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CARBON-13 CARBONYL SHIELDING AND STERIC INHIBITION OF RESONANCE

A NEW AND BETTER METHOD FOR ESTIMATING ANGLES OF TWIST IN CONJUGATED SYSTEMS

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The estimation of angles of twist about single bonds in sterically hindered conjugated systems, θ in Fig. 1, is a problem of theoretical interest and has attracted the attention of several investigators (1). A number of physical methods have been applied to this problem, principal among which are ultraviolet spectroscopy and dipole moment measurements, but suffer from certain disadvantages and, in specific cases, give anomalous results. We wish to report a new method utilizing carbon-13 NMR chemical shift data which yields values for θ which are internally consistent and in agreement with simple steric considerations. These estimates are compared with previous values to show that the C^{13} NMR method avoids some of the difficulties associated with the other methods

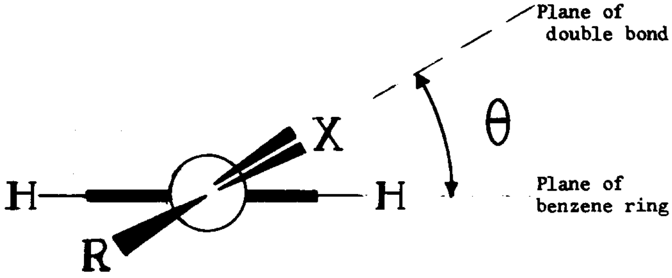

FIG. 1

Diagrammatic representation of the angle of twist, θ, about a single bond in a conjugated system. End view of $\phi\text{-}\underset{R}{\underset{|}{C}}{=}X$.

and possesses certain unique advantages.

Several studies of C^{13} NMR spectra of aromatic molecules have been reported (2a-e) and, as a result, the major factors contributing to the chemical shifts of aromatic carbon nuclei have been established. For these nuclei, good linear correlations of the *para*-carbon chemical shifts of monosubstituted benzenes with the Hammett σ_p parameter have been demonstrated (2d), as well as excellent correlations of these shifts with F^{19} and H^1 NMR data (3) for similarly substituted fluorobenzenes (4) and 2,6-dimethylbenzene derivatives (5), respectively. Furthermore, Lauterbur (3) has shown that the shieldings of the aromatic carbons appear to be more simply related to ground state electronic distributions of these molecules than either H^1 or F^{19} shieldings and that it appears likely that the π electron densities are a major factor determining C^{13} shieldings in aromatic molecules. As a consequence, evidence of steric inhibition of resonance may be obtained from studies of the chemical shifts of aromatic carbon nuclei (2c). Our studies of aromatic carbonyl compounds, extending a general survey of carbonyl chemical shifts (6), permit the examination of C^{13} shieldings of those nuclei bonded to the aromatic ring and, on the basis of results for over 100 aromatic carbonyl compounds (7), provide a new method for the study of steric inhibition of resonance in these systems. We have developed an empirical expression relating the angle of twist, θ, between the carbonyl group and the benzene ring with the shielding of the carbonyl carbon nucleus.

In contrast to the chemical shifts of the aromatic *para*-carbon nuclei, carbonyl shieldings in substituted acetophenones are relatively insensitive to the polar effects of substituents, covering the range, $p\text{-}NMe_2 \rightarrow p\text{-}NO_2$. An examination of thirteen m- and p-substituted acetophenones shows a total variation of 1.2 p.p.m. for the carbonyl carbon and no correlation with the σ parameter is evident. The total change may be compared to the 27.5 p.p.m. difference found for F^{19} chemical shifts in the corresponding p-substituted fluorobenzenes (4) and to the difference of less than 1 p.p.m. in the methyl C^{13} resonances of the corresponding toluenes (2a). Clearly, polar factors are of minimal importance for these carbonyl resonances.

Significant changes in the carbonyl chemical shifts are observed, however, for ortho-substituted derivatives (15 examples) for which the carbonyl carbon absorbs at lower fields than in the corresponding m- and p-substituted compounds, while a more pronounced low-field shift is found for the 2,6-disubstituted compounds (8 examples). Furthermore, the shift to lower field increases with increasing bulk of the substituents* (see Fig. 2). Some representative data in Table I illustrate this.

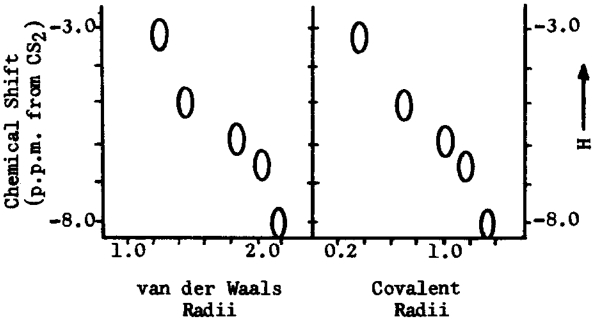

FIG. 2

Plot of carbonyl carbon resonance position for o-substituted acetophenones vs. the van der Waals and covalent radii of the following ortho substituents: H, O(as OMe), Cl, Br, I.

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*We feel that any effects acting through space due to magnetic anisotropy are of secondary importance for the reasons discussed elsewhere (6).

TABLE I

C^{13} Chemical Shifts of some Alkyl-Substituted Acetophenones

Substituent(s)	Chemical Shifts (p.p.m. from CS_2)		
	C=O	para-C*	CH_3-CO
H	-3.2	61.2	167.9
4-Me	-3.2	(58.9)	166.9
3-Me	-2.7	(60.6)	167.7
2-Me	-6.5	(62.7)	164.2
2,4-Me_2	-5.8	(64.8)	164.2
2,5-Me_2	-5.7	(64.8)	164.4
2,6-Me_2	-12.9	(66.2)	162.0
2,4,6-Me_3	-13.4	(64.5)	161.7
2,3,5,6-Me_4	-15.3	(62.6)	160.2
2-Et	-6.9	(62.5)	164.2
2-*i*-Pr	-8.0	(63.7)	164.3
2,5-*t*-Bu_2	-15.3	-	161.6
2,6-Et_2	-13.0	(64.6)	161.5
2,4,6-*i*-Pr_3	-15.1	(63.5)	-

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* Data in parentheses have been corrected for the contribution of the alkyl substituent assuming additivity of alkyl effects (1b, c,e,6). These figures may be compared with the benzene C^{13} shift of 65.0 p.p.m. (1b).

TABLE II

Estimates of θ for some Ortho-Substituted Acetophenones by Various Methods

Substituent(s)	Method of Estimation		
	C^{13} NMR (corr.)*	UV Spectra (8)	Dipole Moment (8)
2-Me	24° (28°)	40°	34°
2,4-Me_2	21° (25°)	24°	-
2,5-Me_2	21° (25°)	35°	46°
2,6-Me_2	44° (50°)	55°	-
2,4,6-Me_3	46° (51°)	63°**	62°
2,3,5,6-Me_4	51° (57°)	-	-
2-Et	25°	-	-
2-*i*-Pr	29°	-	-
2-*t*-Bu‡	51°	-	-
2-MeO	17°	-	-
2-Cl	22°	30°●	-
2-Br	24°	-	-
2-I	29°	-	-

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* Data in parentheses have been corrected for "ortho" effect of methyl group(s). (See text).

‡ Using the data for 2,5-di-t-butyl acetophenone.

● Reference 10.

** The value 67° has also been reported (8).

A comparison of the carbonyl shift data for a large number of saturated and conjugated compounds of both the aliphatic and aromatic series clearly shows that the conjugated carbonyl carbon nuclei are shielded relative to the corresponding saturated derivatives (6), an effect which may be attributed to an increase in the electron density about that carbon, as in the aromatic series (2). If this were true, the electron-withdrawing effect of the carbonyl grouping on the carbonyl-methyl bond in methyl ketones would be reduced in a conjugated system relative to its saturated analogue, and hence lead to a reduced polarization of this bond which would increase the electron density at the methyl carbon nucleus. In fact this is found to be the case since the acetyl methyl carbons absorb _ca_. 4 p.p.m. to higher field in the conjugated systems. It follows, therefore, that any factor which could reduce the degree of conjugation in a substituted acetophenone would be expected to reduce the shielding at the carbonyl and acetyl methyl carbons. Inhibition of resonance between the carbonyl group and the benzene ring caused by a bulky _ortho_ substituent should be indicated by comparison of these shifts with those in a planar system such as acetophenone (see Table I). An additional check on the origin of this shift toward lower field is provided by an examination of the variation of the shielding of the aromatic carbon _para_ to the carbonyl grouping. On the basis of Lauterbur's results for hindered dimethylanilines, iodobenzenes and nitrobenzenes (2c), one would expect the _para_ carbon of these acetophenones to move up-field in hindered systems since the acetyl group tends to deshield at the _para_ position in acetophenone relative to benzene (2d). In all cases, as the carbonyl peak moves toward lower field the _p_-carbon resonance moves up-field (see Table I). Throughout this series of compounds we have observed an additive relation for the substituent effects on the aromatic carbon shieldings in agreement with earlier work (2b,c).

On the basis of the results for the carbonyl carbon resonances, it is evident that the most important factor, unique to the conjugated systems, contributing to the shielding of the carbonyl carbon nucleus in the aromatic ketones is the degree of conjugation between the carbonyl group and the aromatic ring. This suggests the possibility of correlating the carbonyl chemical shifts with the interplanar angle, θ between these groups and the development of an empirical expression follows. It is reasonable that the conjugative interaction between the two π systems is maximal for a coplanar system, $\theta = 0^{\circ}$, and minimal for systems in which $\theta = 90^{\circ}$. It has been shown that the extra resonance energy due to the conjugative interaction for the system R-S relative to R + S varies approximately as $\cos^2\theta$ (9). Also, the chemical shift of the carbonyl carbon in acetophenone, 3.2 p.p.m., may be taken as that typical of the planar system. Finally, it remains to estimate the chemical shift for the hypothetical system in which $\theta = 90^{\circ}$. A comparison of the C^{13} data for a number of derivatives of the type, $\phi_n\mathrm{CH}_{(3-n)}\mathrm{X}$, where n=0, 1 or 2 and X=H, Cl, OH, and Me, indicates that substitution of phenyl for hydrogen tends to deshield the α-carbon by ca. 17 p.p.m., for systems in which conjugative interactions may be considered minimal. For the substitution, $\mathrm{CH_3CHO} \rightarrow \mathrm{CH_3CO}\phi$, however, the α-carbon (i.e., the carbonyl carbon) is shielded by 3.5 p.p.m. Thus, a reasonable estimate of the conjugative shielding effect of the phenyl group appears to be 20 p.p.m. Using this value, one would predict the carbonyl shift for the case, $\theta = 90^{\circ}$, to be -23.2 p.p.m. On the basis of these assumptions, one can relate θ with the observed carbonyl carbon chemical shift by the expression,

$$\cos^2\theta = \left[\frac{\delta_c^{x} - \delta_c^{90^{\circ}}}{\delta_c^{0^{\circ}} - \delta_c^{90^{\circ}}}\right] = \frac{\delta_c^{x} + 23.2}{20}$$

where δ_c^x represents the C^{13} carbonyl shift of a substituted acetophenone, relative to CS_2. Some typical values for Θ obtained from this expression are collected in Table II, together with estimates obtained by other means (9,10). It can be noted that the estimate of the conjugative effect of the phenyl group (20 p.p.m.) is not particularly critical since variations of $\pm$ 10% change Θ by $\leq \pm 5^\circ$.

Studies of substituted o-xylenes have shown that the methyl carbons appear at slightly higher field (1 p.p.m.) than for the cases in which the methyls are further separated (2b,2c,7), indicating the presence of a small additional "ortho" effect. Assuming that this additional factor is operative in the acetophenones, one can estimate Θ using carbonyl shifts corrected for this effect and representative values have been included in parentheses in Table II. Support for including this correction is given by the carbonyl data for the series: benzaldehyde, o-tolualdehyde, mesitylaldehyde whose resonances appear at 2.0, 0.9 and 1.9 p.p.m., respectively. These data, on the basis of the present interpretation, indicate that there is more hindrance in the monosubstituted case than in the di-*o*-substituted example, contrary to normal expectations, whereas inclusion of the correction for the "ortho" effect of the methyl groups restores order in this series.

An examination of the data in Table II shows that the calculations based on C^{13} NMR data yield values for Θ which are consistent with simple steric considerations without further qualifying assumptions. This is in contrast to the results obtained by other methods. For example, there appears to be no reason to expect a significant difference in Θ for the 2-methyl and 2,5-dimethyl substituted compounds, although estimates based on dipole moment data indicate this (8). Also it is difficult to understand why a para-methyl group reduces Θ in the

2,4-dimethyl system relative to the 2-methyl derivative but increases θ in the 2,4,6-trimethyl compound relative to 2,6-dimethylacetophenone, according to the estimates from UV spectra (8). A more rational set of values result from the analysis of the C^{13} data and, in view of the parameters used to develop the equation, it is suggested that these estimates are within ± 5° of the true value. It is interesting to note, also, the clear indication of a "buttressing" effect in the case of 2,3,5,6-tetramethylacetophenone (acetyldurene).

The major difficulty associated with obtaining estimates of θ from UV spectra is a precise knowledge of the particular band chosen. Cases involving overlapping bands are not uncommon and an overlap of absorption bands combined with the ever-present possibility of slight shifts of these due to other factors may make accurate intensity measurements of a specific band very difficult. Even in the most favorable case, one is observing an energy difference between an excited state and the ground state in an attempt to evaluate a property of the ground state. The limitations of the method have been discussed in detail (1,9). The C^{13} data, however, are characteristic of the ground electronic state alone and the absorption band due to the carbonyl carbon nucleus appears in a relatively uncluttered region of the C^{13} spectrum. In addition, the changes in carbonyl chemical shifts observed in the hindered systems are large relative to the effects of other factors such as polar substituents, solvents (excluding those capable of hydrogen-bonding) and neighboring magnetically anisotropic groups. Furthermore, it appears that an examination of suitable model compounds allows one to correct for these non-steric effects as illustrated above for the methyl group.

Extension of this method to ortho-substituents other than alkyl groups is straightforward and a few uncorrected data are given in Table II.

Although less general, an alternative approach to θ values involves the use of the acetyl methyl C^{13} shifts which are less susceptible to non-steric factors. Both of these aspects, together with the data for other aromatic systems will be reported in full elsewhere. The marked dependency of carbonyl carbon resonances on the degree of planarity in conjugated systems is also observed in aliphatic and alicyclic carbonyl compounds (11), studies of which will be described in detail in due course.

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