JOURNAL OF PHYSICAL ORGANIC CHEMISTRY
J. Phys. Org. Chem. 2004; **17:** 686–693

Steric inhibition of resonance: revision of the principle on the electronic spectra of methyl-substituted acetophenones

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Received 8 September 2003; revised 27 November 2003; accepted 19 January 2004

ABSTRACT: The principle of steric hindrance to resonance (SIR) was revised on the well-known example of the electronic spectra of methyl-substituted acetophenones. The spectra were reinvestigated on an extended series **1–14**, and computer separation of bands was undertaken. The conformation of these molecules, total energy, rotational barrier, geometry of the transition state and electronic spectra were calculated within the framework of the density functional theory. The classical literature was correct that some molecules of the series are twisted from the planar arrangement by a variable angle ϕ. However, these angles do not agree with the values anticipated; the main difference is that all derivatives with only one *ortho*-methyl group are planar ($\phi = 0$). Our main objection is that the rotational barrier is in some cases very low; hence ϕ does not have the same importance with all derivatives. A better measure of steric hindrance is the calculated energy $\Delta_4 E$ of the isodesmic reaction Eqn (4), in which the molecule of the substituted acetophenone is formed from acetophenone and a methyl-substituted benzene. In contrast to the angles ϕ, there was good agreement between calculation and experiment in electronic spectra, viz. between the extinction coefficients of the ^1L_a band and the calculated oscillator strengths, at least in the relative values. Summarizing, SIR is valid as a qualitative principle but the reported angles ϕ based on several experimental quantities are often wrong. Each case must be examined separately as to the actual shape of the molecule. The classical paper by Braude *et al.* is a particularly bad example: the basic hypothesis of a planar excited state was not confirmed by our calculations.

KEYWORDS: acetophenone; density functional theory; isodesmic reaction; resonance; steric hindrance

INTRODUCTION

The principle of steric inhibition to resonance[1–3] (SIR) assumes that substitution by bulky groups can change the conformation of an originally planar molecule: part of the molecule is rotated out and the electron delocalization is reduced. SIR has been included in textbooks and applied broadly, for instance to electronic[2,4,5] and IR[4] spectra, ^{13}C[6–8] and ^{17}O[9] NMR spectra, acid–base equilibria,[3–5,10–12] dipole moments[1,2,13] and molar refraction.[5,14] The most recent applications are typically in kinetics.[15] In a more sophisticated version of this theory,[2] attempts were made to estimate quantitatively the torsion angle ϕ from the experimental quantities. (Most work deals with benzene derivatives; then ϕ is the angle between the planes of the ring and of the substituent.) It was assumed that ϕ increases within a series of compounds according to the size of the substituent; the observable quantities dependent on the electron delocalization are then reduced proportionally to $\cos\phi$. Hence ϕ was estimated[2] from the molecular extinction coefficient ε by means of Eqn (1) or from the dipole moment μ by Eqn (2):

$$\cos\phi = \varepsilon/\varepsilon_0 \tag{1}$$

$$\cos\phi = (\mu - \mu_\infty)/(\mu_0 - \mu_\infty) \tag{2}$$

The values ε_0 and μ_0 relate to the unsubstituted compound with $\phi = 0$; μ_∞ refers to the compound (sometimes hypothetical) with the extreme steric hindrance and $\phi = 90°$. The NMR shifts or pK values were treated according to equations similar to Eqn (2). Equations (1)

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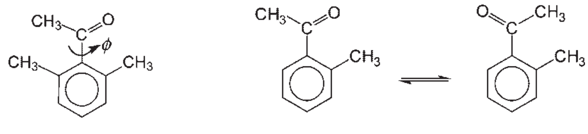
Contract/grant sponsor: Academy of Sciences of the Czech Republic; *Contract/grant number:* Z4 055 905.
Contract/grant sponsor: Ministry of Education of the Czech Republic; *Contract/grant numbers:* LN00A032, CI 253 100001.

and (2) were modified using[4–7] $\cos^2\phi$ or even only[9] ϕ instead of $\cos\phi$; the difference seems not to be important.[8]

We already had the opportunity to criticize the SIR theory—not overall but in some particular applications—from two points of view.[16–18] First, some molecules are undoubtedly twisted but their observable properties can be explained even without appealing to resonance and its inhibition (such as the dipole moments of nitro compounds[18]). Second and more important, SIR predicts that certain molecules, particularly substituted benzoic acids, should be twisted by non-negligible angles,[3,7,9,10b,14] whereas they are in fact planar,[16] as shown in an unambiguous way.[19]

In this work, we proceeded to a more fundamental revision of SIR, both in general and in its particular application to electronic spectra. We used the classical model, the methyl-substituted acetophenones. This was one of the series on which SIR was based[2a] and was investigated by the electronic spectra[2,4,20] and also by other methods;[2,4,6,9a,11,21] the assumed angles ϕ were estimated several times[2,4,6,9a] according to Eqns (1) and (2). We used an extended series of compounds, **1–14** (Table 1), and calculated their energy and geometry, including the minimum-energy angle ϕ, within the framework of the density functional theory[22] (DFT) at the B3LYP/6–311 + G(d,p) level. In important cases we calculated also the rotational barrier and course of the potential-energy curve. We also reinvestigated experimentally the electronic spectra and attempted computer separation of the bands with particular attention to the ^1L_a UV band on which the SIR correlations[2,4,20] were based. The experimental wavelengths λ and molecular extinction coefficients ε were compared with the calculations at the RCIS/6–311 + G(d,p)//B3LYP/6–311 + G(d,p) level. We calculated also the energy and geometry of the first three excited states, one of which was given particular importance in the SIR theory.[2]



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

Our first goal was to find which derivatives exist actually in a twisted conformation (shown for compound **8**), which is anticipated by SIR for all *ortho* derivatives. The alternative possibility is equilibrium

Table 1. Calculated energies and some geometric parameters of methyl-substituted acetophenones

No.	Substituents and conformation	E (DFT) (a.u.)	ϕ (°)	ϕ est.[a] UV (°)	ϕ est.[b] μ (°)	ϕ est.[c] NMR (°)	Population[d] (%)	C(1)—C(O) (Å)	C=O (Å)	Δ_4E[e] (kJ mol^{-1})	$\Delta_4E^{e}_{corr}$ (kJ mol^{-1})
1	H	−385.0016932	0.0	0		0		1.502	1.217	0	0
2	2-Me *sp*	−424.3251100	0.5	41	30[f](31)	28	98.7	1.500	1.219	11.01[g]	13.19
	ac	−424.3213794	148.4				1.3	1.508	1.217		
3	3-Me *sp*	−424.3295711	0.0				57.9	1.501	1.217	−0.55[g]	0
	ap	−424.3292696	180.0				42.1	1.501	1.218		
4	4-Me	−424.3300643	0.0					1.498	1.218	−2.18	0
5	2,3-Me_2 *sp*	−463.6491420	23.8			32	96.5	1.501	1.218	13.69[g]	16.42
	ac	−463.6462679	138.3				3.5	1.507	1.216		
6	2,4-Me_2 *sp*	−463.6536231	0.0	35	58	25	98.9	1.496	1.218	8.15[g]	12.51
	ap	−463.6496947	151.3				1.1	1.506	1.220		
7	2,5-Me_2 *sp*	−463.6525710	0.8	54	61	25	98.2	1.499	1.217	10.55[g]	13.28
	ac	−463.6491203	148.3				1.8	1.508	1.219		
8	2,6-Me_2	−463.6457513	73.3	71	55[f](86)	50		1.510	1.214	28.66	33.02
9	3,4-Me_2 *sp*	−463.6573014	0.0				59.7	1.498	1.218	−7.68[g]	−4.95
	ap	−463.6569285	180.0				40.3	1.498	1.218		
10	3,5-Me_2	−463.6569911	0.0					1.501	1.217	−0.85	0.25
11	2,3,4-Me_3 *sp*	−502.9742208	24.5				96.8	1.499	1.218	11.03[g]	15.94
	ac	−502.9712674	141.1				3.2	1.505	1.216		
12	2,4,6-Me_3	−502.9731043	68.8	80	78	51		1.507	1.215	27.54	34.08
13	3,4,5-Me_3	−502.9817839	0.0					1.498	1.218	−9.15	−5.87
14	2,3,5,6-Me_4	−542.2972744	90.0			57		1.516	1.213	23.74	29.20
Excited states											
1*	H	−382.5557067	0.0					1.449	1.216		
2*	2-Me	−421.5972970	23.4[h]					1.481	1.251		
8*	2,6-Me_2	−460.6287899	50.1[h]					1.517	1.252		

[a] Estimated from the extinction coefficients, Eqn (1), Ref. 2a.

[b] Estimated from the dipole moments, Eqn (2), Ref. 2a (in parentheses from the molar refraction, Ref. 14).

[c] Estimated from the ^{13}C NMR shifts, Eqn (2), Ref. 6.

[d] Calculated population of rotamers when they are present.

[e] Δ_4E is reaction energy of the reaction in Eqn (4); Δ_4E_{corr} is corrected according to the principle in Eqns (3a) and (3b).

[f] Ref. 13a.

[g] Related to the equilibrium mixture of conformers.

[h] Dihedral angle O=C—C(1)—C(2). The other dihedral angles on the same bond are different since the configuration on the carbonyl carbon atom is pyramidal: the sum of the three bond angles is 357.9° in the case of **2*** and 352.9° in the case of **8***.

of two planar conformers, as shown in the formulas $\mathbf{2A} \rightleftharpoons \mathbf{2B}$; the equilibrium may be sometimes strongly shifted to one side. Our ultimate intention was to give some suggestions for how to evaluate the numerous reported angles ϕ and how to treat the new examples of SIR.

EXPERIMENTAL

Materials. Compounds **2**, **5**, **8** and **10** were prepared from the corresponding benzonitriles by reaction with methylmagnesium iodide[23] and **7**, **11** and **12** from the appropriate methylbenzenes with acetyl chloride.[24] In the synthesis of **11** it was necessary to remove the byproducts by chromatography. Compound **13** was obtained by isomerization[25] of **12**. The remaining compounds were commercial. The purity of all samples was checked in a parallel investigation of ^{1}H and ^{13}C NMR spectra.[26]

Spectral measurements. The electronic absorption spectra were measured at 25 °C in methanol at a concentration of $5 \times 10^{-5}\,\mathrm{mol\,l^{-1}}$ using a Hewlett-Packard HP8453 spectrometer with extent of the diode field 190–1100 nm.

Separation of bands was carried out with the program Galactic Peaksolve.[27]

RESULTS AND DISCUSSION

When SIR is now applied to methyl-substituted acetophenones, its basic statements may be summarized at four levels:

1. In the ground state, the molecules of *ortho*-substituted acetophenones are twisted by a variable angle ϕ, which increases with the steric crowding.
2. The angle ϕ can be calculated from the experimental quantities, particularly from the extinction coefficient ε of the ^1L_a band[2] according to Eqn (1), from the dipole moment[2] or from the ^{13}C shift[6] according to Eqn (2). This procedure was improved[2a] when the experimental quantities were corrected for the polar effect of the methyl group with respect to its effects in the *meta* and *para* positions. For instance, ε of 2-methylacetophenone or 2,3-dimethylacetophenone are corrected according to the equations

$$\varepsilon_{\mathrm{corr}}(2\text{-Me}) = \varepsilon(2\text{-Me}) - \varepsilon(4\text{-Me}) + \varepsilon_0 \qquad (3a)$$

$$\begin{aligned}\varepsilon_{\mathrm{corr}}(2,3) = \varepsilon(2,3\text{-Me}_2) - \varepsilon(3\text{-Me})\\ - \varepsilon(4\text{-Me}) + 2\,\varepsilon_0\end{aligned} \qquad (3b)$$

3. Changes in the observable quantities with ϕ are connected with the electron distribution. They may be denoted as resonance and its inhibition and depicted more or less closely by the common resonance formulas.
4. In the case of electronic spectra, reduction of ε is accompanied only by minute shifts of the wavelength λ. This was explained[2] by assuming that resonance in the excited state is strengthened and the pertinent angle ϕ_{exc} is smaller than ϕ, almost $\phi_{\mathrm{exc}} \approx 0$. Reduction of ε was explained by transition from the higher vibrational levels. This is an additional hypothesis, not really SIR, and was not accepted by some later workers.[20]

These four statements will be successively re-examined in the following sections.

Conformation and energy in the ground state

The calculated torsion angles ϕ are given in Table 1, column 4. Derivatives **2**, **5**, **6**, **7** and **11** exist in equilibrium of two conformers but the equilibrium is strongly shifted. One can say that they exist in the *sp* conformation (as for example **2A**); minute populations of the *ap* or *ac* conformers, not exceeding 4% (Table 1, column 8), do not affect further conclusions. Derivatives **3** and **9** exist each in two conformers, almost equally populated. Since the energies of these two conformers are virtually equal, their presence need not be taken into account.

As anticipated, ϕ increases roughly with the steric hindrance but agreement with the SIR estimates (Table 1, columns 5–7) is poor. Our calculated values do not show the anticipated continuous rise but can be better rationalized when the compounds are divided into two classes. Derivatives without an *ortho*-methyl group (**1**, **3**, **4**, **9**, **10** and **13**) and those bearing one *ortho*-methyl group (**2**, **6** and **7**) are essentially planar, the *sp* conformation being preferred. Compounds of the second class, with methyl groups in both *ortho* positions (**8**, **12** and **14**), exist in a non-planar conformation with ϕ not far from 90°. Compounds **5** and **11**, with two adjoining methyl groups (buttressing effect), belong into the first class with a certain approximation.

Let us examine the conformation of the most important members of our series that have been separately investigated. The planar conformation of acetophenone (**1**) has been proven by several methods;[28] a few contrary claims were in our opinion based on inaccurate techniques.[29] The greatest difference between ϕ calculated by DFT and estimated by SIR is observed for the derivatives **2**, **6** and **7**, bearing one *ortho*-methyl group: the exact conformation of 2-methylacetophenone **2** may appear to be the central problem. Most of the experimental data may be interpreted by a non-planar conformation and by the equilibrium $\mathbf{2A} \rightleftharpoons \mathbf{2B}$ also. The former possibility was generally accepted[2,4,6,13a,14,21a,d] but some authors claimed the equilibrium[21c] or the conformer **2A** as the only one present.[21b] In a parallel investigation,[26] we measured the $^{3}J_{C,C}$ coupling constants of some acetophenones labeled with ^{13}C in the acetyl-CH_3 group. We confirmed conformation **2A** to be strongly prevailing if not the only one present but a small deviation from planarity could not be excluded. Similarly, gas-phase electron diffraction (D. Hnyk, S. Samdal and O. Exner, unpublished work) cannot distinguish between the planar form **2A** and a small torsion angle, say $\phi = 20°$.

The above problem is seen in the proper light when the whole potential-energy curves were calculated for the rotation around the C(O)—C(1) bond (Fig. 1). Neglecting the small irregularities, it is evident that the curves differ fundamentally for the individual compounds. For acetophenone (**1**), the symmetrical curve shows a barrier of 23.6 kJ mol^{-1}, in agreement with the low-temperature ^{13}C NMR measurement[28c] (22.4 ± 0.4 kJ mol^{-1}) but not with some other experimental values.[30] This value can be considered as a rough estimate of the resonance energy when the steric hindrance in the planar form is neglected. For **8**, the curve is also symmetrical but reversed: the two minima are placed at $\phi = 73$ and 107° but their energy is practically equal to that at 90°. The barrier of 20.2 kJ mol^{-1} can be interpreted as the steric hindrance in the planar form diminished by the resonance energy (greater than in **1**). The curve for **2** is strongly unsymmetrical, since the form **2B** is populated only to 1% (Table 1); the barrier measured from **2A** is 15.1 kJ mol^{-1}. The minimum-energy angle $\phi = 0°$ is not well defined since the minimum is very shallow; the values up to 20° cannot be excluded. With **5** the ground state is more sterically hindered owing to the buttressing effect, hence the barrier is lower (9.5 kJ mol^{-1}). The curve is still less regular. Values of ϕ between 0° and 40° must be admitted.

One conclusion that is evident from Fig. 1 is that the values of ϕ cannot be directly compared and cannot form a continuous scale since their significance differs from one member of the series to another. With certain compounds, ϕ defines a stable conformation, whereas with the others it is of uncertain magnitude and does not correspond to any real molecule. Within a series such as **1**–**14** it is more meaningful to distinguish only compounds of two classes: one with the energy minima near to 0 and 180° and the other with one minimum near to 90°. These two cases can be distinguished unambiguously.

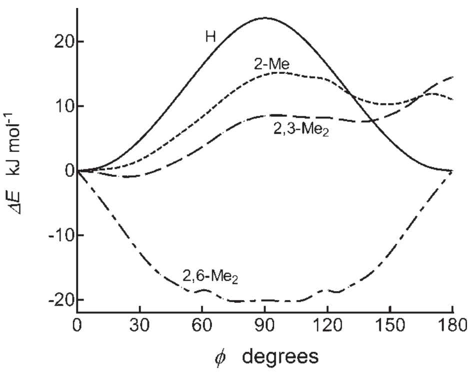
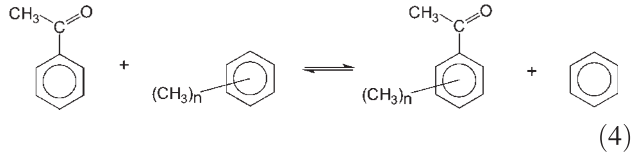


Figure 1. Calculated potential-energy curves of acetophenone (**1**), 2-methylacetophenone (**2**), 2,3-dimethylacetophenone (**5**) and 2,6-dimethylacetophenone (**8**): dependence of the relative DFT energy on the torsion angle ϕ

Since the angle ϕ is a bad measure of SIR or of the steric hindrance, a more suitable quantity needs to be searched for, preferably in the terms of energy. Energies of non-isomeric compounds can be compared within the framework of isodesmic reactions[31] applied broadly also in our previous work.[16a,c,17] For **1**–**14**, the reaction has the form of Eqn (4); it is not only isodesmic but also homodesmotic.[32]



(4)

Its reaction energy Δ_4E is a measure of the total substituent effect exerted on the functional group by all methyl groups together. It has a clear physical meaning and can be calculated unambiguously (Table 1, last but one column). Similarly to ε, even Δ_4E can be corrected for the polar effect of the methyl groups as for instance, in Eqns (3a) and (3b). The corrected Δ_4E is then a measure of the substituent steric effect assuming that the polar effect of a substituent is equal in the *ortho* and *para* positions. The assumption was doubted[33] but was applied broadly in the previous work[16a,c,17] with reasonable success. In the present case, it is certainly sufficiently precise since the polar effect of the methyl group is small.

Correlation of the electronic spectra with structure

The electronic spectra of **1**–**14** were treated by the standard computer program for the separation of bands,[27] but the results depend somewhat on the details of the separation procedure. Therefore, we tried a number of possibilities and compared the statistics given by the program also with some respect to the visual fitting. The Gaussian form of bands was sufficient in all cases; mixed Gaussian–Lorentzian bands brought no improvement. Separation in terms of the absorptivities A was more effective than in terms of $\log A$. The input number of bands and range of wavelengths appeared to be most important. Of the three bands of benzene derivatives, $^{1}E_{2u}$, $^{1}B_{1u}(^{1}L_a)$ and $^{1}B_{2u}(^{1}L_b)$, we were interested only in the second, $^{1}L_a$. Therefore, the most efficient procedure was fitting only by one band within the range 218–260 nm; the first band was fitted separately in the range 200–218 nm. This procedure was not possible in the case of **8**, **12** and **14** since the two bands come together: in the literature the $^{1}L_a$ band is described only as an inflex.[20,34] In these cases, the region 200–260 nm was treated

Table 2. Experimental electronic spectra of methyl-substituted acetophenones

		^1L_a band			First band	
No.	Substituent	λ (nm)	ε	ε_{corr}(rel.)	λ (nm)	ε
1	H	241.3	11660	0	209.0	18000
2	2-Me	242.0	7890	−4780	207.8	16240
3	3-Me	245.6	10490	0	210.9	10380
4	4-Me	251.4	12670	0	212.7	8030
5	2,3-Me_2	245.8	5240	−6260	209.2	18180
6	2,4-Me_2	252.2	10410	−3270	209.1	18150
7	2,5-Me_2	246.8	6690	−4810	211.5	17190
8	2,6-Me_2	230.2	1420	−12260	209.8	9250
9	3,4-Me_2	254.8	12290	790	213.6	13970
10	3,5-Me_2	250.7	10970	1650	212.7	19470
11	2,3,4-Me_3	255.5	8350	−4160	212.9	17100
12	2,4,6-Me_3	246.9	1140	−13550	213.5	10070
13	3,4,5-Me_3	258.4	13630	3300	214.3	20510
14	2,3,5,6-Me_4	241.3	312	−11030	214.3	8150

together and the search for two bands was input into the program.

The results of the above procedures are given in Table 2. We calculated also the integrated absorption intensities but they were practically proportional to the extinction coefficients and did not give better correlation with the calculated spectra. Therefore, we preferred discussion in terms of ε, better comparable to previous results. The progress of our separation as compared with previous simple recording of spectra[2a,4,20,34] concerns mainly **8**, **12** and **14** with low-intensity bands. With the other compounds, there is reasonable agreement with the previous measurements on smaller sets: our wavelengths agree with those of Forbes and Mueller[20] within 1 nm (four compounds), the values of Suzuki[34] are systematically 5 nm lower. Agreement of ε with Forbes and Mueller[20] is very good (correlation coefficient $R = 0.991$, six compounds) when the erroneous value[20] for **14** is omitted; with Suzuki[34] it is somewhat worse ($R = 0.970$).

The calculated UV spectra are presented in Table 3 as the transition wavelengths λ and the oscillator strengths f for the first three excited states. The spectra are more complex than originally believed.[2] In the place of the experimental absorption band ^1L_a two transitions have been found theoretically, corresponding to the second and third excited states. They differ only by 1–10 nm and cannot be separated experimentally. Therefore, we

Table 3. Calculated electronic spectra of methyl-substituted acetophenones

No.	Substituent	λ_1 (nm)	10^4f_1	λ_2 (nm)	10^4f_2	λ_3 (nm)	10^4f_3	$10^4(f_2+f_3)$[a]
1	H	250.6	2	215.3	632	212.6	878	1510
2	2-Me	*sp* 253.0	2	220.1	845	212.8	700	1545
		ac 249.5	38	215.4	440	212.5	685	1125
3	3-Me	*sp* 250.9	2	219.4	478	216.4	1126	1604
		ap 251.1	2	221.4	818	215.0	678	1496
4	4-Me	248.7	3	217.8	1749	215.0	257	2006
5	2,3-Me_2	*sp* 251.9	7	220.7	560	214.7	555	1115
		ac 250.3	43	215.5	302	211.8	354	656
6	2,4-Me_2	*sp* 250.9	3	220.7	1177	215.0	833	2010
		ap 248.0	57	217.0	1000	215.6	559	1559
7	2,5-Me_2	*sp* 253.4	2	226.6	1059	215.3	523	1582
		ac 249.7	35	220.8	683	214.8	461	1144
8	2,6-Me_2	251.2	19	214.0	285	210.7	201	486
9	3,4-Me_2	*sp* 249.1	2	218.4	1748	218.0	234	1982
		ap 249.2	2	221.0	1363	216.1	552	1915
10	3,5-Me_2	251.5	2	224.6	709	219.2	994	1703
11	2,3,4-Me_3	*sp* 250.4	11	220.0	460	216.8	856	1316
		ac 249.5	63	216.3	174	214.8	695	869
12	2,4,6-Me_3	251.0	29	216.0	378	214.0	343	721
13	3,4,5-Me_3	249.6	2	222.8	976	220.1	1038	2014
14	2,3,5,6-Me_4	243.5	8	210.4	113	206.5	142	255

[a] Sum for the two bands.

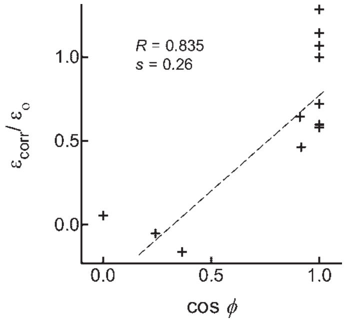


Figure 2. Dependence of the relative experimental extinction coefficients $\Delta\varepsilon_{corr}$ (corrected for the inductive effect) of acetophenones **1–14** on the calculated torsion angle ϕ

calculated the sum $f_2 + f_3$ for these two bands; in addition, the values for the two conformers were summed as the case may be. (The latter correction is of little importance since either one conformer is negligibly populated or the two conformers are very similar.) The values of $f_2 + f_3$ are given in Table 3, last column. The essential agreement of the calculated and experimental UV spectra is based on their correlation with the experimental $\varepsilon (R = 0.944$, 14 points). We obtained no correlation of the experimental and calculated λ owing to the small range of their values.

The central test of the SIR theory is now comparison of the experimental ε with the calculated ϕ, which we believe to represent the real geometry. We used corrected values[2] of ε but the correction is insignificant. Although the correlation coefficient of 0.832 could suggest some relation, Fig. 2 reveals no linear dependence. Instead, the points are divided into two groups: one with a planar conformation and the other with rather high values of ϕ. This is the conclusion drawn already in the previous section from the mere values of ϕ. We conclude that SIR fails in the critical point.

On the other hand, there is a good correlation of the corrected ε with the corrected energies of the isodesmic reactions $\Delta_4 E$ (Fig. 3); in the latter quantity the correction must not be omitted. It follows that the extinction coefficient depends on the intensity of steric hindrance whether the molecule is planar or not. Similar results to those in Figs 2 and 3 can be obtained on replacing ε by the ^{13}C NMR shifts[6] or by the gas-phase basicities;[11] in all cases the energies $\Delta_4 E$ are strongly preferable to the minimum-energy angles ϕ. This is the fundamental objection against the SIR theory: not only are the observable quantities controlled by ϕ, they are also modified by the steric hindrance existing in the planar derivatives (Fig. 3, the points in the middle).

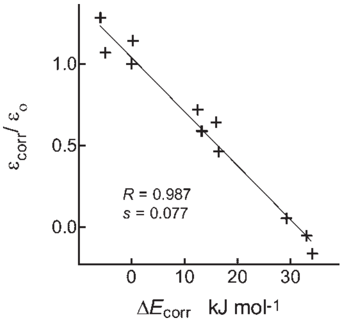
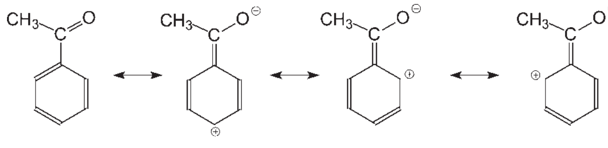


Figure 3. Dependence of the relative experimental extinction coefficients $\Delta\varepsilon_{corr}$ (corrected for the inductive effect) of acetophenones **1–14** on the similarly corrected energies $\Delta_4 E$ of the isodesmic reaction, Eqn (4); these corrected energies represent the substituent steric effect

Resonance and its inhibition

There is no doubt that SIR is broadly valid as a qualitative principle: many proofs have been reported in accord with the classical resonance theory. For acetophenone, this theory gives the formulae **1A–1D**, predicting some changes of geometry, in particular shortening of the C(1)—C(O) bond. Inhibited resonance in the crowded derivatives should be seen on lengthening this bond. The data in Table 1, column 9, confirm the prediction; see particularly the derivatives **8**, **12** and **14**.



1A **1B** **1C** **1D**

A quantitative extension of SIR would require a dependence of the C(1)—C(O) bond length on ϕ. The shape of the potential-energy curve should be of less importance with this test since we are dealing with fixed structures, not with real molecules. Figure 4 reveals a good correlation for the stable conformations of **1–14**: the greater is ϕ, the shorter is the C(1)—C(O) bond. The formulae **1A—1D** express the real structure well in this point. Deviation of the minor conformations in Fig. 4 means that the bond length is controlled partly also by the steric hindrance in nearly planar molecules (it is lengthened). Changes of other geometric parameters are less evident and no important correlations were found. In

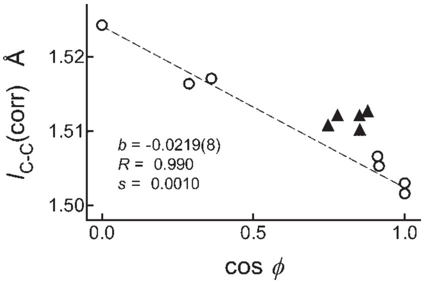


Figure 4. Dependence of the C(1)—C(O) bond length in all conformers of **1–14** (corrected for the inductive effect) on the torsion angle ϕ: ○, minimum-energy conformers; ▲, minor conformers (the statistics and the regression line belong to the former group)

particular, the changes of the C═O bond length (Table 1, column 10) are small; only in strongly twisted derivatives is the longer C(1)—C(O) bond connected with a shortened C═O bond. Note that in some other cases the resonance formulae express the real structure only in certain aspects; the exceptions concern just the C═O bond.[35]

We may conclude this section by our opinion that when the resonance formulae are once accepted as a reasonable expression of certain structural features, the steric inhibition of resonance is to be accepted by the same token.

The excited state

Electronic spectra were the first experimental method on which the SIR theory was based but just this application is problematic. Since in most cases ε was strongly affected by SIR whereas λ was almost unchanged, a special explanation was proposed[2] based on the assumption that the molecule in the excited state is almost planar, or in any case much nearer to planarity than in the ground state. This has not been confirmed by our calculations (Table 1, bottom). The geometry in the second excited state (^1L_a transition) of **1***, **2*** and **8*** is relatively similar to that in the ground state. This means that **1*** is planar and **2*** near to planar, and the non-planar conformation of **8*** could be decisive for the above theory. The angle ϕ_{exc} in the excited state is not very different from that in the ground state but is badly defined since the configuration at the carbonyl C atom in **8*** is not planar. (The sum of the three angles at this atom is less than 360°, Table 1, footnote f). Pyramidalization at this atom is accompanied by lengthening the C═O and C(1)—C(O) bonds, the latter at variance with the assumed strengthening of resonance. On the other hand, it is true that the C(2)—C(3) and C(5)—C(6) bonds are shortened compared with the ground state. The geometries of the planar molecules of **1*** and **2*** are of course different, particularly the C(1)—C(O) bond is shortened (Table 1).

In general, the geometry of the excited state is different from that of the ground state and can hardly be discussed in terms of common structural formulae. It is only certain that the simple assumption about the strengthened resonance and planarity[2] is not valid: the changes during excitation are much more complex to be described by changes of the single angle ϕ. In addition, the assumed transition from the vibrationally excited states[2] was from the beginning improbable, since it is at variance with the Franck–Condon principle.

We conclude that the particular application of SIR to electronic spectra using the extinction coefficient as the observed quantity was less justified than in the other cases. It needed additional hypotheses, which were not correct. It is strange that just the fundamental paper by Braude *et al.*,[2a] establishing the SIR theory, was wrong in the essential points. In the case of methyl-substituted acetophenones, more suitable observable quantities are, for instance, the gas-phase basicities[11] or ^{13}C NMR shifts.[6,26]

CONCLUSIONS

The theory of SIR is evidently right as a qualitative principle within the framework of the resonance theory, which is also qualitative in character. The quantitative extension operating with variable angle ϕ was inadequate in all examples revised. Several molecules certainly do not possess the conformation attributed to them by this theory; moreover, the angle ϕ cannot serve as a physical characteristic for comparing individual compounds since the rotational barrier is in some cases too low. Instead of a continuous series of ϕ values, there is a better description to distinguish only two groups of compounds: nearly planar ($\phi \approx 0$) and non-planar (ϕ not far from 90°).

In any new application of this theory, it is advisable to determine the actual conformation of each derivative by direct methods, say by calculations; the strength of the steric hindrance is better evaluated in energy terms (reaction energy of an isodesmic reaction) than in any geometric parameter (angle ϕ). The numerous values of ϕ reported in the literature should be viewed as bad estimates of an ill-defined quantity and should not be given credence. Application of SIR to electronic spectra is still less trustworthy than the other owing to the problems mentioned above.

CALCULATIONS

The DFT calculations of the ground state were performed at the B3LYP/6–311+G(d,p) level according to the original proposal[22] using the Gaussian program.[36] No symmetry preconditions were presumed. All energy-optimized structures were checked by the vibrational analysis. The population of the conformers was calculated with the approximation $\Delta G^\circ(298) \approx \Delta E$. The calculated energies, minimum-energy conformations and reaction energies of the isodesmic reaction, Eqn (4), are given in Table 1.

Energies of the conformations with frozen rotation were calculated with a given fixed torsion angle ϕ; all remaining geometry parameters were optimized. These results are given only in the form of potential energy curves, Fig. 1.

Electronic transitions were calculated at the RCIS/6–311+G(d,p)//B3LYP/6–311+G(d,p) level; the results are given in Table 3. Geometry and energy of the excites states were calculated at the RCIS/6–311+G(d,p) level.

Acknowledgments

This work was carried within the framework of research project Z4 055 905 of the Academy of Sciences of the Czech Republic, and supported by the Ministry of Education of the Czech Republic, Projects LN00A032, Center for Complex Molecular Systems and Biomolecules (to O.E.) and CI 253 100001 (to J.K.).

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