Proc. Estonian Acad. Sci. Chem., 40, N 2, 122—128
https://doi.org/10.3176/chem.1991.2.07

УДК 539.193

Toomas TAMM and Mati KARELSON**

ELECTRONIC AND SOLVENT EFFECTS IN DISUBSTITUTED BENZENES: A QUANTUM-CHEMICAL INVESTIGATION

A quantum-chemical study of disubstituted benzenes, both neutral and charged, was carried out using AM1 SCF and SCRF semiempirical models. The intramolecular interaction energies between the substituents were calculated according to three different formulae. The applicability of the corresponding definitions of resonance and inductive interactions is discussed.

1. Introduction

Inclusion of the Self-Consistent Reaction Field (SCRF) model of dielectric medium into semiempirical quantum-chemical calculations to mimic solvent effects has proven successful in casting more light on non-specific solvatation [1–4]. In order to find out the applicability of the model for the description of the solvent field on the intramolecular electronic properties of larger molecules, and to check the conclusions made earlier (cf. [2]), a SCRF study of mono- and disubstituted benzenes was carried out.

2. Calculations

Semiempirical LCAO—MO calculations were carried out using the MOPAC quantum-chemical program package [5] (version 3.01) modified in order to enable the inclusion of the effects caused by dielectric medium [6]. The seven basic structures whose properties were calculated were the following: benzene, benzoic acid, benzoate anion, phenol, phenolate anion, aniline, anilinium cation. Additionally the respective meta- and para-substituted derivatives of these compounds were also investigated, the substituents being $—NO_2$ and —CN. The latter compounds will be termed as «heterosubstituted» in the following discussion.

For reference, the properties of the meta- and para-isomers of the «homosubstituted» compounds, i. e. those having two identical substituents of any in the aforementioned list attached to the benzene ring, were also calculated. All geometries of molecules were fully optimized, using the one-point finite difference for finding the gradients of energy in respect of geometrical variables. Introduction of this variation of the standard optimization algorithm used in the original version of MOPAC is necessary for correct optimization, whereas the one presented in [6] results in unreasonably early termination of geometry optimization and gives too high values for heats of formation of several compounds in the set. The problems of gradient calculation with SCRF model will be discussed elsewhere.

The cavity radii r_c, necessary for SCRF calculations [1], were calculated additively from the respective molecular refraction increments corresponding to individual bonds [7], and the cube root of the respective refraction (in cm^3/mole) was used directly as the radius of

* Tartu Ülikooli füüsika-keemia teaduskonna keemia osakond (Department of Chemistry, Tartu University). 202400 Tartu, Jakobi 2, Estonia.

cavity. All calculations were carried out using both the normal SCF procedure (corresponding to the gas phase), and the SCRF model, the dielectric permittivity of the medium being $\varepsilon=78.5$ (equal to the corresponding value of ε of water).

The cavity radii, AM1 calculated heats of formation, and dipole moments of the compounds are listed in Tables 1 and 2.

As already noted in connection with earlier SCRF calculations [1,2], the dipole moments of the compounds increase in the dielectric medium as compared to those of the gas phase, and the heats of formation drop to some extent. Only if the compound does not have any dipole moment and small changes in geometry do not lead to its emergence from zero, there is no change in energy in different media (as in the case of benzene).

3. Definitions of interaction energy

In classical models, the intramolecular interactions between substituents attached to a benzene ring are divided into inductive and resonance effects [8,9]. Polar resonance is considered to be energetically insignificant, if the corresponding substituents are in the meta-position to each other. Both the induction and resonance effects are normally considered to be independent of solvent influence.

The interaction energy corresponding to a particular intramolecular electronic effect can be defined as the energy of a metathetic reaction leading to the formation of the compound under discussion from some compounds in which this effect can be considered negligible, provided also that no other geometrical or electronic alternations of the structure are present. In our previous work, involving disubstituted ethylenes [2], we used the following reaction:

$$1/2\, X{-}C{=}C{-}X + 1/2\, Y{-}C{=}C{-}Y = X{-}C{=}C{-}Y, \qquad (1)$$

whose energetic effect can be calculated according to the formula:

$$E_{\text{int}}=\Delta H_f(X{-}C{=}C{-}Y)-1/2[\Delta H_f(X{-}C{=}C{-}X)+ +\Delta H_f(Y{-}C{=}C{-}Y)]. \qquad (2)$$

In these formulae X and Y represent substituents of different resonance types ($+R$ and $-R$), E_{int} is the energy of intramolecular interaction, and ΔH_f are the calculated heats of formation of the respective compounds. This formula yields reasonable results when applied to ethylenes [2], and was initially used also by us for the definition of interaction energy in disubstituted benzenes.

For reasons discussed in more detail in the next section, we have also used an alternative formula, corresponding to the reaction

$$X{-}C{=}CH + Y{-}C{=}CH = X{-}C{=}C{-}Y + HC{=}CH \qquad (3)$$

with the energetic effect being

$$E_{\text{ent}}=\Delta H_f(X{-}C{=}C{-}Y)-[\Delta H_f(X{-}C{=}CH)+ + \Delta H_f(Y{-}C{=}CH)-\Delta H_f(HC{=}CH)]. \qquad (4)$$

It is important to note that, according to this definition, if one of the substituents X or Y is charged, there is no compound with more than one charged substituent in the reaction.

Also, a slightly modified classical definition of resonance energy in substituted benzenes [10],

$$\Delta\Delta E_f=\Delta H_f(\text{para})-\Delta H_f(\text{meta}), \qquad (5)$$

was used for comparison.

Table 1

Cavity radii, AM1/SCRF-calculated heats of formation and dipole moments of heterosubstituted compounds

Compound	a_0, Å	Heat of formation, kcal/mole		Dipole moment Debye	
		ε=1	ε=78.5	ε=1	ε=78.5
Benzoic acid	3.190	—67.6	—66.3	2.040	2.951
m—CN	3.329	—33.4	—34.8	2.267	2.880
p—CN	3.129	—33.4	—34.3	1.753	2.342
m—NO_2	3.299	—60.1	—65.0	4.113	5.399
p—NO_2	3.299	—60.3	—64.4	3.543	5.201
Benzoate (—)	3.130	—86.7	—167.5	15.035	18.521
m—CN	3.274	—59.9	—134.1	13.170	15.971
p—CN	3.274	—60.7	—134.5	10.615	14.902
m—NO_2	3.243	—91.5	—170.5	12.492	16.185
p—NO_2	3.243	—93.3	—169.4	8.397	12.726
Phenol	3.026	—16.7	—17.3	1.236	1.535
m—CN	3.180	9.8	8.2	2.096	2.827
p—CN	3.180	8.9	4.9	3.286	4.744
m—NO_2	3.147	—17.7	—23.4	3.963	5.605
p—NO_2	3.147	—19.4	—30.4	5.234	8.051
Phenolate (—)	2.964	—41.0	—102.3	5.864	7.297
m—CN	3.124	—19.6	—76.5	5.070	5.944
p—CN	3.124	—25.6	—79.5	0.129	1.097
m—NO_2	3.090	—54.3	—112.9	5.803	6.838
p—NO_2	3.090	—64.9	—118.8	2.918	1.773
Aniline	3.093	20.5	19.9	1.537	1.697
m—CN	3.241	52.2	46.8	4.053	5.486
p—CN	3.241	50.9	41.9	4.916	7.519
m—NO_2	3.299	24.4	14.1	5.839	7.839
p—NO_2	3.299	21.8	2.5	7.244	12.590
Anilinium (+)	3.153	176.5	109.5	9.773	11.460
m—CN	3.296	215.0	127.6	11.208	14.672
p—CN	3.296	215.0	113.7	12.126	16.684
m—NO_2	3.265	192.5	75.1	12.363	17.688
p—NO_2	3.265	193.2	50.1	13.951	20.350

Table 2

Cavity radii, AM1/SCRF-calculated heats of formation and dipole moments of homosubstituted benzenes (reference compounds)

Substituent(s)	a_0, Å	Heat of formation, kcal/mole		Dipole moment Debye	
		ε=1	ε=78.5	ε=1	ε=78.5
H	2.969	22.0	22.0	0.000	0.000
NO_2	3.095	25.5	15.3	5.216	7.235
CN	3.129	53.4	49.3	3.336	4.500
m—COOH, COOH	3.384	—155.3	—139.5	0.862	1.817
p—COOH, COOH	3.384	—155.5	—141.5	2.121	3.415
m—CN, CN	3.273	86.2	83.4	3.162	4.149
p—CN, CN	3.273	86.2	86.2	0.012	0.010
m—COO^-, COO^-	3.276	—140.2	—354.4	14.623	21.726
p—COO^-, COO^-	3.276	—145.0	—335.3	0.268	2.001
m—NH_2, NH_2	3.208	19.6	20.0	2.409	3.350
p—NH_2, NH_2	3.208	20.9	22.5	0.729	3.145
m—NH_3^+, NH_3^+	3.318	408.5	199.9	9.993	12.800
p—NH_3^+, NH_3^+	3.318	405.4	210.7	0.129	0.253
m—NO_2, NO_2	3.211	33.3	40.5	4.815	8.173
p—NO_2, NO_2	3.211	33.4	45.3	0.058	1.052
m—O^-, O^-	2.959	—7.8	—234.0	7.190	9.784
p—O^-, O^-	2.959	1.1	—219.4	0.139	0.312
m—OH, OH	3.080	—60.8	—62.5	3.029	3.451
p—OH, OH	3.080	—65.6	—66.6	2.276	2.879

Table 3

Energies of intramolecular interaction in disubstituted benzenes, calculated according to Eq. (2)

Compound	meta		para	
	$\varepsilon=1$	$\varepsilon=78.5$	$\varepsilon=1$	$\varepsilon=78.5$
CN-phenol	—2.91	0.81	—1.31	—4.74
NO_2-phenol	—3.92	—2.18	—3.27	—14.59
CN-phenolate	—58.78	1.04	—69.25	—12.29
NO_2-phenolate	—67.04	—4.94	—82.14	—25.22
CN-benzoic acid	1.13	0.45	1.31	—0.99
NO_2-benzoic acid	0.86	—0.45	0.81	—3.60
CN-benzoate	—32.87	—4.42	—31.27	—16.16
NO_2-benzoate	—38.08	—9.53	—37.47	—17.01
CN-aniline	—0.70	—4.20	—2.59	—13.36
NO_2-aniline	—2.06	—9.06	—5.32	—29.63
CN-anilinium	—32.35	—14.66	—30.74	—33.21
NO_2-anilinium	—28.40	—35.13	—26.19	—70.49

Table 4

Energies of intramolecular interaction in disubstituted benzenes, calculated according to Eq. (4)

Compound	meta		para	
	$\varepsilon=1$	$\varepsilon=78.5$	$\varepsilon=1$	$\varepsilon=78.5$
CN-phenol	—4.91	—1.84	—5.72	—5.40
NO_2-phenol	—4.47	0.84	—6.18	—6.97
CN-phenolate	—10.00	1.70	—16.03	0.12
NO_2-phenolate	—16.81	1.39	—27.42	—4.53
CN-benzoic acid	2.82	6.54	2.85	6.21
NO_2-benzoic acid	3.99	11.30	3.85	11.89
CN-benzoate	—4.54	30.59	—5.34	34.19
NO_2-benzoate	—8.30	31.14	—10.04	41.63
CN-aniline	0.26	—0.99	—1.01	—7.99
NO_2-aniline	0.36	—0.19	—2.23	—15.97
CN-anilinium	7.06	11.78	7.11	0.89
NO_2-anilinium	12.46	—3.02	13.17	—28.09

Table 5

Energies of polar resonance in disubstituted benzenes, calculated according to Eq. (5)

Compound	$\Delta\Delta E_f$		Compound	$\Delta\Delta E_f$	
	$\varepsilon=1$	$\varepsilon=78.5$		$\varepsilon=1$	$\varepsilon=78.5$
CN-phenol	—0.81	—3.56	CN-benzoate	—0.80	3.60
NO_2-phenol	—1.71	—7.80	NO_2-benzoate	—1.74	10.49
CN-phenolate	—6.03	—1.58	CN-aniline	—1.27	—7.00
NO_2-phenolate	—10.61	—5.92	NO_2-aniline	—2.59	—15.78
CN-benzoic acid	0.03	—0.33	CN-anilinium	0.05	—10.89
NO_2-benzoic acid	—0.15	0.59	NO_2-anilinium	0.70	—25.07

4. Results and discussion

The numerical values of the energies of intramolecular interaction are given in Tables 3—5.

It can be noted that the calculated energetic effect depends on the calculation scheme used, and the results are in most cases even not proportional to each other. The following details should be outlined:

Interaction energies calculated according to Eq. (2) for charged compounds tend to become more positive when the molecule is placed into a dielectric medium. Also, the absolute values of the interaction energies for ions seem to be unrealistically large.

This contradicts to the earlier observations on the related systems [1,2]. However, in the SCRF model the interaction energy between the species with charged substituents and the medium includes the following term (for details see e. g. [1]):

$$E_{tot}=E_{tot}+(1-\varepsilon)Q^2/(\varepsilon a_0^3), \quad (6)$$

where E_{tot} is the total energy of the system, ε is the dielectric permittivity of the medium, r_c is the cavity radius, and Q is the ionic charge on the system.

For reactions with unequal total ionic charge on the compounds at the left side of Eq. (1), the respective difference in ionic electrostatic solvation energies will be included into interaction energy (2). Therefore we considered the definition of interaction energy according to Eq. (2) not appropriate if systems with ionic charges are involved.

As a substitution, we propose (similar to [11]) a definition based on reaction (3) and the corresponding interaction energy (Eq. (4)). As it can be seen from Table 4, the large absolute values of energy differences for ionic compounds have now been reduced, but the effects of destabilization (in terms of intramolecular interactions) when a molecule is placed into a dielectric medium, remain substantial in many cases.

Aniline and anilinium ions behave almost as expected according to the solvent-assisted resonance stabilization theory [1,2]: the respective interaction energies become more stabilizing in "solution" whenever resonance effects in the molecule permit a redistribution of charges. However, phenols are quite insensitive towards the changes in dielectric medium and phenolate anions experience a destabilization.

Nitro- and cyano-substituted benzoic acids are a good classical example, where only inductive effect is present, with no resonance possible between the substituents. It should be noted that in accordance with this model the calculated interaction energies for meta- and para-substituted molecules are very close to each other in different media. Benzoate anions, however, are destabilized considerably when the dielectric permittivity of the medium increases.

Using definition (5) it is possible to calculate «pure» resonance energy, if the changes in inductive interactions between meta- and para-substituted compounds are considered negligible. In most cases, the resonance energy increases with the growth of ε, whereas the benzoate disubstituted species show a notable decrease of the corresponding value. This observation is in accordance with the classical resonance theory as no polar conjugation will be expected between carboxylate, —CN or —NO_2 groups whether in meta- or in para-position. It can be outlined that the nitro-group has approximately twice the influence of the cyano-group, which agrees with the relative values of the corresponding σ_R^- substituent constants (0.29 for —CN and 0.45 for —NO_2 [12]) in Linear Free-Energy Relationships (LFER) theory.

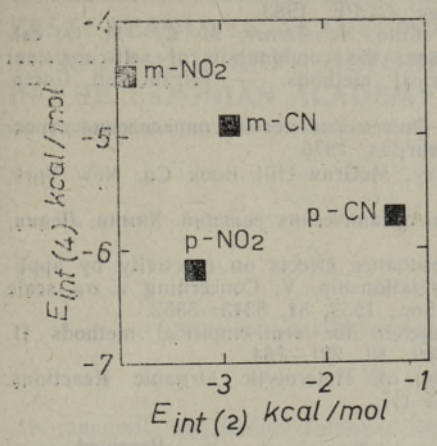

Fig. 1. Poor correlation between interaction energies calculated according to Formulae (2) and (4) for substituted phenols in gas phase.

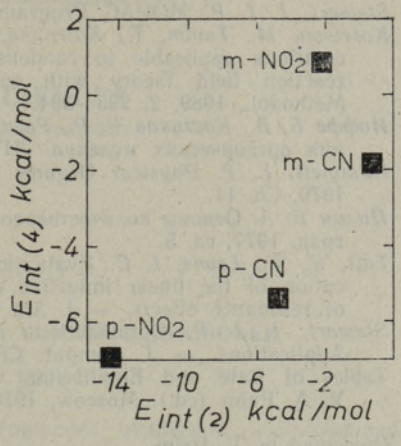

Fig. 2. Poor correlation between interaction energies calculated according to Formulae (2) and (4) for substituted phenols in dielectric medium.

It is important to note that there is a poor correlation between the interaction energies defined by different methods (see e. g. Figs. 1 and 2 for substituted phenols). Therefore, no universal substituent constants referring to resonance effect in different media or different chemical processes can be defined.

5. Conclusions

It has been shown that the reaction field effects by polarizable solvent have significant influence on the intramolecular inductive and resonance effects in substituted benzenes. However, the numerical values of this effect are dependent on the definition of the interaction energy by the corresponding intramolecular interaction mechanism. Therefore no simple LFER-type formulae for the numerical prediction of polar solvent influence on the various energetic and electronic properties of molecules in solutions are applicable. For the detailed theoretical analysis of the solvent effects on an intramolecular electron redistribution and energy of solute a full quantum-mechanical description of both the specific and non-specific solvation effects is needed.

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Presented by V. Palm

Received
Jan. 29, 1991

Toomas TAMM, Mati KARELSON

ELEKTROONSED JA SOLVENDIEFEKTID KAHE ASENDUSRÜHMAGA BENSEENIDES: KVANTKEEMILINE UURIMUS

On tehtud kahe elektroneutraalse või laetud asendusrühmaga benseenide kvantkeemiline arvutus, kasutades poolempiirilisi AM1 SCF- ja SCRF-meetodeid. Asendusrühmadevahelise sisemolekulaarse vastastikmõju energia on arvutatud kolme erineva valemi järgi. On analüüsitud nende valemite rakendatavust induktsioon- ja resonantsinteraktsiooni kvantitatiivseks hindamiseks eri keskkondades.

Тоомас ТАММ, Мати КАРЕЛСОН

ВЛИЯНИЕ ДИЭЛЕКТРИЧЕСКОЙ СРЕДЫ НА ЭЛЕКТРОННЫЕ ЭФФЕКТЫ В ДВУХЗАМЕЩЕННЫХ БЕНЗОЛАХ: КВАНТОВОХИМИЧЕСКОЕ ИССЛЕДОВАНИЕ

Проведено квантовохимическое исследование электронейтральных и заряженных двухзамещенных бензолов с использованием полуэмпирических методов AM1 ССП и ССРП. Энергии внутримолекулярного взаимодействия между заместителями вычислены по трем различным формулам. Обсуждена возможность использования этих формул для количественного определения резонансного и индукционного взаимодействия в разных средах.