of absolute shift values if they are required. This is because of shift additivity.

In terms of an additivity theory we might write

$$\nu_X(Z,X) = \nu_X(X) + \nu_X(Z) \quad (5)$$

where the subscript indicates the substituent ortho to the proton being observed and the letter in parentheses designates which substituent has influenced the shift. The internal shift correlation has the form

$$\Delta_{Z,X} = m\Delta_{Z,Y} + b \quad (6)$$

which expands to

$$[\nu_X(X) + \nu_X(Z)] - [\nu_Z(X) + \nu_Z(Z)] = m\Delta_{Z,Y} + b \quad (7)$$

Insertion of the shift value,  $\Delta_{Z,Y}$ , the slope,  $m$ , and the intercept,  $b$ , gives the estimate of the internal shift,  $\Delta_{Z,X}$ .

The meta shift correlation gives

$$M_X(Z,X) = m'M_Y(Z,Y) + b' \quad (8)$$

which expands to

$$\nu_X(Z) + \nu_X(X) = m'M_Y(Z,Y) + b' \quad (9)$$

by shift additivity. Substitution of  $M_Y(Z,Y)$ ,  $m'$ , and  $b'$  into (9) estimates the meta shift as influenced by both substituents and substitution of that value into (7) gives  $[\nu_Z(X) + \nu_Z(Z)]$ . That is, the estimated ortho shift in compound  $ZC_6H_4X$  includes the contributions of both substituents. It is not surprising, then, that the estimated ortho shifts are in such good agreement with the observed values despite the lower quality of the meta shift correlations.

Another important application of the internal shift correlations is estimation of the internal chemical shifts for monosubstituted benzenes. Because the 2,2'-proton multiplet of a monosubstituted benzene is almost always separated from the 3,3'- and 4-proton multiplets, one can immediately ascertain the center of the 3,3' multiplet once the internal shift is known. Then only assignment of the 4-proton shift remains before one can analyze the spectrogram of a monosubstituted benzene.

Perhaps of greater significance, the sharp singlet peaks observed for 4-iodonitrobenzene (7.899 ppm), methyl 4-nitrobenzoate (8.211 ppm), 4-nitrobenzoyl chloride (8.318 ppm), methyl 4-iodobenzoate (7.702 ppm), 4-iodobenzoyl chloride (7.776 ppm), and 4-*tert*-butylbenzotrile (7.488 ppm) are predicted from the internal shift correlations. One would not expect sharp singlets for these compounds on the basis of Hammett  $\sigma$  constants<sup>8</sup> or any other substituent parameters. The fact that each singlet occurs at a different absolute shift is not predicted by the internal shift

Table III. Internal Chemical Shifts and Equations of Correlation for the 1,4-Disubstituted Benzenes<sup>a</sup>

Z	X								
	F			Cl			Br		
	$\delta_F(Z)$	$\delta_Z(F)$	$\Delta_{Z,F}$	$\delta_{Cl}(Z)$	$\delta_Z(Cl)$	$\Delta_{Z,Cl}$	$\delta_{Br}(Z)$	$\delta_Z(Br)$	$\Delta_{Z,Br}$
N(CH <sub>3</sub> ) <sub>2</sub>	6.86	6.55	0.31	7.12	6.55	0.57	7.21	6.48	0.73
NH <sub>2</sub>	6.81	6.48	0.33	8.08 <sup>a</sup>	7.55 <sup>a</sup>	0.53	8.15 <sup>a</sup>	7.41 <sup>a</sup>	0.74
OCH <sub>3</sub>	6.95	6.77	0.18	7.80 <sup>a</sup>	7.38 <sup>a</sup>	0.42	7.85 <sup>a</sup>	7.32 <sup>a</sup>	0.52
OH	6.92	6.72	0.20	7.12	6.64	0.48	7.25	6.60	0.65
CH <sub>3</sub>	6.83	7.05	-0.22	7.18 <sup>a</sup>	7.04 <sup>a</sup>	0.14	7.33 <sup>a</sup>	6.98 <sup>a</sup>	0.35
CH <sub>2</sub> CH <sub>3</sub>									
CH(CH <sub>3</sub> ) <sub>2</sub>									
C(CH <sub>3</sub> ) <sub>3</sub>				7.19	7.19	0			
H	6.94 <sup>b</sup>	7.22 <sup>b</sup>	-0.28	7.29 <sup>b</sup>	7.22 <sup>b</sup>	0.07	7.44 <sup>b</sup>	7.15 <sup>b</sup>	0.29
F	7.33	7.33					7.42	6.90	0.52
Cl				7.22 <sup>a</sup>	7.22 <sup>a</sup>	0			0.25
Br	6.90	7.42	-0.52	7.12	7.39	-0.27	7.67	7.67	0
I				7.03 <sup>a</sup>	7.57 <sup>a</sup>	-0.54	7.39 <sup>a</sup>	7.50 <sup>a</sup>	-0.11
CN	7.17	7.67	-0.50	7.43	7.56	-0.13			
COOH	7.29	8.03	-0.74	7.52	7.96	-0.44	7.68	7.96	-0.44
COOCH <sub>3</sub>	7.07	7.99	-0.92	7.07	7.91	-0.84	7.52	7.82	-0.30
COCl	7.14	8.06	-0.92	7.41	7.94	-0.53	7.63	7.92	-0.29
NO <sub>2</sub>	7.20	8.28	-1.08	7.45	8.91	-0.66	7.61	8.02	-0.41
NHCOCH <sub>3</sub>	6.93	7.60	-0.67	7.23	7.80	-0.57	7.39	7.77	-0.38

Z	X								
	I			CN			COOH		
	$\delta_I(Z)$	$\delta_Z(I)$	$\Delta_{Z,I}$	$\delta_{CN}(Z)$	$\delta_Z(CN)$	$\Delta_{Z,CN}$	$\delta_{COOH}(Z)$	$\delta_Z(COOH)$	$\Delta_{Z,COOH}$
N(CH <sub>3</sub> ) <sub>2</sub>	7.37	6.37	1.00	7.33	6.57	0.77	7.72	6.64	1.08
NH <sub>2</sub>	7.34	6.32	1.02	7.30	6.57	0.73	7.67	6.61	1.05
OCH <sub>3</sub>	7.53	6.62	0.90	7.56	6.97	0.59	7.92	7.03	0.89
OH				7.51	6.95	0.56	7.83	6.88	0.95
CH <sub>3</sub>	7.54 <sup>a</sup>	6.86 <sup>a</sup>	0.68	7.46	7.22	0.24	7.88	7.30	0.58
CH <sub>2</sub> CH <sub>3</sub>				7.52	7.27	0.25	7.85	7.28	0.57
CH(CH <sub>3</sub> ) <sub>2</sub>				7.49	7.26	0.23	7.88	7.33	0.56
C(CH <sub>3</sub> ) <sub>3</sub>				7.49	7.49	0	7.90	7.49	0.41
H	7.65 <sup>b</sup>	7.02 <sup>b</sup>	0.63	7.56 <sup>b</sup>	7.39 <sup>b</sup>	0.17	8.01	7.51	0.50
F				7.67	7.17	0.49	8.03	7.29	0.74
Cl	7.57 <sup>a</sup>	7.03 <sup>a</sup>	0.54	7.56	7.43	0.13	7.96	7.52	0.44
Br	7.50	7.39 <sup>a</sup>	0.11				7.88	7.68	0.20
I	7.62	7.62	0	7.35	7.80	-0.46	7.86	7.70	0.17
CN									
COOH									
COOCH <sub>3</sub>	7.70	7.70	0						
COCl	7.78	7.78	0						
NO <sub>2</sub>	7.90	7.90	0	7.90	8.33	-0.43			
NHCOCH <sub>3</sub>	7.58	7.58	0						

Z	X								
	COOCH <sub>3</sub>			COCl			NO <sub>2</sub>		
	$\delta_{COOCH_3}(Z)$	$\delta_Z(COOCH_3)$	$\Delta_{Z,COOCH_3}$	$\delta_{COCl}(Z)$	$\delta_Z(COCl)$	$\Delta_{Z,COCl}$	$\delta_{NO_2}(Z)$	$\delta_Z(NO_2)$	$\Delta_{Z,NO_2}$
N(CH <sub>3</sub> ) <sub>2</sub>							8.07	6.56	1.51
NH <sub>2</sub>	7.79	6.61	1.17				8.05	6.61	1.44
OCH <sub>3</sub>	7.90	6.85	1.06	7.94	6.89	1.05	8.09	6.89	1.21
OH	7.88	6.87	1.01				8.10	6.92	1.18
CH <sub>3</sub>	7.87	7.19	0.68	7.91	7.22	0.68	7.97	7.20	0.78
CH <sub>2</sub> CH <sub>3</sub>	7.89	7.20	0.69	7.95	7.28	0.68	8.00	7.22	0.78
CH(CH <sub>3</sub> ) <sub>2</sub>	7.89	7.21	0.68	7.96	7.31	0.65	8.06	7.35	0.71
C(CH <sub>3</sub> ) <sub>3</sub>	7.89	7.39	0.51	7.99	7.49	0.50	8.07	7.50	0.57
H	7.99	7.38	0.62	8.03	7.45	0.58	8.13	7.47	0.65
F	7.99	7.07	0.92	8.06	7.14	0.92	8.23	7.22	1.00
Cl	7.91	7.07	0.84	7.94	7.41	0.53	8.11	7.45	0.66
Br	7.82	7.52	0.30	7.92	7.63	0.29	8.02	7.61	0.41
I	7.70	7.70	0	7.78	7.78	0	7.90	7.90	0
CN									
COOH									
COOCH <sub>3</sub>							8.21	8.21	0
COCl							8.32	8.32	0
NO <sub>2</sub>	8.21	8.21	0	8.32	8.32	0	8.34	8.34	0
NHCOCH <sub>3</sub>									

<sup>a</sup> Shift data are relative to TMS and given in parts per million. A benzene shift of 7.285 ppm was used to convert referenced data to absolute shift values. <sup>b</sup> T. K. Wu and B. P. Dailey, *J. Chem. Phys.*, **41**, 2796 (1964).

correlations, of course, but is predicted precisely by the meta shift correlations. For that reason the singlet behavior must result from normal substituent interactions.

Having analyzed the relationships between nine families of disubstituted benzenes, we find that only five or six members need be studied to establish the behavior of the entire family. Those should be selected

from the three principal classes of substituent: strongly directing, little directive ability, and antidirecting. The classification of substituents as strongly directing, weakly directing, or antidirecting will be discussed in a second paper.<sup>14</sup> Examples are  $\text{NH}_2$  or  $\text{OCH}_3$ , the halogens F, Cl, or Br, and carbonyl-containing functions such as  $\text{COCH}_3$ ,  $\text{COCl}$ , or  $\text{COOCH}_3$ , respectively.

In a previous study<sup>6</sup> we suggested the use of the relative internal chemical shift when relating substituent effects on chemical shifts to Hammett constants. The relative internal chemical shift was defined by

$$\delta_{Z,X}^{\text{rel}} = \Delta_{Z,X} - \Delta_{H,X} \quad (10)$$

where  $\Delta_{Z,X}$  is the internal shift in the disubstituted benzene and  $\Delta_{H,X}$  is the internal shift in the parent, monosubstituted benzene. If one plots  $\delta_{Z,X}^{\text{rel}}$  for the families of disubstituted benzenes included in this report he will obtain the same slopes given in Table II for comparable internal shift correlations, and the coefficients of correlation will be identical. The intercepts will be shifted, however. It can be shown that the intercepts differ from zero by the quantity  $(\Delta_{H,Y} - m\Delta_{H,X})$  for the  $y$  intercept and

$$\frac{m\Delta_{H,X} - \Delta_{H,Y} - b}{m}$$

for the  $x$  intercept in all cases studied. Thus we see another aspect of shift additivity. In the case of relative internal shifts the substituent effect of the parent substituent, X, subtracts out.

The relative internal shifts for each family of 1,4-disubstituted benzenes were plotted against the internal shifts of the monosubstituted benzenes to test further the additivity theory of Diehl. A typical plot is shown in Figure 3 and other equations of correlation are given in Table IV. If eq 10 is expanded in terms of contributing shifts

$$\delta_{Z,X}^{\text{rel}} = [\nu_X(Z,X) - \nu_Z(Z,X)] - [\nu_X(H,X) - \nu_H(H,X)] \quad (11)$$

while for the monosubstituted benzenes

$$\Delta_{Z,H} = \nu_H(Z,H) - \nu_Z(Z,H) \quad (12)$$

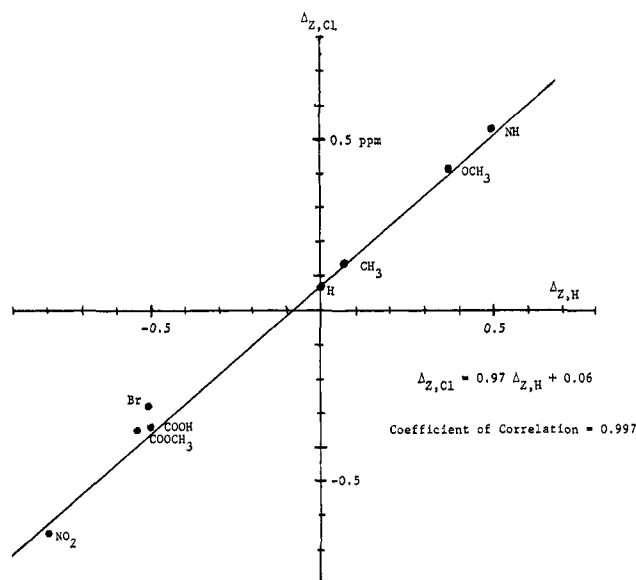
**Table IV.** Equations of Correlation for Relative Internal Shifts in Parts Per Million<sup>a</sup>

Y	X	$m''$	$b''$	Coefficient of correlation
$\Delta_{Z,F}$	$\Delta_{Z,H}$	1.04	0.00	0.975
$\Delta_{Z,Cl}$	$\Delta_{Z,H}$	0.97	-0.01	0.997
$\Delta_{Z,Br}$	$\Delta_{Z,H}$	0.92	-0.03	0.993
$\Delta_{Z,I}$	$\Delta_{Z,H}$	0.87	-0.05	0.984
$\Delta_{Z,COOH}$	$\Delta_{Z,H}$	1.42	-0.24	0.962
$\Delta_{Z,COOCH_3}$	$\Delta_{Z,H}$	1.45	-0.13	0.953
$\Delta_{Z,COCl}$	$\Delta_{Z,H}$	1.52	-0.11	0.944
$\Delta_{Z,NO_2}$	$\Delta_{Z,H}$	1.68	-0.03	0.938

<sup>a</sup> The slope is  $m''$  and the intercept is  $b''$  in the equation  $Y = m''X + b''$ , where  $Y$  is the internal shift in the 1,4-disubstituted benzene family and  $X$  is the internal shift in the monosubstituted benzenes.

For a slope of 1 and intercept of 0 in a correlation of eq 11 and 12, it would appear that the effect of X sub-

(14) D. W. Beistel, *J. Amer. Chem. Soc.*, submitted for publication.



**Figure 3.** Relative internal shift correlation, 4-substituted chlorobenzenes vs. the monosubstituted benzenes.

tracts out of eq 11 to give

$$\delta_{Z,X}^{\text{rel}} = \nu_H(H,X) - \nu_Z(Z,X) \quad (13)$$

an equation of the same form as eq 12.

More specifically for a slope of 1 and intercept of 0 the equation of correlation between (11) and (12) is

$$[\nu_X(Z,X) - \nu_Z(Z,X)] - [\nu_X(H,X) - \nu_H(H,X)] = [\nu_H(Z,H) - \nu_Z(Z,H)] \quad (14)$$

which when written in terms of shift additivity becomes

$$[\nu_X(Z) + \nu_X(X) - \nu_Z(Z) - \nu_Z(X)] - [\nu_X(H) + \nu_X(X) - \nu_H(H) - \nu_H(X)] = [\nu_H(Z) + \nu_H(H) - \nu_Z(Z) - \nu_Z(H)] \quad (15)$$

This reduces to

$$\nu_X(Z) - \nu_Z(X) + \nu_H(X) - \nu_X(H) = \nu_H(Z) - \nu_Z(H) \quad (16)$$

which appears to give

$$\nu_H(Z) = \nu_H(X) + \nu_X(Z) \quad (17)$$

and

$$\nu_Z(H) = \nu_Z(X) + \nu_X(H) \quad (18)$$

That is, a chain rule relationship seems to exist for substituent effects.

Thus it would appear from Table IV that the halobenzenes provide the best support for the additivity concept. Yet Diehl<sup>8</sup> suggested that the halogens might be treated separately in correlating shift data with  $\sigma$  constants. In addition the seemingly anomalous behavior of the halobenzenes contributed to the theories of inductive, resonance, and steric influences on chemical shifts.<sup>15-17</sup> But it is obvious from the present study

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(17) R. W. Taft, E. Price, I. R. Fox, I. C. Lewis, K. K. Anderson, and G. T. Davis, *J. Amer. Chem. Soc.*, **85**, 3146 (1963).

that no anomalous shifts are induced by the halogens or by any of the 16 substituents singly or in combination at the 1,4 positions, suggesting perhaps that qualitative correlations of shift data with  $\sigma$  constants provide little useful information concerning the nature of substituent effects.

Finally while qualitative agreement has been found between the internal shifts and the coupling constants for each family of disubstituted benzenes,<sup>13</sup> no strong correlations were noted. In general as the internal shift increases, the magnitudes of  $J(2,3) = J(2',3')$  and  $J(2,2') = J(3,3')$  increase; the largest internal shift and coupling values are found for the nitrobenzenes. In terms of trends the halogens influence abnormally large coupling values as does the *tert*-butyl group.

## Conclusions

We have seen that shift additivity relationships allow the accurate prediction of proton shifts in disubstituted benzenes. No inductive and/or resonance interactions between substituents have been noted despite the rather broad range of substitution examined. This study suggests the need for a fresh approach to the question of how aromatic substitution influences the shifts of ring protons. Group anisotropy effects do not explain the variations observed for different families of 1,4-disubstituted benzenes, nor can they account for the singlet proton resonances observed for compounds such as 4-iodonitrobenzene.

## Experimental Section

Spectral data were obtained on Varian A56/60, A60, and HA-100 spectrometers. Deuteriochloroform was the solvent for all families of 1,4-disubstituted benzenes except the benzoic acids. The latter were prepared in perdeuteriodimethyl sulfoxide. All spectra were analyzed by an IBM 360/50 computer using the program LAOCOON III.<sup>18</sup> The maximum permissible probable error was 0.03 Hz for the shift and coupling parameters. Standard least-squares programming was used to obtain the reported shift correlations.

Because of the scope of the investigation, a complete tabulation of synthetic procedures would be too voluminous. Commercially available compounds were purified before use by recrystallization or gas chromatography and authenticated by measurements of physical properties and by spectrophotometric identification procedures. Compounds not available from commercial sources were synthesized by standard techniques and verified by elemental analysis, measurements of physical properties, and spectrophotometric methods. Complete discussions are available on request.

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(18) A. A. Bothner-By and S. Costellano, LAOCN3, Mellon Institute, Pittsburgh, QCPE 111.

# Molecular Orbital Theory of the Hydrogen Bond. VII. A Series of Dimers Having Ammonia as the Proton Acceptor

Janet E. Del Bene

Contribution from the Department of Chemistry, Youngstown State University, Youngstown, Ohio 44503. Received April 11, 1973

**Abstract:** *Ab initio* SCF calculations with a minimal STO-3G basis set have been performed on the series of dimers  $\text{ROH} \cdots \text{NH}_3$ , where R may be H, or one of the isoelectronic substituents  $\text{CH}_3$ ,  $\text{NH}_2$ , OH, or F. The equilibrium structures and energies of these dimers are presented and analyzed. The dimer structures are well described in terms of the general hybridization model for the hydrogen bond. While the electrostatic interaction is of primary importance in stabilizing hydrogen bonded dimers, dipole-dipole and long-range interactions are also shown to be important in determining hydrogen bond strengths. Comparisons are made between corresponding dimers in the two series  $\text{ROH} \cdots \text{OH}_2$  and  $\text{ROH} \cdots \text{NH}_3$ .

Within the past several years, *ab initio* molecular orbital theory has been applied to the problem of interacting molecules in studies of a rather wide variety of dimers in which the principal mode of intermolecular interaction is through hydrogen bond formation.<sup>1-19</sup>

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While the results of these studies may differ in certain specific details, collectively they have demonstrated that *ab initio* molecular orbital theory can be applied to the problem of hydrogen bond formation. Certainly, an ultimate aim of theoretical investigations of this type

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