The Torsional Barrier in Aromatic Carbonyl Compounds

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$\Delta G^{\ddagger}$ Values for the torsional barriers of *para*-substituted benzaldehydes, protonated *para*-substituted propiophenones, and various *p*-methoxyacylbenzenes have been measured by dynamic ^{13}C n.m.r. The regression analysis performed for these and other available ^{1}H and ^{13}C n.m.r. data with a variety of inductive and resonance parameters, allowed us to rationalize the effects of different acyl substituents in terms of steric and electronic contributions.

DURING the last 20 years torsional barriers around single bonds with some double bond character have been studied by various methods. The aim has often been to gain deeper insight in the π-electron delocalization which is supposed to be the main reason for this type of barriers.

The first reasonably accurate value for such a barrier is probably that published by Gutowsky *et al.*[1] for the rotational barrier in *NN*-dimethylformamide, obtained from a ^{1}H n.m.r. study. Since then n.m.r. has become a very popular method in kinetic studies.[2,3] Along with the n.m.r. method, other techniques such as i.r., microwave, and ultrasonic relaxation have been used.

The amides are probably a group of compounds most frequently used for this type of kinetic study, at least as far as n.m.r. techniques are concerned,[4] which is due to the fact that measurements can be performed at temperatures not too far from room temperature. Another torsional barrier which has received a great deal of interest is that about the Ph–CO bond. The double

TABLE 1

Rotational barriers in *para*-substituted benzaldehydes

Substituent	Method	Solvent	$\Delta G^{\ddagger}$ [a]	$\Delta H^{\ddagger}$ [a]	$\Delta S^{\ddagger}$ [b]	V_2 [a]	Ref.
NMe_2	^{1}H N.m.r.	$CHCl_2$	45.2				5
	^{1}H N.m.r.	CH_2Cl_2	44.8	46.5			7
	^{1}H N.m.r.	$PhCD_3$	43.9				6
	^{1}H N.m.r.	CH_2CHCl	42.7				6
	^{13}C N.m.r.	CD_2Cl_2	43.9	41.9	−10		18
	^{13}C N.m.r.	$C_6D_5CD_3$	41.4	25.1	−80		18
	^{13}C N.m.r.	$CHCl_2$–CCl_2F_2	44.9	46.6	+7		*c*
	I.r.					55.7	9
OMe	^{1}H N.m.r.	CH_2Cl_2–$C_2F_4Br_2$	38.9				7
	^{1}H N.m.r.	$PhCD_3$	39.3				6
	^{1}H N.m.r.	CH_2CHCl	38.5				5
	^{13}C N.m.r.	CD_2Cl_2	37.5	38.5	+7		18
	^{13}C N.m.r.	$C_6D_5CD_3$	34.3	27.2	−30		18
	^{13}C N.m.r.	$CHCl_2F$–CCl_2F_2	37.7	38.7	+6		*c*
	T_1	*d*		36.25			19
	I.r.					37.8	9
Me	^{1}H N.m.r.	CH_2Cl–CH_2CHCl	35.0				7
	^{13}C N.m.r.	$CHCl_2F$–CCl_2F_2	34.1	35.2	+5		*c*
	I.r.					26.7	10
Pr^{i}	^{13}C N.m.r.	$CHCl_2F$–CCl_2F_2	34.0	32.5			*c*
F	^{13}C N.m.r.	CH_2Cl–CH_2CHCl	35.2				7
	^{13}C N.m.r	$CHCl_2F$–$CHClF_2$	33.6				*c*
	I.r.					21.9	8
Cl	^{13}C N.m.r.	$CHCl_2F$–CCl_2F_2	32.3				13
	I.r.					19.2	10
	I.r.					20.4	9
Br	I.r.					15.6	9
H	^{1}H N.m.r.	CH_2Cl_2	33.0				5
	^{13}C N.m.r.	$(CH_3)_2O$	32.2	34.7	15		20
	^{13}C N.m.r.	$CHCl_2F$–$CHClF_2$	31.7				13
	^{13}C T_1			30.5			19
	Microwave	Gas phase				20.5	11
	I.r.					28.4	9
	I.r.	Gas phase				20	10
	I.r.					28.0	10
	I.r.					26.7	8
	Ab initio					27.6	21
	Force field					20.5	22
CF_3	^{13}C N.m.r.	$CHCl_2F$–$CHClF_2$	28.9				13
CHO	^{13}C N.m.r.	$CHCl_2F$–$CHClF_2$	28.8				*c*
CN	^{13}C N.m.r.	$CHCl_2F$–$CHClF_2$	28.5				*c*
NO_2	^{13}C N.m.r.	$CHCl_2F$–$CHClF_2$	27.7				*c*
	I.r.					18.1	9
OCF_3	^{13}C N.m.r.	$CHCl_2F$–$CHClF_2$	32.0				*c*

[a] In kJ mol^{-1}. [b] In J mol^{-1} K^{-1}. [c] This work. [d] Not quoted.

bond character of this bond is less marked than for the amide bond and therefore the torsional barrier is also considerably lower. This has somewhat hampered n.m.r. studies of these torsional barriers,[5-7] but also made it easier to study them with i.r.[8-10] and microwave spectroscopy.[11]

Some time ago it was shown by Sommer *et al.*[12] that protonation of the carbonyl oxygen in benzaldehydes drastically increases the torsional barrier, roughly speaking a doubling, compared with the unprotonated compounds. This made that these barriers could be easily studied by ^1H dynamic n.m.r. methods.

Routine Fourier transform ^{13}C n.m.r. provides a powerful tool for rate studies which allowed the investigation of many previously inaccessible systems. For this reason we have continued our previous n.m.r. studies on barriers to internal rotation in benzaldehydes [13] and alkyl phenyl ketones [14] and their conjugate acids [15-17] using mainly this technique. We have now the possibility of comparing our data for several carbonyl compounds and their conjugate acids and we try there to rationalize our and others' work in terms of steric and electronic contributions.

RESULTS

The barriers in carbonyl compounds determined in the present work, together with others from the literature are collected in Tables 1—4. Among the compounds discussed in this paper, the benzaldehydes are those that have gained most attention in previous work. Most of the data have been obtained by means of variable temperature, preferably ^{13}C n.m.r., spectroscopy. A comparison of the data collected in Table 1 shows that there is very good consistency in the barriers obtained from n.m.r. studies as regards the free energy of activation, normally within ± 1 kJ mol^{-1}. Also, for the enthalpy and entropy of activation there is, when data are available, reasonable consistency, except for the case where toluene was used as solvent.[18]

TABLE 2

Torsional barriers in *para*-substituted acetophenones

Substituent	Method	Solvent	$\Delta G^{\ddagger}$	V_2	Ref.
NMe_2	^1H N.m.r.	CH_2Cl_2–CH_2CHCl	34.7		18
	^1H N.m.r.	$PhCD_3$	35.6		6
OMe	^1H N.m.r.	CH_2Cl_2–CH_2CHCl	27.6		18
	^1H N.m.r.	$PhCD_3$	30.5		6
	^1H N.m.r.	CH_2CHCl	27.2		6
	^{13}C N.m.r.	$CHClF_2$–$CHCl_2F$	28.6		14
Me	^{13}C N.m.r.	$CHClF_2$–$CHCl_2F$	24.7		14
F	^{13}C N.m.r.	$CHClF_2$–$CHCl_2F$	24.7		14
	I.r.	Gas		14.6	10
Cl	^{13}C N.m.r.	$CHClF_2$–$CHCl_2F$	22.7		14
Br	^{13}C N.m.r.	$CHClF_2$–$CHCl_2F$	22.6		14
H	^{13}C N.m.r.	$CHCl_2F$–$CHClF_2$	22.4		14
	I.r.	Gas		13.0	10
	Ab initio			18.4	21
	Force field			13.1	22
CF_3	^{13}C N.m.r.	$CHCl_2F$–$CHClF_2$	19.7		14
NO_2	^{13}C N.m.r.	$CHCl_2F$–$CHClF_2$	18.4		14

DISCUSSION

(1) *Comparison of Data obtained by Different Techniques.*—As can be seen from Table 1 studies on benzaldehydes are plentiful and the n.m.r. data may be compared with data obtained by other methods. For a series of *para*-substituted benzaldehydes, with the substituent varying from the strongly electron-donating NMe_2 to the electron-withdrawing NO_2 group, the torsional barriers have been obtained from the i.r. frequency of the torsional modes of vibration.[10] These data ought to be the best for a comparison with the n.m.r. data as they are also obtained using liquid samples. It can also (as expected), be seen that the *p*-nitro has the lowest and the *p*-dimethylamino compound the highest torsional barrier. However, the difference between the highest and the lowest barrier is either 17 or 37 kJ mol^{-1} depending on the method of investigation, n.m.r. or i.r. respectively. We strongly believe that the n.m.r. data are the more reliable and that the discrepancy can be explained from a critical examination of the method of evaluating the torsional barrier from the i.r. torsional frequency. We do not mean to say that the values from n.m.r. and i.r. ought to be the same, which they should probably not be as the

TABLE 3

Torsional barriers in protonated *para*-substituted benzaldehydes, acetophenones, and propiophenones

	$\Delta G^{\ddagger}$/kJ mol^{-1}		
Substituent	CHO [a]	$COCH_3$ [b]	COC_2H_5 [c]
OMe	78.0	61.4	
Me	67.4	54.2	49.3
Et	66.3		47.7
Pr^i	66.1		49.0
Bu^t	65.7		49.8
F	64.7	50.9	48.1
Cl	60.8	49.1	43.9
Br	60.6	48.9	43.1
H	61.3	48.1	43.1
CF_3	49.5	39.8	
NH^+Me	45.2		
OH^+Me	54.0	41.4	
$CHOH^+$	41.2		

[a] Ref. 15. [b] Ref. 16. [c] This work.

TABLE 4

Torsional barriers of some acyl and protonated acyl groups in *p*-methoxyacylbenzenes and protonated *p*-methylacylbenzenes

R	*p*-MeO(C_6H_4)C(=O)R [a]		*p*-Me(C_6H_4)C(=O^+–H)R [b]
H	37.7	(44.8) [c]	67.4
Me	28.0	(34.7) [c]	54.2
Et	21.8	(33.9) [c]	49.4
Pr^i	26.4	(32.6) [c]	48.1
Bu^t		(27.6) [c]	42.8
CH_2F	25.1		53.8
CHF_2			59.1
CF_3			63.2
CH_2Cl			53.4
$CHCl_2$			54.3
CCl_3			50.3
CH_2Br			53.1
Cl	32.7	(26.8) [d]	
Br		(25.5) [d]	
F		(29.3) [d]	
CN		(35.1) [d]	
OEt	19.3		

[a] This work, ^{13}C n.m.r. in $CHCl_2F$–$CHClF_2$. [b] Ref. 17. [c] *p*-Dimethylamino-substituted compound, see ref. 7. [d] Unsubstituted benzoyl compounds, F. A. L. Anet, personal communication.

n.m.r. experiments result in a $\Delta G^{\ddagger}$ value and the i.r. in a V_2 value. We, however, believe that the variation of these two parameters should be parallel or almost so.

For some *para*-substituted benzaldehydes the barrier has also been estimated for the gas phase from i.r. or for benzaldehyde itself from microwave spectra.[11] The gas-phase torsional barriers are invariably found to be lower than those obtained from the liquid phase by at least 4 kJ mol^{-1}. This is not surprising as the intermolecular interactions in the liquid phase will tend to stabilize the more polar ground state more than the transition state.[23] The experimental gas-phase data on benzaldehyde are also in reasonable agreement with an *ab initio* STO 3G calculation [21] of the barrier, as well as with force field calculations.[22]

Klinck and Stothers have studied the torsional barrier in *p*-methoxy- and *p*-dimethylamino-benzaldehyde in two different solvents, CD_2Cl_2 and [$^2H_8$]toluene.[18] For the methylene chloride solutions they obtained, as normal, an entropy of activation close to zero, whereas for the toluene solutions they found a strongly negative entropy of activation, which they explained to be due to various solvent–solute interactions in the ground state and the transition state. There have been many examples of reports of entropies of activation different from zero, which later have been shown to be due to inadequate treatment of the n.m.r. bandshapes.[24] In this case, however, the negative entropy of activation must be regarded as real. It is not possible at this stage to draw any further conclusions regarding the reason for this anomalous entropy of activation before more data have been collected. There has, however, been demonstrated in other experiments that there exists an interaction between electron-rich and electron-poor aromatic ring systems.[25,26]

(2) *The* para-*Substituent Effect on the Height of the Rotational Barrier.—Correlation of* $\Delta G^{\ddagger}$ *with the* para-*substituent* σ *constant.* Since the pioneering work of Hammett on the ionization rates of *p*-substituted benzoic acids,[27] many free energy relationships have been developed involving rate constants and substituent parameters. Hammett plots have been applied as a probe of π-electron delocalization to n.m.r. data, such as ^{19}F chemical shifts in aromatic compounds [28] and ^{13}C chemical shifts in substituted benzenes.[29] It is now well known that the free energy of activation of a torsional process can be correlated with the σ_p and σ_p^+ constants. In order to compare the sensitivity to *para*-substitution in different aromatic compounds, we examine here the correlations of these two sets of substituent parameters with $\Delta G^{\ddagger}$ for five series of carbonyl compounds, benzaldehydes (I), acetophenones (II), protonated benzaldehydes (III), protonated acetophenones (IV), and protonated propiophenones (V).

Considering Table 5, we notice as expected that the torsional barrier energy correlates better with σ^+ constants than with the original Hammett constants. The data in Table 5 also clearly show that the sensitivity to *para*-substitution is about three times as high in the protonated as in the non-protonated species, even though the barrier itself has increased by only a factor of two. Thus the barrier in the protonated compound is more sensitive to the *para*-substituent effect than one should expect from the change in barrier caused by protonation. This might indicate that there is more than one contribution to the barrier height and that these contributions are affected in various ways by protonation and *para*-substitution. It is also interesting to note that the protonation also increases the sensitivity to α-substitution as can be seen by comparing the slopes for the free bases and the conjugate acids. We must here remember that it might be misleading to use the free energy of activation when comparing non-protonated and protonated compounds because the entropy of activation is by no means close to zero for the protonated compounds.[15] However, we have not made any attempts to use the enthalpy and entropy of activation in these comparisons because these parameters are much less reliable than the free energy of activation.

TABLE 5

Correlations of $\Delta G^{\ddagger}$ *versus* σ_p and σ_p^+ constants

Series	Slope	Intercept	r [c]	n [c]	s_{y-x} [c]
Correlations versus σ_p constants [a]					
(I)	−9.50 ±0.90	34.01 ±0.45	0.965	10	1.39
(II)	−9.83 ±0.99	24.46 ±0.42	0.971	8	1.21
(III)	−25.40 ±4.47	64.30 ±1.08	0.895	10	4.22
(IV)	−17.90 ±4.01	51.09 ±1.07	0.913	6	2.18
(V)	−13.32 ±3.82	46.50 ±0.64	0.817	8	3.83
Correlations versus σ_p^+ constants [b]					
(I)	−6.75 ±0.27	32.69 ±0.20	0.994	10	0.61
(II)	−6.27 ±0.34	23.34 ±0.24	0.992	8	0.60
(III)	−19.37 ±1.09	61.83 ±0.40	0.988	10	1.21
(IV)	−15.19 ±1.70	49.68 ±0.50	0.976	6	1.16
(V)	−13.52 ±2.75	45.14 ±0.59	0.895	8	1.39

(I) (NMe_2, OMe, Me, Pr^i, F, H, Cl, CF_3, CN, NO_2), (II) (NMe_2, OMe, Me, F, H, Cl, Br, CF_3), (III) (OMe, Me, Et, Pr^i, Bu^t, F, H, Cl, Br, CF_3), (IV) (Me, F, H, Cl, Br, CF_3), (V) (Me, Et, Pr^i, Bu^t, F, H, Cl, Br).

[a] Taken from ref. 30. Expected $\sigma_p(NMe_2)$ −0.972 from ref. 31. [b] From ref. 30. [c] r = correlation coefficient, n = number of data points, s_{y-x} = standard deviation of regression.

We have taken the opportunity here to estimate σ_p^+ values for the following substituents for which these constants were not generally available: OCF_3 (0.09), CHO (0.56), OH^+CH_3 (0.48), $N(CH_3)_2H^+$ (0.86), and $CHOH^+$ (1.06).

The field and resonance contributions to the torsional barrier. Various attempts have been made to simplify, consolidate, and better understand different sets of substituent parameters. The procedure is to divide substituent effects into field effects (inductive effects) and resonance effects.[32] The first attempt was made by Swain and Lupton [33] who proposed the equation $x = fF + rR$ where F represents the field or inductive con-

tribution and R the mesomeric contribution of a given substituent. They tried in this way to describe all types of reactions with a single set of constants. Ehrenson *et all* have shown that a significantly better description can be obtained if the reactions are divided into four different classes with various σ_R sets for each class but with a single set of σ_I values. Here we have chosen to use the σ_R^+ and σ_R constants, since the carbonyl group, especially the protonated one is a strong π-electron acceptor and, for comparison, the Swain and Lupton parameters. The different regressions are gathered in Table 6.

TABLE 6

Correlations of $\Delta G^\ddagger$ *versus* various sets of field and resonance parameters.

$\Delta G^\ddagger = fF + rR + i$ [a]

Series	n	f	r	i	r	s_{y-x}	F (%)	R (%)
(I)	9 [b]	−2.37 ± 0.57	−12.04 ± 0.61	32.21 ± 0.40	0.994	0.53	23.9	76.1
(II)	9 [b]	−2.46 ± 0.43	−11.51 ± 0.47	22.82 ± 0.30	0.996	0.41	25.5	74.5
(III)	9 [b]	−9.66 ± 1.52	−37.12 ± 2.97	61.23 ± 0.82	0.978	1.48	29.4	70.6
(IV)	6 [c]	−7.50 ± 1.68	−24.56 ± 3.51	49.26 ± 0.95	0.958	1.18	32.8	67.2
(V)	7 [d]	−8.73 ± 0.96	−33.05 ± 3.96	43.77 ± 0.55	0.969	0.66	29.7	70.3

$\Delta G^\ddagger = \rho_I\sigma_I + \rho_R\sigma_R^+ + i$ [e]

Series	n	ρ_I	ρ_R^+	i	r	s_{y-x}	I (%)	R (%)
(I)	9 [b]	−4.84 ± 0.43	−7.45 ± 0.18	31.86 ± 0.21	0.999	0.27	39.4	60.6
(II)	9 [b]	−4.68 ± 0.45	−7.10 ± 0.18	22.50 ± 0.21	0.998	0.27	39.8	60.2
(III)	7 [f]	−19.15 ± 1.67	−22.51 ± 1.05	61.02 ± 0.66	0.994	0.83	46.0	54.0
(IV)	6 [c]	−15.16 ± 1.81	−19.27 ± 1.89	48.51 ± 0.67	0.981	0.81	44.0	56.0
(V)	5 [g]	−15.45 ± 0.34	−22.28 ± 0.44	43.11 ± 0.10	0.999	0.10	41.0	59.0

$\Delta G^\ddagger = \rho_I\sigma_I + \rho_R\sigma_R + i$ [e]

Series	n	ρ_I	ρ_R	i	r	s_{y-x}	I (%)	R (%)
(I)	9 [b]	−6.21 ± 3.09	−16.70 ± 3.15	32.88 ± 4.38	0.921	1.94	27.1	72.9
(II)	9 [b]	−6.61 ± 2.69	−16.63 ± 2.95	23.30 ± 1.25	0.927	1.68	28.4	71.6
(III)	7 [f]	−22.93 ± 3.15	−45.50 ± 3.89	61.87 ± 1.18	0.981	1.51	33.5	66.5
(IV)	6 [c]	−15.94 ± 2.01	−30.33 ± 3.26	49.25 ± 0.71	0.977	0.89	34.5	65.5
(V)	5	−20.85 ± 1.41	−45.11 ± 2.96	43.32 ± 0.31	0.992	0.31	31.6	68.4

[a] Values of F and R taken from ref. 33. [b] NMe_2, OMe, Me, F, H, Cl, CF_3, CN, NO_2. [c] Me, F, H, Cl, Br, CF_3. [d] Me, F, H, Cl, Br, Et, But. [e] Values of σ_I, σ_R, or σ_R^+ from ref. 34. [f] MeO, Me, F, H, Cl, Br, CF_3.

As the values of F and R for the p-dimethylamino group were not reported by Swain and Lupton, we have estimated these data as indicated by these authors and obtained F ±0.11 and R −1.03, values consistent with the inductive and mesomeric effects of the NMe_2 group. We must however observe that our values do not agree with those estimated by Hamer [35] from σ_p constants (F −0.097 and R −0.568).

If we now compare the three sets of dual parameters, we note that the set with σ_I and σ_R^+ in each case gives a better correlation with our data than the other two sets (Table 6) as expected on the basis of the Ehrenson results. We also note, for all sets of substituent parameters, that there is a large contribution from field or inductive effects to the barrier height, which might be surprising. Even more surprising is that the proportion of the inductive effect increases upon protonation as judged from the values of $\lambda^p = \rho_R{}^p/\rho_I{}^p$, which are *ca.* 1.5 and *ca.* 1.1 for the non-protonated and protonated series, respectively. One explanation to this somewhat unexpected finding could be that not the same σ_R scale applies to both the protonated and non-protonated series. But the various tests performed using for example the σ_R scale for the free bases and the σ_R^+ scale for the protonated compounds result in even greater discrepancy with predictable R and F values.

The free energy of activation of the torsional barrier in aromatic carbonyl compounds is not compatible with a Swain and Lupton treatment for the dissociation in field and resonance effects. We have no explanation for this now.

To further stress this point we can compare with the results of Jones and Wilkins,[36] who have reported a resonance contribution to the substituent effect on the barrier to internal rotation in *NN*-dimethylbenzamides of 63% using the Swain and Lupton parameters. This is slightly less than what we have found (Table 6). In general it seems that the Swain and Lupton separation of the field and resonance contributions results in a close to 1 : 1 ratio of the two effects and a clear trend moving away from this ratio could never be observed for systems in which this trend would be expected.

TABLE 7

Correlations of $\Delta G^\ddagger$ with C-13 chemical shifts [a]

Series	Carbon	n	a	b	r	s_{x-y}
(I)	C-1	11	−1.03 ±0.07	171.35 ±9.55	0.979	1.03
(II)	C-1	8	−0.87 ±0.05	142.09 ±6.42	0.991	0.42
(III)	C-1	10	−2.91 ±0.31	431.37 ±39.93	0.957	2.11
	C=O	9	−2.03 ±0.10	473.17 ±30.62	0.981	1.57
(IV)	C-1	6	−2.20 ±0.39	331.29 ±50.36	0.942	1.93
	C=O	7	−2.03 ±0.10	492.80 ±23.15	0.993	0.63
(V)	C-1	8	−2.31 ±0.63	339.39 ±79.81	0.832	1.73
	C=O	8	−2.01 ±0.27	491.31 ±59.84	0.948	0.99

[a] The previously non-reported ^{13}C chemical shifts (refs. 14, 16, and 17) are gathered in Tables 8 and 9.

(3) *Correlation of the Free Energy of Activation with* ^{13}C *Chemical Shifts.*—It has been shown by Levy [29] that the ring carbon *para* to a substituent is extremely well correlated with the substituent σ^+ constant. It is there-

fore not surprising that we also have found a good correlation between the C-1 chemical shift and $\Delta G^{\ddagger}$ (Table 7). We would like to stress the usefulness of the ^{13}C chemical shifts in estimates of the torsional barrier. From the correlations in Table 7 and known chemical shifts, the barrier can be estimated to within a few kJ mol^{-1}. Complete bandshape analysis, however, is necessary when $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values are needed.

TABLE 8

^{13}C N.m.r. chemical shifts for some *para*-substituted benzaldehydes in Freon solution (in p.p.m. from Me_4Si)

Substituent	Temp. (°C)	C-1	C-2	C-3	C-4	C-5	C-6	C=O
NMe_2	−101	124.5	128.8	112.5		110.7	137.8	
OMe	−118	130.0	129.0	116.7	165.2	114.0	138.0	
Me	−142	134.1	126.8	131.2	147.7	130.8	135.7	194.8
Pr^i	−150	134.7	127.0	128.8	158.3	128.4	136.0	
F	−145	132.9	129.7	118.1	167.5	117.3	138.1	194.2
Cl	−150	135.0	128.5	130.9	142.4	130.6	136.6	
OCF_3	−146	134.0	129.4	122.3	154.8	121.6	137.5	194.9
H	−123	136.5	126.8	130.0	136.3	130.3	135.5	
CF_3	−150	138.7	127.3	127.5		127.5	135.4	
CHO	−160	140.3	128.3	128.3	140.3	136.5	136.5	195.2
CN	−148	139.6	127.8	135.0		134.4	135.7	196.2
NO_2	−150	141.0	128.8	126.1	152.2	125.7	136.4	195.9

The carbonyl carbon chemical shift which is generally very sensitive to conjugation, appearing over a 70 p.p.m. range in organic compounds, has however been observed to be ' insensitive ' to ring substituent effects.[37] This is also observed here for the free bases. In the conjugate acids, however, the substituent dependence is striking as the carbonyl carbon shifts over 20 p.p.m. depending on the electron-releasing power of the substituent and is also well correlated with the free energy of activation (Table 7).

However, the sensitivity of the C-1 chemical shift in the *para*-substitution remains unchanged on protonation in contrast to the three-fold increase in the sensitivity of the torsional barrier. These results indicate that protonation affects mainly the polarisability of the carbonyl group.

(4) *The Carbonyl Substituent Effect.*—Katritzky and his co-workers [38] have related the barrier to internal rotation in monosubstituted benzenes to the σ_R° constant of the rotating group by the relationship (1). In equation (1), σ_{Rtw}° is the value of the σ_R° constant that

$$\Delta G^{\ddagger} = E = a(\sigma_R^{\circ} - \sigma_{Rtw}^{\circ}) - S \qquad (1)$$

should apply for the rotating group in the transition state geometry and has been shown to be small for acyl groups,[38] and thus set to zero. S represents the steric strain in the ground state, strictly speaking, the difference in strain energy between the ground state and the transition state. The constant a was evaluated by Katritzky to be 138 kJ mol^{-1}, and assuming $S = 0$ for the formyl group the steric strain for the acetyl group was estimated to be *ca.* 4 kJ mol^{-1}. At that time there was, however, no experimental value for the barrier to internal rotation in acetophenone available and this value has now been shown to be too low. With our data on the torsional barriers in benzaldehyde and acetophenone we found a 132 and S_{COMe} 6.6 kJ mol^{-1}. Using equation (1) we can also estimate the σ_R° values for the protonated formyl and acetyl group (Table 10). Refining equation (1), Katritzky has introduced an interaction term for the *para*-substituent. Since the *para*-effect correlates well with σ^+ it is natural to use this parameter as the interaction term keeping in mind that the strength of the interaction is dependent on the rotor as well as on the *para*-substituent [equation (2)]. If equation (2) holds

$$\Delta G^{\ddagger} = \sigma_R^{\circ}(a + b\sigma^+) - S \qquad (2)$$

there should be a linear relationship between the barrier to rotation in benzaldehydes with those in, *e.g.* acetophenones, which is verified by the correlation of the barrier to internal rotation in acetophenones and protonated acetophenones with the corresponding barrier in benzaldehydes [$\Delta G^{\ddagger}_{MeCO(H^+)} = 0.893\Delta G^{\ddagger}_{HCO(H^+)} - 5.77$, $r = 0.999$, $n = 14$]. From this correlation the steric interaction in the ground state of acetophenones is found to be 5.8 kJ mol^{-1}, in good agreement with the above estimate and a previously made estimate of this steric interaction with the aid of *o*-methylbenzaldehyde.[14,16]

TABLE 9

^{13}C N.m.r. chemical shifts (in p.p.m. from external Me_4Si) in protonated [a] *para*-substituted propiophenones

Substituent	C-1	C-2	C-3	C-4	C-5	C-6	C=O
OMe [b]	121.1	142.4	118.5	174.5	116.7	137.7	213.3
Me	126.0	139.0	132.8	162.0	132.8	134.6	219.9
Et	126.1	139.1	131.6	167.5	131.6	134.7	220.0
Pr^i	126.5	139.4	130.5	171.6	130.5	135.0	220.8
Bu^t	126.0	139.1	129.3	173.4	129.3	134.4	219.9
F	125.3	142.8	120.5	165.3	119.1	138.7	220.6
Cl	127.1	139.3	132.4	154.3	132.4	135.7	222.2
Br	127.4	138.9	135.4	144.1	135.4	134.9	222.7
H	128.6	138.4	131.8	146.4	131.8	134.2	223.3
MeOH$^+$	129.2	139.6	119.0	160.5	119.0	139.6	224.7

[a] At −70 °C in HSO_3F–SbF_5–SO_2ClF (1 : 1 : 2). [b] In pure HSO_3F.

We therefore feel confident to say that the steric interaction between the acetyl group and the benzene ring is 6 ± 1 kJ mol^{-1} in the ground state of acetophenones. The same treatment of propiophenone data results in

TABLE 10

Energy terms for torsional barriers in monosubstituted benzenes

Substituent	$\Delta G^{\ddagger}$	σ_R^0	a	$R = a\sigma_R^0$	σ_{Rtw}^0	S
CHO	31.7	0.24	132.2 [a]	31.7	0 [b]	0 [b]
$CHOH^+$	61.3	0.46_4 [a]	132	61.3	0 [b]	0 [b]
MeCO	22.4	0.22	132	29.0	0 [b]	6.64 [a]
$MeCOH^+$	48.1	0.41_5 [a]	132	54.7	0 [b]	6.64 [c]

[a] Calculated from the other data using equation (1). [b] Assumed equal to zero. [c] S can be considered unchanged by protonation.

S 12 kJ mol^{-1}, which seems a slight overestimate however. As there are only two data points for the non-protonated propiophenones this is less reliable than for acetophenones; an error of 1 kJ mol^{-1} in the value of $\Delta G^{\ddagger}$ for the non-protonated propiophenones will result in an error of *ca.* 2 kJ mol^{-1} on the estimated steric effect. We believe that this method could be very useful in calculating the steric effect in the ground state of various acylbenzenes. No sufficient data are available at present to apply this to other acyl compounds.

In the α-halogenocarbonyl compounds the barrier-lowering effect due to the increase in size competes with the barrier-increasing electronic effect. This effect is most dramatic in the protonated *p*-methyl-ααα-trifluoroacetophenone as can be seen from Table 4.

The comparison of $\Delta G^{\ddagger}$ data of protonated alkyl and α-tolyl halogenoalkyl ketones with $\Delta G^{\ddagger}$ in *NN*-dimethylamides [39] shows similar effects of the α-substitution on the barrier height. But by using the same approach as Wunderlich *et al.*,[39] we find that the correlation of $\Delta G^{\ddagger}$ with the inductive parameters $\sigma_I(pK)$ and the steric parameter v is poor (r 0.796). This can be explained by the fact that in our case, the barrier is also related to the resonance contribution of the *para*-group and this contribution is dependent on the electron-releasing or -attracting power of the acyl group.

EXPERIMENTAL

Most of the benzaldehydes were commercially available and were purified when necessary by distillation or recrystallization. The preparation of *p*-ethylbenzaldehyde has been described previously.[15] The alkyl and halogenoalkyl *p*-tolyl (*p*-methoxyphenyl) ketones, as well as the *p*-substituted propiophenones were synthesized by Friedel–Crafts acylation of the appropriate monosubstituted benzene. The *p*-methoxybenzoyl chloride was obtained by treating *p*-methoxybenzoic acid with PCl_5 and the ethyl ester by refluxing the acid with ethanol.

Protonation was performed by dissolving the carbonyl compound in SO_2ClF and adding at −78 °C a mixture of HSO_3F–SbF_5 (1 : 1) in SO_2ClF. The base-to-acid molar ratio was 0.2 : 1.[40]

The n.m r spectra were recorded either on a XL-100 Varian spectrometer or a JEOL FX 60 (protonated propiophenones) in the Fourier transform mode The temperature was monitored by a thermocouple placed inside the probe and calibrated against another thermocouple.

Simulation of the experimental spectra was made using the $DNMR_2$ program.

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