# CONFORMATION OF AROMATIC CARBONYL DERIVATIVES: AN INFRARED STUDY

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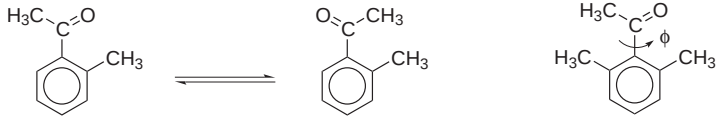
Infrared spectra of 14 methyl- and polymethyl-substituted acetophenones and of 14 equally substituted methyl benzoates were investigated in the carbonyl region in tetrachloromethane solution and correlated with their conformation. The ν(C=O) frequency depends moderately on the inductive effect of substituents and more sensitively on the steric effect of ortho substituents. Steric effects are not simply related to the torsion angle ϕ (calculated by the density functional theory) but are better described by dividing the methyl substituents into three classes: nonplanar derivatives with methyl groups in the two ortho positions, slightly nonplanar derivatives with two methyl groups in the positions 2 and 3 (buttressing effect), and the remaining derivatives existing in two equilibrium planar conformations. Eleven various physical properties of methyl-substituted acetophenones, measured or calculated previously, were now correlated by principal component analysis (PCA). Two components are necessary to explain 93% of variance; they relate roughly to the steric and inductive effects. Steric effect affects all properties while inductive effect is of importance mainly for the gas-phase basicities and wavelengths in the UV spectra. Both can be separated very effectively using the classic comparison of ortho and para derivatives; in this way, the steric effect is isolated and in a subsequent PCA only one component is sufficient to explain 94% of variance.

**Keywords**: Steric effects; Substituent effects; Inhibition of resonance; Conformation; Ketones; Acetophenones; Methyl benzoates; Chemometrics; IR spectroscopy.

Conformation of aromatic carbonyl compounds such as substituted benzaldehydes, acetophenones, benzoic acids and their esters has been of importance for explaining their reactivities, particularly their acid-base properties. When attention was focused on steric effects, the substituents chosen were mostly alkyl groups. Commonly, the main part of the effect was attributed to the steric inhibition of resonance[1–3] and the observable quantities were directly correlated with the torsion angle ϕ between the benzene ring and the carbonyl plane[1–4], see for instance the formula of 2,6-dimethylacetophenone **8**. The angle ϕ itself was derived either from various

physical properties (mostly from electronic[2], IR [5], $^{13}$C NMR [6] and $^{17}$O NMR [7] spectra, rarely from other quantities[8]), or from semiempirical[4c,7,9] and ab initio[10] calculations. According to the classic theory[2], it was mostly assumed[1,6-8] that $\phi$ varies between 0 and 90° according to the intensity of the steric hindrance. This view was challenged by us[4,10,11] since certain, less hindered compounds exist in the planar conformation or as two equilibrium forms, as for instance 2-methylacetophenone **2A** $\rightleftharpoons$ **2B**. In addition to acetophenones[12–14], this was proven also for similarly substituted benzoic acids[4]. The exact value of $\phi$ cannot be recommended as a characteristic structural parameter since the potential energy curve is often very flat[10,12]. For this reason, most values of $\phi$ reported in the literature are very inaccurate, often quite wrong.




**2A** **2B** **8**

In our opinion, there is a better description dividing various sterically hindered derivatives into two classes: planar molecules with $\phi \cong 0$ and nonplanar with $\phi$ greater than say 50°. Certain derivatives with small $\phi$ (approximately up to 15°) may be classified as nearly "planar" when their energy has been calculated: just the energy and not the geometry is deciding[10c]. Methods for experimental determination of the conformation can be classified into two categories.

Methods of the first category allow finding the most abundant conformation of a given compound in the given state. Of them the X-ray analysis[10c,11,15] is of limited value for the isolated molecule, electron diffraction is near the limits of its applicability to the molecules of this size[16]. Determination of the $^3J_{13C,13C}$ coupling constants was attempted[13] but is possible only in particular cases. In our opinion, ab initio calculations at a higher level[10,12] are most reliable at present.

Methods of the second category are empirical in character and belong to the field of the correlation analysis. They process a set of compounds with variable substituents and divide it into two or more subsets. Any interpretation in terms of certain steric arrangement lies then outside the correlation analysis and must be based on further arguments. Nevertheless, very convincing results were obtained in certain cases as for instance from the car-

bonyl stretching frequency of polymethyl-substituted benzoic acids[17] and from the UV intensity[12] or $^{13}C$ NMR shifts[6a,13] of similarly substituted acetophenones.

In this communication, we applied the IR approach to methyl-substituted acetophenones **1**–**14** (Table I) and methyl-substituted methyl benzoates **15**–**28** (Table II). The results of the former set can be compared to the less empirical NMR approach[13] and to the calculations[12] within the framework of the density functional theory (DFT) with the same compounds. The latter set may be related to the pertinent benzoic acids investigated previously both by calculations[4c,10] and physical measurements[4,17], including several X-ray structures[10c,11,15]. Our intention was to explore whether the IR spectroscopy itself can distinguish compounds of different conformation as it was done in the case of similarly substituted benzoic ac-

TABLE I
Infrared spectral characteristics of methyl-substituted acetophenones

| Compound | Substituents | ν(C=O) | | | |
|---|---|---|---|---|---|
| | | ν, $cm^{-1}$ | SE[a], $cm^{-1}$ | $\Delta\nu_{1/2}$, $cm^{-1}$ | AF, % |
| **1** | H | 1690.6 | 0 | 9.7 | +3 |
| **2** | 2-Me | 1688.6 | 2.0 | 11.7 | –2 |
| **3** | 3-Me | 1689.1 | 0 | 9.9 | +2 |
| **4** | 4-Me | 1686.6 | 0 | 9.3 | –1 |
| **5** | 2,3-$Me_2$ | 1691.6 | 6.5 | 15.5 | –2 |
| **6** | 2,4-$Me_2$ | 1684.0 | 1.4 | 11.3 | –4 |
| **7** | 2,5-$Me_2$ | 1686.3 | 1.2 | 14.2 | –6 |
| **8** | 2,6-$Me_2$ | 1706.8 | 24.2 | 17.1 | +21 |
| **9** | 3,4-$Me_2$ | 1685.9 | 0.8 | 11.1 | +2 |
| **10** | 3,5-$Me_2$ | 1686.2 | –1.4 | 10.4 | –5 |
| **11** | 2,3,4-$Me_3$ | 1686.5 | 5.4 | 13.7 | –6 |
| **12** | 2,4,6-$Me_3$ | 1703.3 | 24.7 | 16.4 | +3 |
| **13** | 3,4,5-$Me_3$ | 1685.4 | 1.8 | 10.8 | +6 |
| **14** | 2,3,5,6-$Me_4$ | 1704.0 | 24.4 | 18.0 | +5 |

[a] Steric effect on ν(C=O) defined by Eq. (*1*) or (*2*).

ids[17]. Finally we wanted to summarize the results on the steric effects in substituted acetophenones using the principal component analysis (PCA).

## EXPERIMENTAL

Methyl-substituted acetophenones[12] **1**–**14** and methyl-substituted methyl benzoates[4a,4b] **15**–**28** were characterized previously.

IR absorption spectra were recorded in tetrachloromethane solution, compounds **1**–**14** on a Bruker IFS 88 FT-IR spectrometer (concentration $c$ = 0.18 mol $l^{-1}$, $d$ = 0.1 mm), compounds **15**–**28** on a Bruker IFS 55 FT-IR spectrometer ($c$ = 0.2 mol $l^{-1}$, $d$ = 0.13 mm, except the less soluble compound **28** for which $c$ = 0.1 mol $l^{-1}$). With the resolution used (2 $cm^{-1}$), the old ATS 89B program on Bruker IFS 88 did not allow an interval of wavenumber reading finer than 0.64 $cm^{-1}$. Therefore, we used a graphical procedure and obtained the apparent maxima of the ν(C=O) bands as the point of intersection of the band axis with the spectral curve. With sufficient magnification, the accuracy of reading was better than 0.1 $cm^{-1}$.

TABLE II
Infrared spectral characteristics of methyl-substituted methyl benzoates

| Compound | Substituents | ν(C=O) | | | | ν(C–O), $cm^{-1}$ | |
|---|---|---|---|---|---|---|---|
| | | ν $cm^{-1}$ | SE[a] $cm^{-1}$ | $\Delta\nu_{1/2}$ $cm^{-1}$ | AF % | | |
| **15** | H | 1728.1 | 0 | 9.8 | +1 | 1278 | 970 |
| **16** | 2-Me | 1726.4 | 0.3 | 12.5 | +6 | 1259 | 969 |
| **17** | 3-Me | 1726.2 | 0 | 11.1 | 0 | 1284 | 977 |
| **18** | 4-Me | 1726.1 | 0 | 14.0 | +2 | 1279 | 970 |
| **19** | 2,3-$Me_2$ | 1726.6 | 2.4 | 16.1 | +4 | 1269 | 970 |
| **20** | 2,4-$Me_2$ | 1724.4 | 0.3 | 11.8 | +6 | 1260 | 974 |
| **21** | 2,5-$Me_2$ | 1726.2 | 2.0 | 13.6 | +5 | 1261 | 971 |
| **22** | 2,6-$Me_2$ | 1733.0 | 8.9 | 11.8 | +2 | 1269 | 961 |
| **23** | 3,4-$Me_2$ | 1724.3 | 0.1 | 11.6 | +3 | 1269 | 975, 961 |
| **24** | 3,5-$Me_2$ | 1725.6 | 1.3 | 11.4 | +1 | 1315, 1220 | 977 |
| **25** | 2,3,4-$Me_3$ | 1724.0 | 1.8 | 13.5 | +4 | 1264 | 976 |
| **26** | 2,4,6-$Me_3$ | 1730.7 | 8.6 | 13.9 | +4 | 1268 | 968 |
| **27** | 3,4,5-$Me_3$ | 1722.9 | 0.6 | 13.9 | +2 | 1313, 1301sh | 997, 989 |
| **28** | 2,3,5,6-$Me_4$ | ≅1733 | 12.7 | 16.5 | –6 | 1310, 1243 | 964 |

[a] Steric effect on ν(C=O) defined by Eq. (*1*) or (*2*).

## RESULTS AND DISCUSSION

### *Effects of Substituents on the Carbonyl Frequency*

In our previous study of benzoic acids[17], a simple Hammett plot was of crucial importance for determining conformation, although it was loaded with an uncertainty of the value of constant σ for the ortho substituent. However, the separation into two subgroups, planar and nonplanar, was so striking that this small uncertainty was of no importance. The same plot for substituted acetophenones **1**–**14** (Fig. 1) is more complex. The steric size of the $COCH_3$ group is evidently greater than that of the COOH group and allows distinguishing substitution of three types: (i) nonplanar molecules with two methyl groups in positions 2 and 6, (ii) less distorted molecules with two methyl groups in positions 2 and 3, (iii) remaining molecules, approximately planar. In the last subgroup, ν(C=O) is controlled by the Hammett equation as expected. The precision is only fair (see the statistics in Fig. 1) since the substituents have weak polar effects. Meta substituents with strong polar effects were correlated[18] with a slope of 15.5 $cm^{-1}$ and $R$ = 0.974. The steric effect of the 2,3-dimethyl substitution is an example of the buttressing effect (BE) in the classic meaning[19]. We have redefined

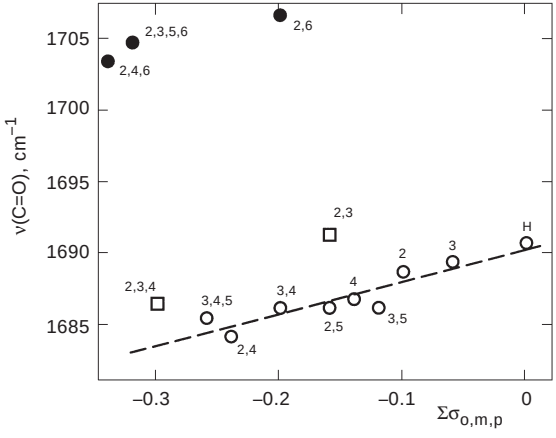



FIG. 1

Hammett plot of the ν(C=O) frequency of methyl-substituted acetophenones **1**–**14** vs the sum of constants $\sigma_o$, $\sigma_m$, $\sigma_p$: ● compounds with two methyl groups in positions 2,6; □ compounds with two methyl groups in positions 2,3; ○ remaining compounds; the regression line belongs to the last group as well as the statistics given: the slope $b$ = 22.9(3) (with the standard deviation in parentheses), correlation coefficient $R$ = 0.926 and standard deviation from the regression line $s$ = 0.83

this term for any trisubstituted compound[4] and claimed its occurrence even in the absence of ortho substituents[4b]. However, some of these findings were based on imprecise experimental values[20] and unquestionable proofs in the aromatic series have remained restricted to 1,2,3 derivatives. In the case of the carbonyl frequency, a significant BE was not observed with 2,3-dimethylbenzoic acid[17], but it is evident here with equally substituted acetophenone.

The same plot for substituted methyl benzoates **15**–**28** (Fig. 2) differs only in the quantitative sense: the steric hindrance is weaker and an evident BE is not observed: the 2,3-dimethyl and 2,3,4-trimethyl derivatives deviate from the Hammett line only insignificantly. The slope of the Hammett line is smaller than in Fig. 1 as can be explained by the conjugation within the $COOCH_3$ group. For similarly substituted benzoic acids, the slope 29 $cm^{-1}$ was obtained[17]. Since the Hammett dependences are little precise, the differences in their slopes are not much important.

Figures 1 and 2 can be thus regarded as a proof that the carbonyl compounds **1**–**28** can be divided into groups with different structure. Our conclusion that one group contains planar molecules and the other groups nonplanar and slightly nonplanar molecules goes beyond the finding of IR spectroscopy and should be supported by more direct proofs. Concerning the methyl esters, there is a direct proof of the planar conformation of 2-methylbenzoate[16]. Also the comparison with the parent benzoic acids, whose conformation is certain[4,11,15], is convincing. Concerning the

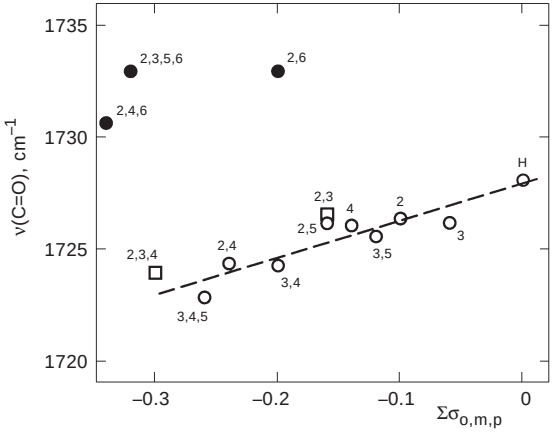



FIG. 2

The same plot as in Fig. 1 for methyl-substituted methyl benzoates **15**–**28** ($b$ = 16.7(3), $R$ = 0.926, $s$ = 0.61)

acetophenones, our recent proofs of the planar conformation of 2-methylacetophenone are based mainly on calculations[12] within the framework of the density functional theory, partly on $^3J_{C,C}$ coupling constants[13].

There is still another approach for distinguishing planar and nonplanar molecules that is based directly on the IR data but it was less compelling in the case of benzoic acids[17] and is still less in the present case. It has been based on the obvious assumption that planar molecules existing as two conformers in equilibrium should show two maxima of the ν(C=O) band. Since two maxima were never observed, at least an asymmetry of the band was searched for as expressed by the asymmetry factor[17] (AF). It turned out that the band was unsymmetrical with all benzoic acids that could exist as two equilibrium planar conformers[17]. In the case of acetophenones, this approach was not successful for two reasons. First, the equilibrium of the two planar conformations is always shifted too far to one side, for instance to **2A**. Second, the ν(C=O) band is often strongly unsymmetrical due to partial overlapping with not identified vibrations. On the other hand, some empirical regularity was observed in the mere half-width $\Delta\nu_{1/2}$ (Table I). It is largest (16.4–18 $cm^{-1}$) with the nonplanar derivatives **8**, **12**, **14**, slightly enhanced by the buttressing effect in **5** and **11** (15.5 and 13.7 $cm^{-1}$, respectively), and smallest but rather variable (9.3–14.2 $cm^{-1}$) with the planar derivatives **1**–**4**, **6**, **7**, **9**, **10**, **13**. In the case of methyl benzoates, some significant differences of AF were observed (Table II, column 6) but there are also exceptions, which can be attributed to overlapping with other vibrations. It is only evident that higher values of AF were found with all planar derivatives existing in two conformations: **16**, **19**, **20**, **21**, **25**. We conclude that observation of the band asymmetry can serve at most as a subsidiary argument.

*Quantitative Separation of Steric Effects*

The traditional estimation of steric effects in the ortho position is based on the assumed additivity of polar and steric effects and on two additional premises: Polar effects are equal in the ortho and para positions, and steric effects are negligible in the meta and para positions. Although the first premise may be only approximate, we used it with reasonable success for methyl derivatives of benzoic acids[4a,4c] and nitriles[21]. Applied to our problem, this concept defines the steric effect (SE) on ν(C=O) in **2** simply as a difference between the ortho and para derivative, Eq. (*1*).

$$SE[2] = \nu[2] - \nu[4] \qquad (1)$$

In the case of poly derivatives, other substituents present must be taken into account; for instance SE in **11** is given by Eq. (*2*).

$$SE[2,3,4] = \nu[2,3,4] - \nu[3] - 2\nu[4] + 2\nu[H] \qquad (2)$$

Steric effects calculated in this way are given in Tables I and II, always in column 4. Their significance and physical meaning can be proven by comparison of SE values derived from different series of compounds or from different properties. Comparison of ν(C=O) of various series of compounds is presented in Figs 3 and 4. When the original experimental values of acetophenones and benzoic acids are compared, a complex picture is obtained (Fig. 3). A linear relationship exists again only for the Hammett derivatives; the remaining compounds deviate strongly since the steric effects in acetophenones are stronger. This is confirmed quantitatively when the steric components SE are compared: One gets a single regression line with the slope of 1.66 and $R$ = 0.933. (The pertinent graph is not shown due to its simplicity.) The series of methyl benzoates and benzoic acids are more similar. Nevertheless, the plot of experimental ν(C=O) does not reveal a simple dependence (Fig. 4), while the plot of the steric components SE is linear with $R$ = 0.984 (graph not shown).

The best example proving the significance of steric components was obtained from the relation to the gas-phase basicities[3,14], $\Delta G_{bas}$. There is no re-

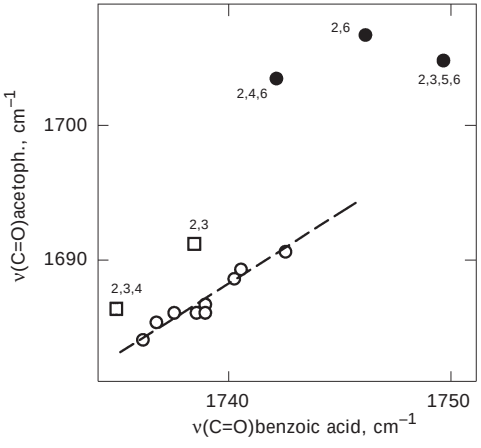



FIG. 3
Plot of the ν(C=O) frequency of methyl-substituted acetophenones vs the ν(C=O) frequency of equally substituted benzoic acids[17]; denotation of points and meaning of the regression as in Fig. 1 ($b$ = 1.00(10), $R$ = 0.965, $s$ = 0.58)

lationship between the direct experimental values of ν(C=O) and $\Delta G_{bas}$ (Fig. 5) and separation into two groups of more and less hindered compounds is clearly seen. The reason is evidently in the stronger sensitivity of $\Delta G_{bas}$ to inductive effects. When the steric components are isolated, they are proportional in the two series with a high correlation coefficient of

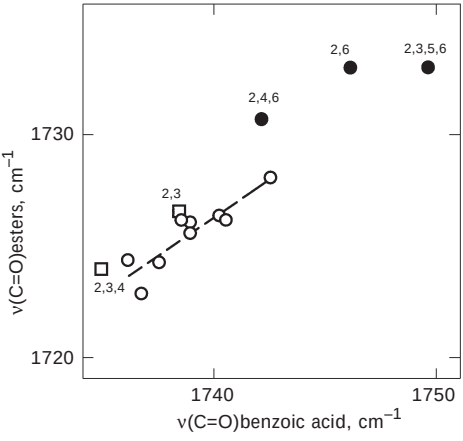



FIG. 4
The same plot as in Fig. 3 for methyl-substituted methyl benzoates ($b$ = 0.68(12), $R$ = 0.904, $s$ = 0.69)

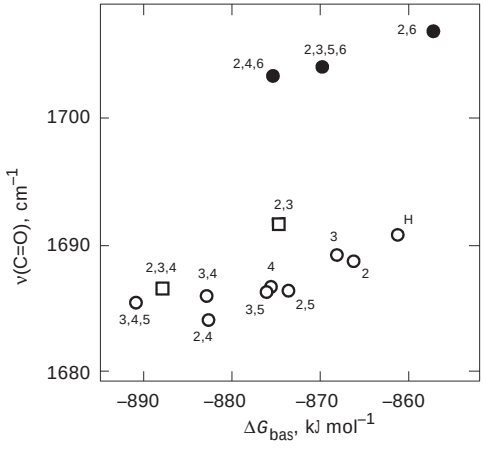



FIG. 5
Plot of the ν(C=O) frequency of methyl-substituted acetophenones vs their relative basicity in the gas phase[3,14]; denotation of points as in Fig. 1

0.966 (Fig. 6), although separation into classes is still evident. In our opinion, the physical meaning of the steric components and the reliability of their approximate values are well proven.

*Substituent Effects on Various Properties*

During the investigation of methyl-substituted acetophenones, several experimental and calculated properties were accumulated and interpreted in terms of steric and polar effects[12–14,22]. We are now able to check this procedure by the principal component analysis summarizing all available data. In PCA the data are considered as various "descriptors" (subscript j) differing further by substitution (subscript i). In the course of the analysis, a given quantity $Y_{ij}$ is expressed by Eq. (*3*) where all empirical constants, $a_i$, $b_i$, $c_i$, $\alpha_j$, $\beta_j$, $\gamma_j$ etc., are optimized in order to reach the minimum sum of the squared deviations $\Sigma\varepsilon_{ij}^2$.

$$Y_{ij} = a_i\alpha_j + b_i\beta_j + c_i\gamma_j + \ldots + \varepsilon_{ij} \qquad (3)$$

Our attention was focused on the number of necessary components ($\alpha$, $\beta$, $\gamma$ in Eq. (*3*)) with the intention to test our standard procedure of separating steric and polar substituent effects. The original data were arranged into a source matrix of the dimension 14 × 14. The lines corresponded to com-

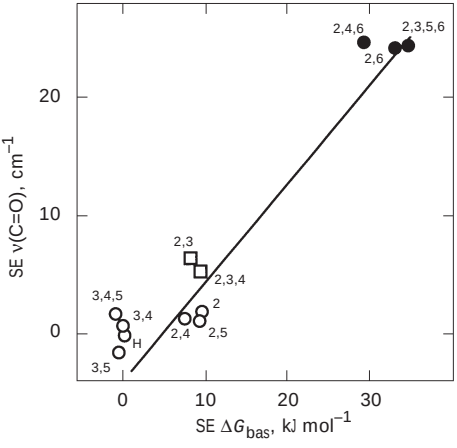



FIG. 6

Plot of the steric component of the ν(C=O) frequency of methyl-substituted acetophenones vs the steric component of their relative basicity in the gas phase; denotation of points as in Fig. 1, the regression line and the statistics relate to the whole set ($R$ = 0.966, $s$ = 2.7)

pounds **1**–**14**. The 14 columns were represented by the independent descriptors, both experimental and calculated: the carbonyl frequency ν(C=O), its half-width $\Delta\nu_{1/2}$ (this work); $^{13}$C NMR shifts[13] of the carbon atoms $^{13}$C(O), $^{13}$C(1) and $^{13}CH_3$; UV spectral characteristics of the $^1L_a$ band[12], viz. the wavelength λ and molar absorption coefficient ε; relative proton affinities (PA, gas-phase basicities)[3,14] PA ≡ $\Delta H_{bas}$; five quantities calculated at the B3LYP/6-311+G(d,p,) level, viz. the relative energy $\Delta E_{is}$ (expressed by an isodesmic reaction[12,14]), the bond length[12] of the C(1)–C(O) bond $l_{C-C}$, function of the torsion angle[12] $\cos^2\phi$, equilibrium of the two configurations of the cation[14] log $K_{E,Z}$, and the oscillator strength of the $^1L_a$ band[12] $f_{cal}$; from the reactivities in solution only p*K* in sulfuric acid[22]. The matrix was complete except three items missing in the last column, which were estimated using the principle of additivity. Originally an additional descriptor was included, the $^1$H NMR shifts[13] of the $CH_3CO$ group, but it was subsequently excluded due to its low modeling power. Note that the descriptors were very different in character, while the compounds **1**–**14** were very similar to each other.

When the descriptors had been standardized by linear transformations to zero mean value and unit variance, PCA required three significant components explaining 80.8, 12.7 and 3.5 per cent of variance. The first component is a blend of inductive (negative) and steric (positive) factors and is most closely related to $^{13}$C(1), less to $f_{cal}$ or ε. The second component accounts mainly for the different sensitivity to the inductive effect. It is particularly important with PA (negative) and λ (positive).

In the next step, the data were processed by separating the steric components SE using Eqs (*1*), (*2*) and similar equations for various substituents. The resulting matrix consisting of SE values (SE matrix) had now only 12 lines corresponding to compounds **1**, **2**, **5**–**14**. Compounds **3** and **4** were omitted since their SE is zero by definition. Only two components were revealed explaining 94.2 and 3.6 per cent of variance, both components describe the steric effects. They are pictured in Fig. 7. The first component, α, is dominated by the strong effect in the nonplanar compounds **8**, **12** and **16**; all descriptors are influenced almost equally strongly. The second component, β, appears as a minor correction, important particular for the buttressing effect in **5** and **11**, to which some descriptors are more sensitive, for instance ν(C=O). A few descriptors were of less modeling power as expected, particularly $\Delta\nu_{1/2}$ ($R$ = 0.936). Any transformation of the components (rotation) was not attempted since the second component is too little important. With a good approximation, the steric effect SE is described by one component: separation of groups in Fig. 7 is more evident in the direc-

tion of the *x*-axis. Seven descriptors can be fitted satisfactorily only by the first component. When this approximation is accepted, the total substituent effect can be expressed by Eq. (*4*) where the polar effect is accounted for by the sum of Hammett constants σ.

$$Y_{ij} = a\alpha + \rho \Sigma \sigma_{o,m,p} \qquad (4)$$

Equation (*4*) holds for 12 from our descriptors with the correlation coefficient $R > 0.94$, for ν(C=O) with $R = 0.924$ and does not hold for $l_{C-C}$. Nevertheless, its range of validity is very restricted. Therefore, we do not claim it as a new empirical relationship and do not want to introduce the constants α as a new set of substituent constants. Qualitative interpretation referring only to groups of compounds is preferable.

Evaluation of SE has been based on the assumption that the polar effects are equal in the ortho and para positions. This assumption was several times questioned as discussed elsewhere[23]. Recently we estimated from ortho-substituted benzoic acids that it is weaker[23] by a factor of approximately 0.81. We repeated the PCA respecting this factor but the results with a modified SE matrix were not significantly different than above (two components, 93.5 and 4.1%). Hence the exact value of the factor cannot be determined in this way. In the case of methyl substituents with their weak polar effects, the assumption of equal polar effects is satisfactory.

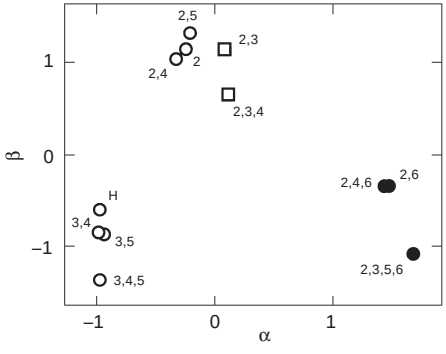



FIG. 7
Plot of the two significant components, α and β, of PCA of the steric effect (SE matrix); denotation of points as in Fig. 1

The physical meaning of SE was confirmed also by cluster analysis (CA, the nearest-neighbour method)) of the substituents in the SE matrix. The compounds were grouped into three classes: compounds **3**, **4**, **9**, **10**, with compound **13** closely related to them, a relatively distant group **2**, **5**, **6**, **7**, **11**, and a very distant group **8**, **12**, **14**. The grouping is essentially the same as seen in Fig. 1, 3 or 7. When CA was carried out in the original matrix, it yielded less definite results: three compounds were classified incorrectly.

PCA and CA yielded two unambiguous results. First the procedure of isolating steric effects is meaningful and the rough assumption that the steric effects are equal in the ortho and para positions is good for methyl substituents. Second factorization of the substituent effects in the ortho position is in principle possible. Our procedure was restricted only to one series of compounds; on the other hand, the variation in the descriptors was very broad including rather heterogeneous properties some of which have not been normally treated by empirical equations.

## CONCLUSIONS

Conformation of a series of aromatic carbonyl compounds has been determined by several independent experimental methods (see[12–14,22] and this work) and by DFT calculations[12,14] in good agreement. The results can be summarized as follows. The classic theory of steric inhibition of resonance is right merely in the qualitative sense. Quantitative dependence on the torsion angle $\phi$ is only very approximate since many derivatives are in fact planar ($\phi = 0$ or 180°). The angles $\phi$ reported in the literature and estimated from various experimental quantities are not reliable. A more realistic description divides the derivatives into two groups: “planar” and “nonplanar”; in some cases still the group “slightly nonplanar” can be distinguished. The differences between these groups are distinct. The well-known estimation of steric effects by comparing ortho and para derivatives is based on reasonable assumptions and can be elaborated to yield a quantitative measure of the steric hindrance.

The carbonyl frequency $\nu$(C=O) can serve as a physical quantity that is easily measured and is rather sensitive to the substituent steric effect. All the above conclusions can be drawn even from this single property.

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