JOURNAL OF PHYSICAL ORGANIC CHEMISTRY
J. Phys. Org. Chem. 2003; **16:** 721–725

Ortho effect and steric inhibition of resonance: basicities of methyl-substituted acetophenones[†]

Eva Otyepková,[1] Tat'jana Nevěčná,[1] Jiří Kulhánek[2] and Otto Exner[3]*

[1]Department of Inorganic and Physical Chemistry, Palacký University, 771 46 Olomouc, Czech Republic
[2]Department of Organic Chemistry, University of Pardubice, 532 10 Pardubice, Czech Republic
[3]Institute of Organic Chemistry and Biochemistry, Academy of Sciences of the Czech Republic, 166 10 Praha 6, Czech Republic

Received 7 January 2003; revised 10 March 2003; accepted 11 March 2003

ABSTRACT: The basicity of 12 methyl-substituted acetophenones was measured spectrophotometrically in 46–90 vol.% sulfuric acid. The acidity function was constructed and the pK_a values were calculated by a new algorithm proposed by Pytela. The substituent effects were divided into polar and steric, assuming that the former are approximately equal in the *ortho* and *para* positions. Polar effects of the methyl group bring about stronger basicity as expected; the effect is more intense than the acid weakening in equally substituted benzoic acids. Steric effects of *ortho* methyl groups are base strengthening. This is not due to steric inhibition of resonance since the conformation remains planar in most derivatives. Two *ortho* methyl groups are necessary to distort the planarity; their steric effect is more than doubled compared with one methyl group. These results do not agree with the common idea of twisted conformations with gradually increasing twisting angle but are better rationalized by the existence of two groups of derivatives, planar and non-planar. Copyright © 2003 John Wiley & Sons, Ltd.

KEYWORDS: acetophenones; acidity function; inhibition of resonance; steric effects

INTRODUCTION

Substituent effects in the *ortho* position of the benzene ring (the *ortho* effect) have often been investigated on methyl and polymethyl derivatives in which the polar effect is small and steric effects can be better observed. The most popular interpretation was by steric inhibition of resonance[1] (SIR) applied, for instance, to substituted nitrobenzenes,[1,2] benzoic acids,[3] their esters,[3a,4] substituted anilines[5] and aryl ketones.[4,6–9] In the more sophisticated version of this theory, it has been assumed that the functional group is twisted out of the ring plane by the angle ϕ variable with the steric hindrance. Any quantity related to electron delocalization then depends on this supposed angle, which has been calculated many times from observable quantities, e.g. from the molecular extinction coefficient[6a] [Eqn (1)] or from other spectroscopic quantities,[5a] even from acid–base equilibria[3b] [Eqn (2)] (the subscript 0 refers to the unsubstituted planar compound and the subscript ∞ to a compound with $\phi = 0$, sometimes hypothetical). The results were similar when cos ϕ was replaced[2,3d,6b,7a,b] by $\cos^2 \phi$ or even by ϕ itself.[3e]

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

$$(\mathrm{p}K - \mathrm{p}K_\infty)/(\mathrm{p}K_0 - \mathrm{p}K_\infty) = \cos\phi \tag{2}$$

We criticized the theory of SIR in the case of benzoic acid derivatives[10] since the calculated ϕ in many cases did not agree with the actual conformation determined by reliable independent methods. In particular, molecules with a small steric hindrance (one *ortho* methyl group) were planar[11] whereas SIR anticipated considerable twisting angles ϕ. The increased acidity of these acids cannot be due to SIR. The steric effect was observable in the acid molecule and somewhat smaller in the anion; the difference causes the increased acidity. We attributed it tentatively to polarization of the methyl group by the charge of the $\mathrm{COO^-}$ group.[10d]

In this work, we extended the investigation to methyl-substituted acetophenones **1a**–**1l** (Table 1) and report here their basicity in sulphuric acid. These compounds were important as models from the early development of the SIR theory;[6a] the supposed angles ϕ based on several observable quantities have been reported.[6a,b,7,9] Their basicity has been measured occasionally in H_2SO_4 on a few compounds,[6b,12] and more recently in the gas phase on a larger series.[8] It was always interpreted in terms of SIR.[6b,8] The second target of our investigation, in our

---

*Correspondence to: O. Exner, Institute of Organic Chemistry and Biochemistry, Academy of Sciences of the Czech Republic, 166 10 Praha 6, Czech Republic.
E-mail: uochb@uochb.cas.cz

[†]Dedicated to Professor T. M. Krygowski on the occasion of his 65th birthday in recognition of his outstanding outstanding contributions to physical organic chemistry.

Contract/grant sponsor: Ministry of Education of the Czech Republic.
Contract/grant number: 1221//2002.
Contract/grant number: CI 253 100001.
Contract/grant number: LN00A032.

Table 1. Basicities of methyl-substituted acetophenones and related quantities

Compound	Substituent	λ (nm)	$c(H_2SO_4)$ (mol dm^{-3})	pK_a	$\Delta_3G°$(w) (kJ mol^{-1})	$\Delta_3G°$(g)[a] (kJ mol^{-1})	pK_a(COOH)[b]	*SE* (kJ mol^{-1})
1a	H	290	9.9–15.1	−4.16 (4)	0	0	4.20	0
1b	2-Me	297	9.9–14.8	−4.12 (7)	−0.2	−5.0	3.90	2.3
1c	3-Me	298	8.8–14	−3.89 (13)	−1.5	−7.1	4.27	0
1d	4-Me	311	8.8–13.1	−3.62 (4)	−3.1	−14.4	4.37	0
1e	2,3-Me$_2$	300	8.8–13.6	−3.89 (6)	−1.5	−13.5	3.72	2.5
1f	2,4-Me$_2$	310	7.8–13.1	−3.42 (3)	−4.2	−21.5	4.22	1.4
1g	2,5-Me$_2$	300	9.0–13.5	−3.81 (10)	−2.0	−12.4	4.00	2.0
1h	2,6-Me$_2$	308	10.4–15.1	−4.83 (14)	3.8	4.1	3.35	8.8
1i	3,4-Me$_2$	315	7.8–13.1	−3.40 (8)	−4.3	−21.7	4.41[c]	0.3
1j	3,5-Me$_2$	310	8.8–14.1	−3.86 (6)	−1.7	−14.9	4.30	1.4
1k	2,3,4-Me$_3$	320	8.8–14.1	−3.67 (6)	−2.8	−26.7	4.06[d]	4.3
1l	3,4,5-Me$_3$	323	7.8–12.9	−3.29 (11)	−5.0	−29.7	4.52[d]	1.2

[a] Ref. 8.

[b] pK_a refers to the acidity of similarly substituted benzoic acids.[3b]

[c] Ref. 3a.

[d] Ref. 3c.

opinion of comparable importance, was to provide additional experimental material for the new approach to acidity functions devised by Pytela,[13] and to compare it with previous theories.[14] Pytela's approach[13] allows the determination of both the pK_a values of the indicators and the acidity function $H°$ simultaneously from the same set of data,[15] and even the basicities in several different acids can be treated together. The results should therefore be thus more reliable than the previous measurements[6b,12] based on $H°$ functions determined on substituted anilines.

EXPERIMENTAL

Materials. Compounds **1b**, **1e**, **1h** and **1j** were prepared from the corresponding benzonitriles by reaction with methylmagnesium iodide,[16] **1g** and **1k** from appropriate methylbenzenes with acetyl chloride[17] and **1l** by isomerization[18] of 2,4,6-trimethylacetophenone. The remaining compounds were commercial. The purity of all samples was checked in a parallel investigation of ^{1}H and ^{13}C NMR spectra (M. Buděšínský, J. Kulhánek, S. Böhm and O. Exner, unpublished work).

Measurement of dissociation constants. Dissociation constants of **1a**–**1l** were measured spectrophotometrically in sulfuric acid solutions using a (Beckman) DU 7500 instrument. Ratio of the concentrations of the base c_B and of the cation c_{BH^+} was determined at 298 ± 0.1 K, at a wavelength λ and in the range of concentration of sulfuric acid as given in Table 1; 10–18 measurements were made for each compound. The exact concentration of the acid was determined by alkalimetry. Further details of the procedure were given previously.[15] The obtained values of $\log(c_B/c_{BH^+})$ at a given concentration $c(H_2SO_4)$ were input into the algorithm designed by Pytela,[13] which requires only anchoring of the scale of pK_a on one or more fixed values. We used published values[12] for **1a** and **1b**. The resulting pK_a values of **1a**–**1l** are given in Table 1 and the acidity functions H_0 in Table 2. Under our

Table 2. Calculated acidity functions in dependence on the concentration of sulfuric acid with respect to acetophenones **1a**–**1l** as indicators

$c(H_2SO_4)$ (mol dm^{-3})	H_0	$c(H_2SO_4)$ (mol dm^{-3})	H_0	$c(H_2SO_4)$ (mol dm^{-3})	H_0
6.6	2.049	9.6	2.880	12.6	4.210
6.8	2.082	9.8	2.984	12.8	4.275
7.0	2.115	1.0	3.049	13.0	4.410
7.2	2.147	1.2	3.162	13.2	4.484
7.4	2.176	1.4	3.250	13.4	4.633
7.6	2.211	1.6	3.313	13.6	4.685
7.8	2.257	1.8	3.379	13.8	4.716
8.0	2.324	11.0	3.487	14.0	4.819
8.2	2.398	11.2	3.610	14.2	4.858
8.4	2.486	11.4	3.679	14.4	4.919
8.6	2.559	11.6	3.766	14.6	5.012
8.8	2.618	11.8	3.867	14.8	5.126
9.0	2.681	12.0	3.936	15.0	5.252
9.2	2.751	12.2	3.997		
9.4	2.802	12.4	4.135		

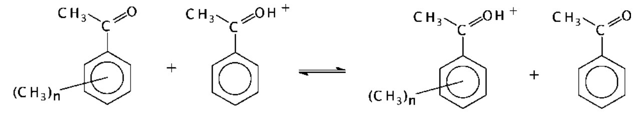
conditions, we were unable to obtain reliable results for 2,4,6-trimethylacetophenone and 2,3,5,6-tetramethylacetophenone owing to their rapid decomposition.[6b]

RESULTS AND DISCUSSION

p*K* and acidity functions

Of our values of pK_a (Table 1, column 5), only a few can be compared with the previous measurements and the comparison will depend strongly on the data chosen as anchoring points. Since we chose the more recent data of dell'Erba *et al.*,[12] a comparison is possible only with the older values of Yates and Scott[6b] for **1a**, **1b**, **1c**, **1d** and **1h**. Our values differ badly; even in the relative values there is merely qualitative agreement. This is just a further example of the fact that the acidity functions cannot be transferred from one class of indicators to another; the values of Yates and Scott were based on H_0 determined on substituted anilines.

The effect of anchoring is eliminated when we confine ourselves to relative values of pK_a related to unsubstituted acetophenone or to the pertinent Gibbs energies. The latter can be understood as reaction Gibbs energies Δ_3G° of the isodesmic reaction in Eqn (3). They are given in Table 1, column 6 and will be used in the following discussion as a measure of the cumulative substituent effect of all methyl groups on the basicity.



1b–1l **1a**

(3)

Basicities in solution and in the gas phase

Correlation analysis of our data will start with comparison of the basicities of **1a–1l** in aqueous sulfuric acid and in the gas phase.[8] Figure 1 reveals deviations of the two most crowded compounds, 2,6-dimethyl- and 2,3,4-trimethylacetophenone, which can be considered as steric hindrance to solvation: when hydration is hindered in the cations, the basicity should be weaker in aqueous solution. The other points in Fig. 1 are situated near a straight line with a slope of 0.19. This value describes the attenuation in water and is of the magnitude observed for molecules of this size.[19] In general, Fig. 1 confirms, on a smaller set, what was found on equally substituted benzoic acids.[10] The compounds are divided into two classes: those with no or one *ortho* methyl group (assumed to be in a nearly planar conformation) and those with two *ortho* methyl groups (strongly non-planar). Derivatives with cumulated methyl groups as in 2,3,4-trimethylacetophenone may be slightly non-planar (buttressing effect) and represent a borderline case.

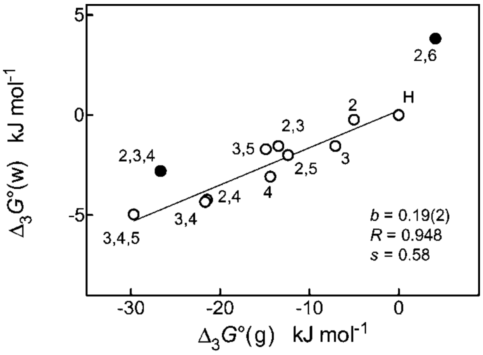
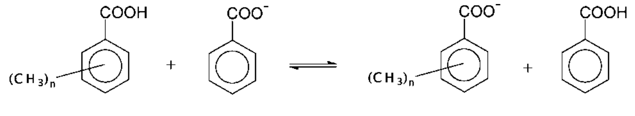


Figure 1. Basicities of methyl-substituted acetophenones, Δ_3G°(w), plotted versus their basicities in the gas phase, Δ_3G°(g): (●) derivatives showing marked steric inhibition of hydration; (○) other derivatives; the regression relates to the latter group

Polar and steric substituent effects

Polar and steric effects are evident from a plot of the basicities of **1a–1l**, Δ_3G°(w), vs the relative acidities Δ_4G°(w) of equally substituted benzoic acids[3a] **2a–2l** [isodesmic reaction in Eqn (4)].



2b–2l **2a**

(4)

In Figure 2 we see first the expected linear dependence for derivatives substituted only in the *meta* and *para* positions; this dependence is required by the general validity of the Hammett equation.[20] The slope of this line, −2.8 equals the reaction constant ρ pertinent to

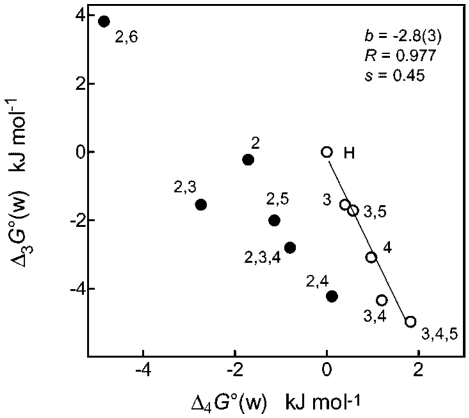
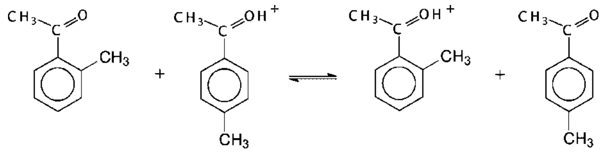


Figure 2. Basicities of methyl-substituted acetophenones, Δ_3G°(w), plotted versus the acidities of similarly substituted benzoic acids, Δ_4G°(w): (○) *meta* and *para* derivatives; (●) other derivatives; the regression line relates to the first group

Eqn (3) (determined here not precisely by means of low-polarity substituents). Its negative sign is evident since electron-releasing substituents make the acids weaker and the bases stronger. Its absolute value, much greater than unity, may be surprising: within the framework of the simple theory one would expect effects of equal intensity in **1** and **2** since the site of protonation is equally distant from the benzene ring.[20] However, it can be understood in terms of crossed conjugation: the conjugated carboxylate group is less sensitive to substituent effects than the simple group —C=OH$^+$.

The deviation of *ortho* derivatives from the straight line in Fig. 2 is evidently due to steric effects. One can estimate only that they are of comparable magnitude in acetophenones and benzoic acids. A more detailed analysis is possible by the classical approach applied by us several times to the gas-phase acidities[10a,b,21] or basicities.[10a,22] It is based on two assumptions: (a) polar effects are equal in the *ortho* and *para* positions and (b) steric effects are zero in the *meta* and *para* positions. Then the steric effect *SE* in 2-methylacetophenone is defined by the difference Δ_3G(2-Me) – Δ_3G(4-Me) and can be expressed by the isodesmic reaction in Eqn (5).



1b **1d**

(5)

When more substituents are present, the definition is more complex, as for instance in the case of the 2,3,4-trimethyl derivative, Eqn (6). An isodesmic reaction would be too complicated in this case but in all cases the quantity *SE* defined in this way can be given a physical meaning.

$$SE(2,3,4\text{-Me}_3) = \Delta_3G(2,3,4\text{-Me}_3) - 2\Delta_3G(4\text{-Me}) - \Delta_3G(3\text{-Me}) \qquad (6)$$

Equal intensity of polar effects in the *ortho* and *para* positions has been questioned several times and the *ortho*:*para* ratio has been claimed to be both greater and smaller than unity.[23] Recently we estimated *ortho:para* = 0.81 on the basis of substituted benzoic acids (O. Exner and S. Böhm, unpublished work). With this correction, Eqn (6) takes the form of Eqn (6a) and similar changes occur for other substituents; representation by an isodesmic reaction is no longer possible.

$$SE(2,3,4\text{-Me}_3) = \Delta_3G(2,3,4\text{-Me}_3) - 1.81\Delta_3G(4\text{-Me}) - \Delta_3G(3\text{-Me}) \qquad (6a)$$

In our case of weakly polar substituents, the above correction is of little importance. The values of *SE* listed in Table 1, last column, were calculated with this correction, but very similar results would be obtained without it. The inaccuracy of the whole approach is clearly seen from the values for **1j** and **1l**, which should equal zero. On the other hand, the essential correctness of this approach is evident from Fig. 3. Steric effects on the basicity of acetophenones were plotted versus steric effects on the acidity of benzoic acids calculated in the same way. The linear dependence is as good, as could be expected with respect to the approximate basic assumptions. Steric effects in the two series are similar, those in acetophenones perhaps being slightly stronger. In our opinion it is possible to transfer the results from the series of benzoic acids, where they were supported by several observable quantities on a large series of compounds,[10,11] to acetophenones where the reaction series is less extended. Derivatives with increasing steric hindrance do not form a series with gradually increasing angle ϕ; more properly they are divided into two groups. Those bearing one or no *ortho* methyl group are assumed to be in a planar (or near to planar) conformation, and those with two *ortho* methyl groups are strongly non-planar with ϕ not far from 90°. Steric effects in the second group are much stronger; the effect of two methyl groups is more than doubled that of one methyl group. The central problem for confirming this interpretation is the conformation of 2-methylacetophenone. Within the framework of SIR it was always assumed to be non-planar[6a,b,7a–c,24] with ϕ between 31 and 40°; only exceptionally did one take into consideration the planar *sp* conformation[7d] (as pictured in formula **1b**), or even the reverse *ap* conformation[25] or an equilibrium of both.[26] Our proofs for the conformation *sp* are based on reinterpretation of ^{13}C NMR spectra,[7a] particularly on a new determination (M. Buděšínský, J. Kulhánek, S. Böhm and O. Exner, unpublished work) of $^3J_{CC}$ coupling constants of labeled **1b**, and on DFT calculations (M. Buděšínský, J. Kulhánek, S. Böhm and O. Exner, unpublished work). The analogous conformation of methyl 2-methylbenzoate was proved by several means; in addition to electron diffraction[11a] and x-ray[11b] methods the analysis of IR spectra[10c] was also fully conclusive.

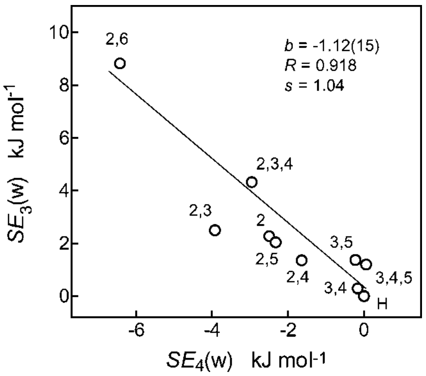
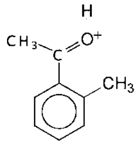
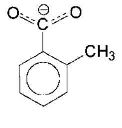


Figure 3. Separated steric effects SE_3 in methyl-substituted acetophenones plotted versus steric effects SE_4 in the acidities of similarly substituted benzoic acids

While the conformation is substantially proven, one unclear point remains, namely why the steric hindrance in the *ortho* position functions as base weakening in acetophenones and as acid strengthening in benzoic acids. Since the main substituent effect takes place in the ions, this means that cation **3** is stabilized by the interaction of CH_3 and $CHOH^+$ whereas anion **4** is destabilized. In our opinion, the solution is to be sought in the detailed charge distribution and cannot be described within the framework of simple electrostatics. In electrostatic terms, one would be obliged to assume that the methyl group behaves in **4** as a polarizable medium[10d] and in **3** rather as a dipole oriented with its positive charge toward the carbonyl. This difference could hardly be justified.



3



4

CONCLUSIONS

The theory of SIR was correct in a qualitative sense and contributed significantly to understanding and predicting the physical properties of sterically congested molecules. However, its refinement assuming that the twisting angle is continuously variable is misleading in many examples. A better description may be that the compounds are divided into two classes: molecules with a weak steric hindrance remain planar whereas those with strong hindrance are strongly twisted. In any application of SIR it is necessary to determine the twisting angle by independent means; its calculation from simple spectroscopic and other quantities using Eqns (1) and (2) often leads to incorrect values.

Acknowledgements

This work was supported by the Ministry of Education of the Czech Republic, projects 1221//2002 (to E. O. and T. N.), CI 253 100001 (to J. K.) and LN00A032 (Center for Complex Molecular Systems and Biomolecules, to O. E.).

REFERENCES

1. Birtles RH, Hampson GC. *J. Chem. Soc.* 1937; 10–15.
2. Wepster BM. *Recl. Trav. Chim. Pays-Bas* 1957; **76**: 335–356.
3. (a) Dippy JFJ, Hughes SRC, Laxton JW. *J. Chem. Soc.* 1954; 1470–1476; (b) Wilson JM, Gore NE, Sawbridge JE, Cardenas-Cruz F. *J. Chem. Soc. B* 1967; 852–859; (c) Lüning B. *Acta Chem. Scand.* 1960; **14**: 321–347; (d) Guilleme J, Diez E, Bermejo FJ. *Magn. Reson. Chem.* 1985; **23**: 442–449; (e) Baumstark AL, Balakrishnan P, Dotrong M, McCloskey CJ, Oakley MG, Boykin DW. *J. Am. Chem. Soc.* 1987; **109**: 1059–1062.
4. Leibfritz D. *Chem. Ber.* 1975; **108**: 3014–3024.
5. (a) Ahlbrecht H, Düber EO, Epsztajn J, Marcinkowski RMK. *Tetrahedron* 1984; **40**: 1157–1165; (b) Wepster BM. *Recl. Trav. Chim. Pays-Bas* 1957; **76**: 357–381.
6. (a) Braude EA, Sondheimer F, Forbes WF. *Nature* (*London*) 1954; **173**: 117–119; (b) Yates K, Scott BF. *Can. J. Chem.* 1963; **41**: 2320–2330; (c) Forbes WF, Mueller WA. *Can. J. Chem.* 1955; **33**: 1145–1154.
7. (a) Dhami KS, Stothers JB. *Can. J. Chem.* 1965; **43**: 479–497; (b) Oakley MG, Boykin DW. *J. Chem. Soc., Chem. Commun.* 1986; 439–441; (c) Grimaud M, Pfister-Guillouzo G. *Org. Magn. Reson.* 1975; **7**: 386–391; (d) Goethals G, Uzan R, Nadjo L, Doucet J-P. *J. Chem. Soc., Perkin Trans. 2* 1982; 885–888.
8. Kukol A, Strehle F, Thielking G, Grützmacher HF. *Org. Mass Spectrom.* 1993; **28**: 1107–1110.
9. Lumbroso H, Liegeois C, Goethals G, Uzan R. *Z. Phys. Chem.* (*Wiesbaden*) 1983; **138**: 167–183.
10. (a) Decouzon M, Ertl P, Exner O, Gal J-F, Maria P-C. *J. Am. Chem. Soc.* 1993; **115**: 12071–12078; (b) Decouzon M, Gal J-F, Maria P-C, Böhm S, Jiménez P, Roux MV, Exner O. *New J. Chem.* 1997; **21**: 561–573; (c) Fiedler P, Exner O. *J. Phys. Org. Chem.* 1998; **11**: 141–148; (d) Böhm S, Exner O. *Chem. Eur. J.* 2000; **6**: 3391–3398.
11. (a) Hnyk D, Borisenko KB, Samdal S, Exner O. *Eur. J. Org. Chem.* 2000; 2063–2069; (b) Tinant B, Declercq J-P, Van Meerssche M, Exner O. *Collect. Czech. Chem. Commun.* 1988; **53**: 301–307.
12. Chimici S, Dell'Erba C, Gruttadauria M, Noto R, Novi M, Petrillo G, Sancassan F, Spinelli D. *J. Chem. Soc., Perkin Trans. 2* 1995; 1021–1026.
13. Pytela O. *Collect. Czech. Chem. Commun.* 1997; **62**: 645–655.
14. Zalewski RI, Sarkice AY, Geltz Z. *J. Chem. Soc., Perkin Trans. 2* 1983; 1059–1067.
15. (a) Pytela O, Kulhánek J, Jirásková E, Nevěčná T. *Collect. Czech. Chem. Commun.* 2001; **66**: 1638–1658; (b) Jirásková E, Kulhánek J, Nevěčná T, Pytela O. *Collect. Czech. Chem. Commun.* 1999; **64**: 1253–1261.
16. (a) Haword RD, Jones B, Way YM. *J. Chem. Soc.* 1943; 10–13; (b) Mukherjee-Müller G, Gilgen P, Zsindely J, Schmid H. *Helv. Chim. Acta* 1977; **60**: 1758–1780; (c) Ulrich R, Ruhdorfer J, Knorr R. *Synthesis* 1993; **10**: 985–992.
17. (a) Fieser LF, Newman MS. *J. Am. Chem. Soc.* 1936; **58**: 2376–2382; (b) Friedman L, Honour RJ. *J. Am. Chem. Soc.* 1969; **91**: 6344–6349; (c) Hufferd RW, Noyes WA. *J. Am. Chem. Soc.* 1921; **43**: 925–935.
18. Baddeley G. *J. Chem. Soc.* 1944; 232–236.
19. Exner O, Nauš P. *J. Phys. Org. Chem.* 2000; **13**: 693–698.
20. Exner O. *Correlation Analysis of Chemical Data.* Plenum Press: New York, 1988; chapter 2.4 and 2.5.
21. (a) Kulhánek J, Exner O. *J. Chem. Soc., Perkin Trans. 2* 1998; 1397–1401; (b) Exner O, Fiedler P, Buděšínský M, Kulhánek J. *J. Org. Chem.* 1999; **64**: 3513–3518.
22. (a) Roithová J, Exner O. *J. Phys. Org. Chem.* 2001; **14**: 752–758; (b) Exner O, Böhm S, Decouzon M, Gal J-F, Maria P-C. *J. Chem. Soc., Perkin Trans. 2* 2002; 168–172.
23. (a) Thompson HW, Steel G. *Trans. Faraday Soc.*; **52**: 1451–1457; (b) Charton M. *Can. J. Chem.* 1960; **38**: 2493–2499; (c) Pytela O, Prusek O. *Collect. Czech. Chem. Commun.* 1999; **64**: 1617–1628.
24. (a) Zaitsev BA. *Izv. Akad. Nauk SSSR, Ser. Khim.* 1974; 780–787; (b) Montaudo G, Caccamese S, Librando V, Maravigna P. *Gazz. Chim. Ital.* 1975; **105**: 85–90.
25. Krueger PJ. *Can. J. Chem.* 1973; **51**: 1363–1367.
26. (a) Baliah V, Aparajithan K. *Tetrahedron* 1963; **19**: 2177–2183; (b) Benassi R, Iarossi D, Folli U, Schenetti L, Taddei F. *J. Chem. Soc., Perkin Trans. 2* 1981; 228–232.