

Conclusion

It has been shown that single determinant RHF theory using an extended basis set with polarization functions is sufficient to describe the equilibrium geometry and barrier to inversion of cyclobutane. Theoretical and experimental data are found to be in good agreement. The quantum mechanical calculations verify a significant coupling between ring puckering and methylene group tilting which was first found by Meiboom and Snyder.¹¹ It seems that this effect plays an important role in puckered ring systems with comparative strain.

Acknowledgment. This work was supported by the Deutsche Forschungsgemeinschaft. The calculations were carried out using the CDC Cyber 72/76 computers of the Cologne Computation Center.

References and Notes

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- (27) The puckering amplitude q is equal to the distance between the two CC diagonals in the cyclobutane ring, i.e., twice the internal coordinate Z used in vibrational studies (ref 8). If α is taken to be the CCC angle, θ the angle between the two ring planes C(4)C(1)C(2) and C(2)C(3)C(4), and $\omega = \frac{1}{2}(180 - \theta)$, then the amplitude q can be calculated from $q = R_{CC} \cos(\alpha/2) \sin \omega$.
- (28) The tilting angle is defined as the angle between the CCC bisector and the HCH bisector.
- (29) D. Cremer, to be published.
- (30) D. Cremer, to be published.
- (31) Recent studies indicate that electron correlation plays a certain role in stabilizing the puckered form (D. Cremer, to be published).

Proton Shift Additivity and Substituent Interaction Parameters

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Abstract: The 4-substituted acetophenone family is characterized and its shifts are correlated with those of nine families of 1,4-disubstituted benzenes reported previously. Then a simple mathematical model is derived to account for the proton magnetic resonance shifts within families of 1,4-disubstituted benzenes. The model suggests that the substituents interact by σ -bond polarization. The polarization model rationalizes shift additivity and is consistent with the qualitative relationship between the number of valence electrons on a substituent and its capacity to induce shifts.

In a recent study the internal and meta proton shifts were correlated for nine families of 1,4-disubstituted benzenes.¹ The equations of correlation were used to predict shifts with an error of less than 3%, a marked improvement over the empirical equations of Diehl² or Dailey.³ It was shown that the shift additivity concept of Diehl² could be applied to the internal shift equations and that 1,4-interactions, induced ring currents, and other effects⁴ might be implicit contributors to the internal shift.

The study of a tenth family, the 4-substituted acetophenones, seems to complement our earlier work and has provided an opportunity to examine the equations of internal shift correlation in greater detail. It will be shown that 1,4 interactions can be written explicitly and may be used to assess the nature of substituent effects.

Results and Discussion

The proton shifts of the 4-substituted acetophenones are given in Table I. The equations of internal shift correlation

relating the acetophenone family to previous data sets¹ are given in Table II and the coefficients of correlation are quite high. The relative magnitudes of the internal shifts suggest that the COCH₃ group provides a magnetic environment similar to the other α -carbonyl containing functions, placing it between the COOH and COOCH₃ groups in the spectrochemical series suggested by our earlier study.¹

If one examines the relative magnitudes of the slope and intercept values for the equations of internal shift correlation in Table II of this and our earlier study,¹ he will note that the slope values range near unity. He might also observe that the coefficients of correlation are highest when the intercept values are small. Those two facts can be used to understand how the internal chemical shift incorporates basic information about substituent effects and chemical bonding in the 1,4-disubstituted benzenes.

The general equation internal shift correlation is

$$\Delta_{Z,R} = m_{R,S} \Delta_{Z,S} + b_{R,S} \quad (1)$$

Table I. Proton Chemical Shifts for the 4-Substituted Acetophenones

Z	$\delta_{\text{COCH}_3}(\text{Z})$	$\delta_{\text{Z}(\text{COCH}_3)}$	$\Delta_{\text{Z,COCH}_3}$
NH ₂	7.803	6.627	1.176
OCH ₃	7.854	6.895	0.959
H	7.710	7.175	0.535
F	7.852	6.973	0.879
Cl	7.838	7.360	0.478
Br	7.736	7.502	0.234
CN	8.037	7.759	0.278
NO ₂	8.280	8.105	0.175

When the 1,4-disubstituted benzenes are correlated against the monosubstituted benzenes we have

$$\Delta_{\text{Z,Y}} = m_{\text{Y,H}}\Delta_{\text{Z,H}} + b_{\text{Y,H}} \quad (2)$$

or

$$\Delta_{\text{Z,X}} = m_{\text{X,H}}\Delta_{\text{Z,H}} + b_{\text{X,H}} \quad (3)$$

depending upon the family of disubstituted benzenes being correlated. Now, the correlations among families of 1,4-disubstituted benzenes gave equations² of the form

$$\Delta_{\text{Z,Y}} = m_{\text{Y,X}}\Delta_{\text{Z,X}} + b_{\text{Y,X}} \quad (4)$$

From (2) and (3)

$$\Delta_{\text{Z,H}} = \frac{\Delta_{\text{Z,Y}} - b_{\text{Y,H}}}{m_{\text{Y,H}}} = \frac{\Delta_{\text{Z,X}} - b_{\text{X,H}}}{m_{\text{X,H}}}$$

giving

$$\Delta_{\text{Z,Y}} = \frac{m_{\text{Y,H}}}{m_{\text{X,H}}} (\Delta_{\text{Z,X}} - b_{\text{X,H}}) + b_{\text{Y,H}}$$

or

$$\Delta_{\text{Z,Y}} = \frac{m_{\text{Y,H}}}{m_{\text{X,H}}} \Delta_{\text{Z,X}} + b_{\text{Y,H}} - \frac{m_{\text{Y,H}}}{m_{\text{X,H}}} b_{\text{X,H}}$$

Comparing these coefficients with those found in eq 4

$$m_{\text{Y,X}} = m_{\text{Y,H}}/m_{\text{X,H}}$$

and

$$b_{\text{Y,X}} = b_{\text{Y,H}} - \frac{m_{\text{Y,H}}}{m_{\text{X,H}}} b_{\text{X,H}} \quad (5)$$

If we let Y = NO₂ and X = COCl the slope eq 5 becomes $m_{\text{NO}_2,\text{COCl}} = m_{\text{NO}_2,\text{H}}/m_{\text{COCl,H}} = 1.11$ (observed, 1.16).¹ A similar prediction for $m_{\text{COOH},\text{COCH}_3}$ gives 0.98 (0.80 is observed).¹ The success of the former prediction can be attributed to shift additivity and to the goodness of fit of the experimental data. The predicted slope value for $m_{\text{COOH},\text{COCH}_3}$ is too large however as are those predicted for $m_{\text{F,Br}}$ and $m_{\text{NO}_2,\text{F}}$. One notes that the intercepts in Table II¹ are large in those cases where the coefficients of correlation are not quite as good. Perhaps the linear-least-squares criteria did not give optimum slope and intercept values in those instances.

One can obtain consistently good predictions of internal chemical shifts for the 1,4-disubstituted benzenes using the shifts and slopes obtained from their monosubstituted counterparts. Noting that the slopes of the shift correlation equations are close to unity, we might assume a slope of the form $m_{\text{Y,H}} = (1 + \alpha_{\text{Y,H}})$ where the $\alpha_{\text{Y,H}}$ represents a perturbation term.

Then eq 1 would be written

$$\Delta_{\text{Z,Y}} = (1 + \alpha_{\text{Y,H}})\Delta_{\text{Z,H}} + b_{\text{Y,H}} \quad (6)$$

or

$$\Delta_{\text{Z,X}} = (1 + \alpha_{\text{X,H}})\Delta_{\text{Z,H}} + b_{\text{X,H}} \quad (7)$$

Table II. Equations of Correlation Relating the Acetophenone Family to Other Families of Proton Shifts^{1,2}

		Slope	Intercept	Corr coeff
$\Delta_{\text{Z,F}}$	$\Delta_{\text{Z,H}}$	1.04	0.00	0.975
$\Delta_{\text{Z,Cl}}$	$\Delta_{\text{Z,H}}$	0.97	-0.01	0.997
$\Delta_{\text{Z,Br}}$	$\Delta_{\text{Z,H}}$	0.92	-0.03	0.993
$\Delta_{\text{Z,I}}$	$\Delta_{\text{Z,H}}$	0.87	-0.05	0.984
$\Delta_{\text{Z,COOH}}$	$\Delta_{\text{Z,H}}$	1.42	-0.24	0.962
$\Delta_{\text{Z,COOCH}_3}$	$\Delta_{\text{Z,H}}$	1.45	-0.13	0.953
$\Delta_{\text{Z,COCl}}$	$\Delta_{\text{Z,H}}$	1.52	-0.11	0.944
$\Delta_{\text{Z,NO}_2}$	$\Delta_{\text{Z,H}}$	1.68	-0.03	0.938
$\Delta_{\text{Z,COCH}_3}$	$\Delta_{\text{Z,H}}$	1.14	-0.66	0.952
$\Delta_{\text{Z,F}}$	$\Delta_{\text{Z,COCH}_3}$	0.752	0.806	0.926
$\Delta_{\text{Z,Cl}}$	$\Delta_{\text{Z,COCH}_3}$	0.874	0.567	0.927
$\Delta_{\text{Z,Br}}$	$\Delta_{\text{Z,COCH}_3}$	0.892	0.386	0.933
$\Delta_{\text{Z,I}}$	$\Delta_{\text{Z,COCH}_3}$	0.962	0.114	0.972
$\Delta_{\text{Z,CN}}$	$\Delta_{\text{Z,COCH}_3}$	0.894	0.439	0.962
$\Delta_{\text{Z,COOH}}$	$\Delta_{\text{Z,COCH}_3}$	1.115	0.001	0.999
$\Delta_{\text{Z,COOCH}_3}$	$\Delta_{\text{Z,COCH}_3}$	0.790	0.059	0.905
$\Delta_{\text{Z,COCl}}$	$\Delta_{\text{Z,COCH}_3}$	0.559	0.143	0.923
$\Delta_{\text{Z,NO}_2}$	$\Delta_{\text{Z,COCH}_3}$	0.735	0.054	0.970
$\Delta_{\text{Z,H}}$	$\Delta_{\text{Z,COCH}_3}$	0.879	0.584	0.952

When Z = X we have from (6) that

$$\Delta_{\text{X,Y}} = (1 + \alpha_{\text{Y,H}})\Delta_{\text{X,H}} + b_{\text{Y,H}} \quad (8)$$

and when Z = Y we have from (7) that

$$\Delta_{\text{Y,X}} = (1 + \alpha_{\text{X,H}})\Delta_{\text{Y,H}} + b_{\text{X,H}} \quad (9)$$

Because $\Delta_{\text{Y,X}} = -\Delta_{\text{X,Y}}$, (9) can be written

$$\Delta_{\text{X,Y}} = -(1 + \alpha_{\text{X,H}})\Delta_{\text{Y,H}} - b_{\text{X,H}} \quad (10)$$

so that adding (8) and (10) will give

$$2\Delta_{\text{X,Y}} = (1 + \alpha_{\text{Y,H}})\Delta_{\text{X,H}} - (1 + \alpha_{\text{X,H}})\Delta_{\text{Y,H}} + b_{\text{Y,H}} - b_{\text{X,H}} \quad (11)$$

When X = H, $\Delta_{\text{H,X}} = \Delta_{\text{H,H}} = 0$ and it is seen from (8) that $\Delta_{\text{H,Y}} = b_{\text{Y,H}} = -\Delta_{\text{Y,H}}$. When Y = H then $\Delta_{\text{H,X}} = b_{\text{X,H}} = -\Delta_{\text{X,H}}$. Substituting into (11) we have $2\Delta_{\text{X,Y}} = (1 + \alpha_{\text{Y,H}})\Delta_{\text{X,H}} + \Delta_{\text{X,H}} - (1 + \alpha_{\text{X,H}})\Delta_{\text{Y,H}} - \Delta_{\text{Y,H}}$. Collecting terms and rearranging one obtains

$$\Delta_{\text{X,Y}} = \Delta_{\text{X,H}} + \Delta_{\text{Y,H}} + \frac{1}{2}(\alpha_{\text{Y,H}}\Delta_{\text{X,H}} + \alpha_{\text{X,H}}\Delta_{\text{Y,H}}) \quad (12)$$

Equation 12 suggests that the internal shifts of the 1,4-disubstituted benzenes can be calculated from the internal shifts of the monosubstituted benzenes using the appropriate parameter, α . To obtain the internal shift for 4-fluoronitrobenzene one would substitute the appropriate shift and values from Table III into

$$\Delta_{\text{NO}_2,\text{F}} = \Delta_{\text{NO}_2,\text{H}} + \Delta_{\text{F,H}} + \frac{1}{2}(\alpha_{\text{F,H}}\Delta_{\text{NO}_2,\text{H}} + \alpha_{\text{NO}_2,\text{H}}\Delta_{\text{F,H}})$$

One obtains 1.00 ppm, which is observed. The agreement with observed shifts is excellent over a broad range of substituents and certainly much better than predictions using the Diehl² or Dailey³ models.

The quantity containing the α 's in eq 12 makes an adjustment of about 5% on the average internal shift. One is tempted to define the α values as shift perturbation terms and use them to assess the nature and extent of a substituent interaction. But the pattern of signs and magnitudes is not consistent with any previous classifications such as Brown⁵ or Taft⁶ suggested.

Only six of the substituents have α values greater than 0.05 and they are NMe₂, F, I, COCH₃, Br, and NO₂, and all but Br and I have positive values. Accordingly all but two require a small added contribution in eq 12 from the shift of the substituent para to them on the benzene ring, suggesting that they

Table III. Internal Shifts and Substituent Interaction Terms from Monosubstituted Internal Shift Plots

Substituents, X	Δ_{XH}	α
I	-0.64	-0.126
Br	-0.30	-0.082
NH ₂	+0.56	-0.024
Cl	-0.06	-0.010
COOCH ₃	-0.60	0.011
CN	-0.17	0.013
COCl	-0.58	0.024
COOH	-0.50	0.043
OCH ₃	+0.39	0.047
N(CH ₃) ₂	+0.50	0.073
F	-0.29	0.081
COCH ₃	-0.54	0.138
NO ₂	-0.65	0.232

have enhanced the contribution of any 4 substituent somewhat. Similarly shifts due to 4 substitution seem to be suppressed by the presence of Br and I. The enhancement or suppression factors represent a constant percentage of the shift of the para substituent regardless of the magnitude of its interaction in a monosubstituted environment.

Clearly the α values do not suggest 1,4 interactions in the sense that conjugation and steric effects have been suggested in the past. They imply that the presence of a 4 substituent has altered the potential of its para neighbor to induce proton shifts. The effect is not steric because the usual comparisons between normal and bulky groups of similar electronic character do not apply. If the origins of the enhancement/suppression are electronic then groups capable of π conjugation do not exert a different level of enhancement from those considered incapable of conjugation.

The nature of the effect seems to require a polarization model involving the σ bonds of the benzenoid skeleton. Polarization effects have been suggested to be short-range perturbations⁷ despite the fact that 4 shifts were noted by Diehl² and α -shifts have been found for several external nuclei.^{6,8,9} The attenuation factor of 1:2.8 per bond¹⁰ would give a perturbation of 1.6% at the α position and the value of the internal shift correction factors is about 3% when the constant, $1/2$, is included. This is certainly suggestive of σ -bond polarization.

The relative magnitudes of the ring proton shifts also suggest a polarization model. The substituent interacts across three σ bonds at the 2 position and 4 σ bonds at position 3. The relative magnitudes of the perturbation should then be 2.8:1 and that is the approximate interaction if one calculates the the shifts at each position relative to the monosubstituted benzene. For example the 2 shift relative to H for 4-aminobenzonitrile is 0.82 ppm while that observed at the 3 position is 0.26 ppm.¹ The ratio of shifts is 3.2:1 which is the expected order of magnitude. In this case the α values for NH₂ and CN are -0.024 and 0.013, respectively. Their values are small and therefore similar enough that essentially no substituent-substituent polarization has occurred and the shift ratio is nearly 3:1 as a consequence.

When one of the substituents has a very large polarizability like the NO₂ group the attenuation factor increases. For instance 4-aminonitrobenzene has an attenuation ratio of 15:1 when its 2- and 3-proton shifts are compared with those of

nitrobenzene. One would expect this attenuation ratio to be large if he compared the α values for NH₂ and NO₂ in Table II. The α values for NH₂ and NO₂ are -0.024 and 0.232, respectively, which suggests that the 3 shift (ortho to NO₂) has been reduced considerably by a polarization of the NO₂ group in its disubstituted environment. Or alternatively, the 2 shift is greater due to the enhanced perturbation from NH₂ due to the presence of NO₂. According to eq 12 either interpretation would seem valid.

It is important to realize that the α value of 0.232 for NO₂ implies that any substituent para to NO₂ will have its shift effect enhanced by 11.6% according to eq 12. The fact that any substituent must behave in this way regardless of its so-called abilities to conjugate, resonate, or act sterically seems to minimize the importance of those complex rationalizations suggested by previous investigators. The deviations from shift additivity that prompted those rationalizations seem illusory and are not real. Equation 12 says as much.

A polarization model for substituent effects is very attractive from several viewpoints. Polarization arises from induced perturbations of the electron clouds and is somewhat independent of the nature of the polarized atom. More important, this perturbation is additive to a first approximation.¹¹ These characteristics can be seen in the proton shift data¹ in terms of shift additivity and in the spectrochemical series as well. There is a degree of similarity between the number of valence electrons on a substituent and the relative shift it induces. The more polarizable substituents, those with the greater number of valence electrons, lie farther down the spectrochemical series and induce downfield shifts relative to groups like NH₂ and F with only seven valence electrons.

Experimental Section

The spectral data for the 4-substituted acetophenones were obtained on commercially available samples in 20% solution in DCCl₃ using a Varian XL-100 magnetic resonance spectrometer at 100.1 MHz. The digitized output was analyzed on an IBM 370/168 computer using the program LAOCOON III, a spectral reduction program used in our previous studies.¹ Linear-least-squares analyses were performed on the IBM 370/168 also. The α values listed in Table II were calculated directly from the definition of α .

Acknowledgment. The authors are grateful to Professor C. A. Wilkins and Mr. Tom Brunner of the University of Nebraska-Lincoln for the fine spectral services provided by their laboratories.

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