JOURNAL OF PHYSICAL ORGANIC CHEMISTRY
J. Phys. Org. Chem. 2001; **14:** 677–683
DOI:10.1002/poc.416

Infrared intensities of benzene derivatives as a measure of the substituent resonance effect

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Received 25 January 2001; revised 25 May 2001; accepted 28 May 2001

epoc ABSTRACT: Infrared spectra of 39 benzene mono-derivatives were recorded in the region 1000–1800 cm^{-1} and the intensities of the bands ν_{16a} and ν_{16b} were determined by computer separation. The intensities correlated with the squared resonance substituent constants σ_R^o as found by Katritzky and co-workers, but band separation does not represent any essential improvement compared with the earlier simpler technique. With substituents including an NH_2 group, there is still an interference with the NH_2 scissoring deformation band: in these cases deuteration is more effective than band separation. Several new constants σ_R^o were determined spectroscopically for substituents of interest in pharmacology and these constants were also calculated by a quantum chemical model. The latter procedure seems to be most efficient and reasonably reliable for calculating new σ_R^o constants; the only problem may be with the conformation in the case of axially unsymmetrical substituents. Copyright © 2001 John Wiley & Sons, Ltd.
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KEYWORDS: benzene derivatives; infrared spectra; resonance; substituent effects

INTRODUCTION

Several attempts have been made[1] to compare quantitatively the resonance of various groups (substituents) with a constant reference system, most often with the benzene ring. They were based on reactivities,[2,3] physical properties,[3,4] quantum chemical calculations[5,6] or a statistical treatment of diverse data.[7,8] The results have been presented as relative values, conventionally scaled, called σ_R constants. It was argued[1] that all these scales are not exactly proportional since it was necessary to create several such scales called σ_R, σ_R^o, σ_R^+ or σ_R^-: the choice between them brings some arbitrariness into the whole procedure. In spite of this, these constants have been applied, mostly in combination with the inductive constants σ_I, with relative success and a number of reactivity data and various physical properties were predicted with reasonable accuracy.

According to Katritzky and co-workers,[4] the constants σ_R^o are determined from infrared intensities. This approach has several merits. First, it makes use of benzene mono-derivatives C_6H_5X in which the phenyl group itself acts as a probe whereas most other methods use bis-derivatives XC_6H_4Y in which the probe group Y may influence the results. The infrared method[4] is also experimentally simple and reasonably precise. The integrated absorption intensity A of the two bands denoted[9] ν_{16a} and ν_{16b} is related to the constant σ_R^o by the empirical relationship[4]

$$\sigma_R^o = 0.0079A^{1/2} - 0.027 \quad (1)$$

There is a disadvantage that the sign of the constant σ_R^o (distinguishing acceptor and donor substituents) remains undetermined and must be assigned in agreement with other evidence, sometimes tentatively.

We became interested in this method in the course of our systematic investigations[6,10] of the physico-chemical properties of the thioamide group and of several related groups are of interest as pharmacophores in tuberculostatics[11] and antimycotics.[12] We intended to determine some new values of σ_R^o by the spectroscopic method[4] and to reinvestigate this method using contemporary spectroscopic techniques. In particular there was a question of whether separation of the bands by a common computer program[13] gives better results than their integration together by the means available in the 1960s.[4] For some of these groups, the constants σ_R^o had already been determined by us[6] using a quantum chemical model,[5] essentially empirical in character; this procedure has another difficulty in that σ_R^o of certain groups depends significantly on their conformation. Hence we calculated σ_R^o for the new substituents also

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Contract/grant sponsor: Grant Agency of the Czech Republic; *Contract/grant number:* 203/99/0030.

Table 1. Selected infrared spectral data for monosubstituted benzenes[a,b]

Substituent	A[c]	$\lvert\sigma_{R\ (IR)}\rvert$[d]	Separation of ν_{16a} and ν_{16b} bands				ν_{13} band A
			$\tilde{\nu}_1$	A_1	$\tilde{\nu}_2$	A_2	
H	0	0	—	0	—	0	922.1
CH_3	240.5	0.10	1604.5	263.0	1585.9	22.4	591.1
$CONH_2$	984.9	(0.22)	1604.6	1055.7	1578.5	1080.5	10.8
					1588.2	565.2	
$COND_2$	548.6	0.16	1603.8	93.7	1579.8	389.2	59.2
$CSNH_2$	8312.5	(0.69)	1600.4	8539.3	—	0	218.4
$CSND_2$	455.9	0.14	1598.9	456.0	1579.3	56.9	182.2
NH_2	5564.0	(0.56)	1618.3	4651.6	1602.1	1404.5	2576.7
ND_2	4071.9	0.48	1604.8	4102.3	—	0	2488.7
NO_2	513.4	0.15	1606.8	491.5	1590.9	79.0	351.2
OH	2809.1	0.39	1605.8	804.2	1597.1	2262.3	2046.7
F	2184.2	0.34	1596.2	2319.2	—	0	2761.4

[a] See Table SI (supplementary material) for more extensive data and additional substituents.
[b] $\tilde{\nu}$ in cm^{-1}, A in 1 mol^{-1} cm^{-2}.
[c] ν_{16a} and ν_{16b} bands integrated together according to Ref. 4.
[d] Absolute values calculated from not separated ν_{16a} and ν_{16b} bands according to Eqn. (1). Values spoiled by the presence of additional bands are in parentheses.

by the quantum chemical method and compared the two approaches.

The selection of substituents included some new groups of interest from the pharmacological point of view and, also, the simplest standard substituents for the sake of comparison. All the substituents are listed in Table SI (supplementary material), those of particular interest being given also in Table 1. They include also substituents, important for our purpose, containing an NH_2 group; in these the scissoring deformation band δ_{NH_2} interferes with the bands being measured. We tried to overcome this difficulty either by measuring the spectra of deuterated derivatives (as done previously for the NH_2 group[4]) or by separating the bands by a computer program.

EXPERIMENTAL

Infrared absorption spectra were recorded on a Nicolet Impact 400 FTIR spectrometer (512 scans, resolution 2 cm^{-1}, DTGS detector) in KBr and NaCl cells (0.0108, 0.0282, 0.0613 cm) in tetrachloromethane, benzene, chloroform or deuterated chloroform. The cell pathlength was calibrated by the interference method. Concentra-

Table 2. Statistics of correlations of infrared data for monosubstituted benzenes

No.	Response function	Explanatory variable	Slope b[a]	R[a]	s[a]	N[a]
1	A (Ref. 4)	A (this work)	0.998 (15)	0.9971	138	27
2	σ_R^o (IR, Ref. 4)	σ_R^o (IR, this work)	0.995 (17)	0.9966	0.023	27
3	σ_R^o (IR, this work)	σ_R (Ref. 7a)	0.70 (5)	0.9411	0.095	27
4	σ_R^o (IR, Ref. 4)	σ_R (Ref. 7a)	0.70 (5)	0.9370	0.099	27
5	σ_R^o (IR, this work)	σ_R (Ref. 3)	1.00 (6)	0.9537	0.085	27
6	σ_R^o (IR, Ref. 4)	σ_R (Ref. 3)	0.99 (7)	0.9490	0.090	27
7	σ_R^o (IR, this work)	σ_R^o (calc., Ref. 6)	1.005 (43)	0.9845	0.052	19
8	σ_R^o (IR, Ref. 4)	σ_R^o (calc., Ref. 6)	1.002 (50)	0.9809	0.059	19
9	σ_R^o (IR, this work)	$\sigma_R^{\pm}$ (Ref. 3)	0.321(21)	0.9487	0.089	27
10	σ_R^o (IR, this work)	$\sigma_R^{\pm}$ (Ref. 3)	0.348 (21)	0.9622	0.078	27
		σ_1 (Ref. 7a)	−0.29 (10)			
11	$A^{1/2}$ of ν_{16a}	σ_R (Ref. 7a)	84 (8)	0.9398	14.53 (0.173)[b]	27
12	$A^{1/2}$ of ν_{16a}	σ_R (Ref. 3)	120 (8)	0.9514	10.56 (0.088)[b]	27
13	$A^{1/2}$ of ν_{16a}[c]	σ_R (Ref. 3)	126 (6)	0.9757	7.83 (0.062)[b]	26
14	A_{v13} (Ref. 4)	A_{v13} (this work)	1.23 (5)	0.9869	244	19[c]
15	$A_{v13}^{1/2}$	σ_R (Ref. 7a)	−49.9 (35)	0.9853	3.06	8[d]

[a] Slope b with its standard deviation in parentheses, correlation coefficient R, standard deviation from the regression s and number of data N.
[b] Standard deviation recalculated on the σ-scale.
[c] NMe_2, COOMe and COCl substituents eliminated.
[d] Only substituents with C_{2v} symmetry.

Table 3. Constants σ_R^o calculated from the quantum chemical model and from IR intensities

Substituent	Conformation[a]	σ_R^o	Energy CH_2=CHX (a.u.)	σ_R^o from IR
CH_2Cl	*sp*	−0.08	−575.3110319	−0.04
	ap	−0.08	−575.3085048	
COOH	*sp*	0.20	−265.2618032	0.26
	ap	0.17	−265.2610632	
$COOC_2H_5$	*sp*	0.17	−343.2120961	0.12
	ap	0.15	−343.2112000	
$CONH_2$	*sp*	0.12	−245.4636424	0.1
	ap[b]	0.07	−245.4594209	
$CONHCH_3$	*sp Z*	0.11	−284.4336309	
	sp E	0.14	−284.4283676	
	ap Z	0.06	−284.4291380	
	ap E	0.09	−284.4192931	
$CSNH_2$	*sp*	0.22	−568.1845415	0.14
	ap[b]	0.12	−567.7586719	
COCl	*ap*	0.25	−648.8945989	0.21
	sp	0.23	−648.8943097	
NHC_2H_5	*sp*	−0.61	−210.8241150	−0.53
	ap	−0.57	−210.8217631	
NHC_4H_9	*sp*	−0.61	−288.7795282	−0.55
	ap	−0.58	−288.7771762	
NHC_6H_5	*ap*	−0.48	−362.0930904	−0.50
	sp	−0.53	−362.0864766	
NCS	*ap*[c]	−0.12	−566.5756573	−0.33
NHC(=NH)NH_2	*ap sp E*	−0.36	−280.5855719	−0.25
	ap sp Z	−0.40	−280.5822546	
N=C$(NH_2)_2$	*ap*	−0.36	−280.5840332	
	sp	−0.45	−280.5797502	
N=NC_6H_5	*ap E*	0.03	−415.8142061	0.07
	sp E	0.01	−415.8081834	
SSC_6H_5	*sp ap*	−0.30	−1101.238791	−0.20
	ap ap	−0.26	−1101.238419	
	ac(100°) *ac*(101°)	−0.04	−1101.254361	

[a] Conformation about the C—X bond is given first, followed by conformations within the X group; conformations about the C—N partial double bonds in amides and configurations on the C=N and N=N double bonds are denoted by *E* and *Z*. The lowest energy conformer is given first.
[b] In Ref. 6 the σ_R^o values were calculated for this conformation.
[c] Conformation is practically irrelevant since the C—N—C angle is 178.7°.

tions of the solutions were between 0.05 and 1.46 mol l^{-1} and were chosen in each case to give peak absorptions between 0.3 and 0.8. The spectra were measured against air as background. The data were processed using standard software.[13] The spectra of solvents were subtracted manually using the program OMNIC 2.0,[13a] and the same program was used for integration of bands. Separation of bands was achieved by the program Peaksolve,[13b] and the method with mixed Gaussian–Lorentzian bands was chosen. All spectral data are listed in Table SI (supplementary material), the most important data for selected substituents are also given in Table 1. Correlation of spectral data with each other and with the σ constants are given in Table 2.

CALCULATIONS

Quantum chemical calculations were performed using the program Hyperchem.[14] For calculating σ_R^o constants, the previously published method[6] was used, the basis set being obtained from the standard database.[15] The original theoretical model[6] (at a relatively low level) was maintained in order to obtain results comparable with the previous ones: the geometry of a molecule XCH=CH_2 was optimized at the RHF/4–31G level and then the single-point calculation was performed. When more conformations (usually planar) with comparable energies are possible, calculations were performed for all of them. The calculated constants σ_R^o were obtained from the equation[5]

$$\sigma_R = 4.167 \sum \Delta q_\pi - 0.06083 \qquad (2)$$

where $\sum \Delta q_\pi$ is the total π-electron population on the two carbon atoms in the molecule XCH=CH_2 minus the

corresponding total π-electron population in the parent ethylene molecule. The results are listed in Table 3.

RESULTS AND DISCUSSION

Comparison of σ_R from different sources

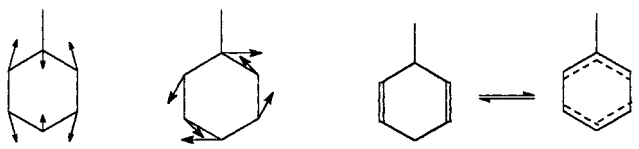
Twenty-seven of our compounds were investigated also by Katritzky's group in the late 1960s.[4] In this section, we shall restrict ourselves to this subset and compare our results with the previous ones. We integrated the bands ν_{16a} and ν_{16b} together as always done in previous work.[4] Our values of *A* (Table SI, supplementary material, column 4) were compared with the previous values[4] by linear regression. Table 2, line 1 reveals good agreement according to the correlation coefficient. The standard deviation from the regression (*s*) may seem relatively large but it is controlled by the compounds with the largest absorption intensities: for these values *s* represents only 3%. More significant may be comparison carried out in the scale of σ_R calculated by Eqn. (1). Table 2, line 2 reveals a standard deviation of 0.02 σ units, comparable to the standard precision of σ constants.[16] We conclude that previous studies[4] were carried out carefully with the means available at that time and our results agree reasonably when the same method is used; the more modern integration technique is not important.

With the small difference between our and previous results, we were unable to decide which of them should be better by comparison with standard σ_R scales. The problem is just in choosing this standard scale based on reliable data, other than IR intensities. The scale most carefully derived from reactivity data[7a] yielded surprisingly poor results: Table 2, lines 3 and 4. Somewhat better is the correlation with σ_R obtained from ^{19}F NMR shifts,[3] Table 2, lines 5 and 6. Relatively closest is the correlation with σ_R^o calculated on a quantum chemical model[6] (Table 2, lines 7 and 8), but the number of available items is smaller. Note that in all three cases correlation with our data was closer than with the literature data,[4] but the difference was not significant and cannot be used as proof that our data are 'better.' We conclude that all the scales of resonance effects differ little but significantly: a unified scale is not possible.[17] The difference between spectroscopic values (IR[4] or NMR[3]) on the one hand, and values derived from reactivities[2,3,7] on the other, seems to be more significant. An explanation could be that derivation from reactivities always used model reactions with charged molecules or with strongly polar transition states. Note that equilibria between uncharged molecules afford a different measure of resonance.[17]

There is still one fundamental problem, that the standard σ_R^o scale has been questioned. Conjugation of some typical acceptor groups such as NO_2 and CN was found to be negligible when a conjugated donor group is not present, hence their σ_R^o should practically equal zero.[18] In particular for the NO_2 group, there is now evidence from various sources that the resonance is negligible.[18c] The small σ_R^o values of acceptors depend in the usual scales on the way in which the inductive effect has been subtracted.[2,3,7] The IR intensities thus served as the main piece of evidence[4] that the σ_R^o values of these substituents are not zero since the corresponding *A* values for these substituents (Table SI, supplementary material) are unambiguously not zero. This contradistinction could be solved in two ways. First, *A* could depend not only on resonance but also slightly on the inductive effect of the substituents.[1] This has not been confirmed here. Correlations with σ_R and σ_I are not better than with σ_R alone: an example is shown in Table 2, line 10. The second possibility could be that resonance in the IR is enhanced, similarly as expressed by the enhanced constants σ_R^+ and σ_R^-; for instance, the values of σ_R^- for NO_2 or CN are fairly large. We attempted also to correlate of our intensities with standard scales of σ_R^+ for donors and σ_R^- for acceptors; the combined scale is denoted here $\sigma_R^\pm$. It revealed an insignificantly worse fit than with common σ_R (Table 2, line 9 as compared with line 5). We conclude that our absorption intensities represent a measure of resonance but it cannot be decided with certainty to which model in reactivity studies (σ_R^o or $\sigma_R^\pm$) this resonance would correspond better: probably resonance in the IR excited state is fairly strong.

Separation of ν_{16} bands

Normal vibrations connected with the ν_{16a} and ν_{16b} bands in benzene mono-derivatives are represented[9] by **1** and **2**, respectively. In terms of chemical structure, **1** was approximately pictured[4] as an equilibrium between **3** and **4**: the C2—C3 and C5—C6 bonds are simultaneously stretched or shortened. Resonance with a substituent would stabilize structure **3**.



1 **2** **3** **4**

In our opinion, a similar interpretation is not possible for the ν_{16b} band. In **2** two equivalent pairs of bonds (C1—C2, C4—C5 and C3—C4, C6—C1) are alternately stretched and shortened: the two deformed structures are equivalent with respect to the position of substituent. It could be supposed that the ν_{16a} vibration is determining for the correlation with the substituent resonance, and the lower and less intense ν_{16b} vibration might represent only noise. Then the intensity of the separated ν_{16a} band

should reveal a better correlation with σ_R^o than when the ν_{16a} and ν_{16b} bands were integrated together. On the basis of the following experiments, we still believe that this principle is correct but difficult to prove.

When we made a computer separation into two anticipated bands, in no case did a third band appear necessary; in several cases only one band was sufficient. We assumed that the ν_{16a} band is that with higher frequency and correlated its intensity as $A_1^{1/2}$ with the σ_R scales. The correlations are not better than for the total intensity A: compare line 11 with 3 and line 12 with 5 in Table 2. However, a detailed analysis revealed significant outliers responsible for the poor statistics. While in most cases the higher frequency band is stronger (sometimes even the only one present), with OH and NHC_6H_5 substituents the intensities are reversed. This may cast some doubts on the correct assignment. When we tentatively reverse the assignment of ν_{16a} to lower frequency, the overall correlation is significantly improved. When still the $NHCOCH_3$ substituent was excluded, the correlation in Table 2, line 13, was better than for unresolved bands, line 5. Its fit could probably still be improved by reinvestigating in detail further substituents. In principle, a fundamental analysis would be necessary when assigning all infrared bands. Obviously, such a procedure would be impractical and in no case can it be recommended as a routine method for determining σ_R^o of new substituents.

Substituents containing an NH_2 group

NH_2, $CONH_2$, $CSNH_2$, $NHNH_2$ and $NHC(=NH)NH_2$ substituents, very important for our purposes, were excluded from the above considerations. The reason is interference with the NH_2 scissoring deformation ($1619\,cm^{-1}$ in aniline[9]) which falls in the integrated region and makes the apparent values of σ_R^o too large. This is seen in Table 1 in the apparent value of σ_R^o for the NH_2 substituent, or still more for $CSNH_2$. There are two possible ways of solving this problem. Isotopic substitution by deuterium shifts the deformation band to $1192\,cm^{-1}$, far from the ν_{16a} and ν_{16b} bands. This procedure was used previously for aniline,[4] and we applied it to three further compounds (Table 1). The second possibility is band separation. In the cases when both ν_{16a} and ν_{16b} are observable, separation into three bands would be necessary. The results of the two procedures were not completely consistent and differed also for individual compounds (see Table 1).

In the case of the NH_2 substituent, the band separation yields two bands (Table 1). By comparison with the deuterated compound, we assign the band at $1602\,cm^{-1}$ as δ_{NH_2} and that at $1618\,cm^{-1}$ as ν_{16a}; the ν_{16b} band is not observable. In the literature[9b] the wavenumber $1618\,cm^{-1}$ is assigned to δ_{NH_2} (without separation). From the intensity of the separated ν_{16a} band, we calculated $\sigma_R^o = 0.51$, in good agreement with the result from ND_2, $\sigma_R^o = 0.48$; this is also a confirmation of the assignment.

The $CSNH_2$ substituent shows only one band; separation from δ_{NH_2} (found[19] at $1604\,cm^{-1}$) is evidently not feasible. In any case, the calculated $\sigma_R^o = 0.69$ is too large and wrong. Surprisingly, two bands are observed after deuteration but one is very weak. With or without separating them, one obtains $\sigma_R^o = 0.14$, and this value seems to be reasonable.

The $CONH_2$ substituent shows three separable bands of which one (at $1588\,cm^{-1}$) disappears after deuteration (Table 1). In contradistinction to the foregoing thioamide, this band cannot be assigned[9b] solely to the δ_{NH_2} vibration and is better denoted conventionally[20] as amide II. The value of $\sigma_R^o = 0.22$ is evidently too large and not altered by band separation; more reliable is the value $\sigma_R = 0.16$ from the deuterated compound.

In the case of the $NHC(=NH)NH_2$ substituent, separation yields two bands but one is weak and does not affect the value $\sigma_R^o = 0.25$, which is too small compared with 0.46 from the deuterated compound. The latter seems better with respect to the calculated values (see the section Calculated σ_R constants), but a reliable value cannot be given.

The ν_{13} band

The normal vibrations of the ν_{13a} and ν_{13b} bands do not result from significant stretching or shortening of some bonds. Hence they do not suggest any connection with resonance. Nevertheless, the intensity estimated only from the half-width[4b] revealed an empirical dependence on σ_R^o but only for axially symmetrical substituents. The other data points were irregularly scattered.[4b] We obtained more reliable intensities (Table SI, supplementary material, last column) using the separation program. However, resolution into ν_{13a} and ν_{13b} was not possible only the neighboring bands were eliminated. Our intensities of the $\nu_{13a} + \nu_{13b}$ bands agreed fairly well with the previous values[4a] except for three substituents. When these were eliminated, the correlation was excellent (Table 2, line 14). Concerning F and Br substituents, there was probably a confusion in ref. 4a since in ref. 4b the intensities are given correctly. The plot of quadratic roots of intensities vs standard[7a] σ_R (Fig. 1) is more informative than previously.[4b] A very good linear dependence for symmetrical substituents is obtained (see the statistics in Table 2, line 15). All the unsymmetrical substituents are shifted downwards and could also be approximately connected by a line [note that ND_2 must be included among unsymmetrical substituents, but not $N(CH_3)_2$]. We confirm that the ν_{13a} band can be used in some cases for determining the sign of σ_R^o, not available from Eqn. (1), provided that the absolute value is not very small.

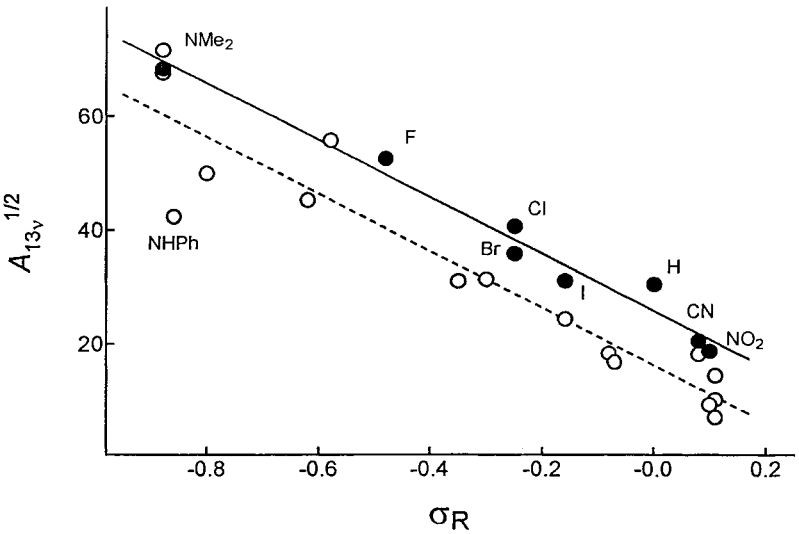
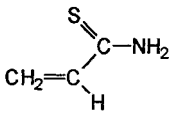


Figure 1. Intensities of the ν_{13} band of benzene mono-derivatives plotted as square roots vs the resonance constants σ_R: ●, substituents with C_{2v} symmetry; ○, other substituents

Calculated σ_R^o constants

Calculation from the quantum chemical model[5] is an apparently unambiguous way to obtain the constants σ_R. It uses an ethene derivative $CH_2{=}CHX$ and records the summarized π-electron density on both carbon atoms: its dependence on σ_R^o was confirmed empirically.[5,6] We calculated the σ_R^o values of the investigated new substituents and also some known values for comparison, keeping exactly the original model[5] (Table 3). A problem was met which was not given sufficient attention in previous work,[5,6] viz. the conformation. While the original authors[5] were satisfied with standard molecular geometry, we made a complete geometry optimization at the RHF level.[6] In some molecules, the lowest energy conformation must be chosen, e.g. about the C—O bond in COOR or about the C—N bond in $CONHCH_3$. These conformations are mostly known and can be checked on an experimental basis, most conveniently on C_6H_5X compounds. Concerning further substituents in Table 3, note that the conformation of $C_6H_5CH_2Cl$ is questionable[21] but the chlorine atom lies with certainty outside the ring plane. Its position has, however, no influence on σ_R^o. In $C_6H_5CONHCH_3$, the *Z*-conformation about the partially double C—N bond is certain.[22] The non-planar conformation of $C_6H_5SSC_6H_5$ is well known from crystal data and supported by other evidence;[23] the dihedral angle CSSC was given[23] as 96°, in fair agreement with our value. Most problematic is the $NHC(=NH)NH_2$ substituent involving even the possibility of tautomeric structures. Our calculations at a small basis (conditioned by the conventional model[5]) prefer the structure as given here, in agreement with more sophisticated calculations,[24] while ^{15}N NMR spectra[25] were in favor of the structure $N{=}C(NH_2)_2$.



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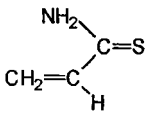

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However, there is a more fundamental problem. Planar, axially unsymmetrical substituents can be bound to the ethenyl group in one of two conformations such as **5** and **6**. It turned out that the calculated σ_R can be different in some cases (see Table 3), in particular for the $CONH_2$ and $CSNH_2$ substituents. Note that the problem exists only for the model ethene derivatives and not for benzene derivatives. It is not clear which value of σ_R^o should be taken as the 'right' one, that based on the lowest energy conformation or an average value of the two planar conformers. Similar problems, possibly still more complex, may appear with non-planar substituents, e.g. CH_2Cl or NHX, but in these cases the differences in σ_R^o values seem to be small. In our opinion, the only solution would be calculations on benzene derivatives instead of ethene derivatives. This possibility was already tested when the original model was designed[5] but ethene derivatives were preferred.

CONCLUSIONS

A universal scale of resonance effects can obviously not be reached. This is prevented by different solvents or states, and even by differences in the structure, e.g.

benzene and ethene derivatives. Various approaches may thus provide scales correlated with reasonable correlation coefficients but a closer examination may reveal differences, even within the narrow field of benzene derivatives. The infrared spectral method requires the simplest compounds and an undemanding technique, but agreement with other methods is limited and cannot be improved by using more refined spectroscopic techniques. Each measurement would require detailed spectral analysis with reliable assignment of several bands; even so, in some cases resolution cannot be achieved. Calculation with the aid of the quantum chemical model is in our opinion more promising. It is quick and the results are reproducible and exactly defined; problems with conformation can be removed. When a universal scale cannot be achieved, the quantum chemical scale can serve as a reference from which the deviations can be measured.

Acknowledgements

The work was supported by the Grant Agency of the Czech Republic, project 203/99/0030.

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