ESTIMATION OF RESONANCE ENERGY FROM FORCED NONPLANAR CONFORMATIONS OF CONJUGATED MOLECULES

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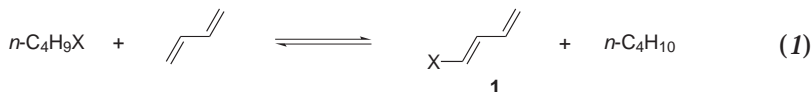166 10 Prague 6, Czech Republic; e-mail: exner@uochb.cas.cz

Energies of 39 derivatives of buta-1,3-diene in the twisted conformation were calculated within the framework of the density functional theory at the B3LYP/6-311+G(d,p) level. By comparing with the same molecules in their natural minimum-energy conformations, a scale of resonance effects of various substituents was obtained and expressed in terms of isodesmic reactions. Comparison with other similar scales revealed that this model is not particularly advantageous, its main shortcoming being the relatively small effect. In any case it confirmed that the scales of resonance effects obtained from different models are only very roughly proportional: the classical model of resonance works well in representative examples but has its clear limitation when unduly extended.

Keywords: Buta-1,3-diene; Inhibited conjugation; Isodesmic reaction; Resonance energy; Substituent effects; Dienes; Chemometrics; DFT; Ab initio calculations.

Several attempts were made to estimate quantitatively resonance of various functional groups with the goal to create a unified scale of their resonance ability[1,2]. They were reviewed and evaluated[3]. In the approach of Taft[1], already classic, the resonance constants σ_R were defined by comparison of dissociation constants of aromatic and aliphatic acids: the functional group COOH was acting as a "probe"[4]. In an alternative approach[5–7], energies of two monofunctional molecules, one saturated and one unsaturated, are compared in isodesmic[8] reactions: no functional group is involved and the conjugative power is referenced only to a hydrocarbon residue. Third model requires determining energy of a conjugated system with an acceptor group and a donor group at the ends[9]. Note that in all these models the term resonance means only the difference between a conjugated and a saturated molecule; there is no direct relation to the resonance theory and to its formulas.

We contributed recently to the two last mentioned approaches with the intention to improve their model systems, in both cases by using derivatives of buta-1,3-diene. In the isodesmic reactions, Eq. (*1*) or (*2*), the *ap*-conformer **1** or *sp*-conformer **2** were compared with substituted *n*-butanes[10]; essential was comparison of molecules of similar size. *n*-Butyl derivatives were recommended as standard[11] since the interaction energy with the functional group is closely similar to that in *n*-pentanes and does not further change in the homologous series.

$$n\text{-}C_4H_9X \quad + \quad \diagup\!\!\!\diagup \quad \rightleftharpoons \quad X\!\!-\!\!\diagup\!\!\!\diagup \quad + \quad n\text{-}C_4H_{10} \qquad (1)$$
$$\mathbf{1}$$

$$n\text{-}C_4H_9X \quad + \quad \diagup\!\!\!\diagdown \quad \rightleftharpoons \quad X\!\!-\!\!\diagup\!\!\!\diagdown \quad + \quad n\text{-}C_4H_{10} \qquad (2)$$
$$\mathbf{2}$$

Disubstituted *sp*-buta-1,3-dienes **3** were involved[12] in Eq. (*3*), which describes the interaction of the groups X and Y and can be a measure of resonance when the small inductive effect is subtracted. Equation (*3*) is not only isodesmic but also homodesmotic[13], in contrast to Eqs (*1*) and (*2*).

$$X\!\!-\!\!\diagup\!\!\!\diagdown \quad + \quad \diagup\!\!\!\diagdown\!\!-\!\!Y \quad \rightleftharpoons \quad X\!\!-\!\!\diagup\!\!\!\diagdown\!\!-\!\!Y \quad + \quad \diagup\!\!\!\diagdown \qquad (3)$$
$$\mathbf{3}$$

Our results indicated that a unique scale of resonance is not possible or is possible only with quite a low accuracy[10]; in any case one should have one scale for acceptors and one for donors[12]. In this communication we intended to test an additional model based on the steric inhibition of resonance (SIR). This classic principle[14,15] was recently seriously criticized[16] since certain molecules involved possess actually planar conformation. Nevertheless, SIR undoubtedly exists in many compounds. The nonplanar conformation can be forced by steric hindrance, e.g. by *ortho* substituents on a benzene ring[14,17]. When the energies are obtained by calculations, there is a possibility of investigating frozen conformations with a fixed dihedral angle[8a,18], usually 90°. Either approach has its shortcomings. The former introduces additional substituents whose effect must be accounted for. With the latter there is an objection that its objects are not real molecules: the quantum chemical methods can be less dependable and the results need not be transferable to the real world. Nevertheless, both possibilities were exploited broadly but only for certain substituents, which are planar

and take normally a coplanar conformation, such as NO_2, CHO, $COCH_3$, OH. In spite of the possible fundamental objections, we returned once more to this approach and suggest here a model applicable for all substituents based on substituted buta-1,3-dienes twisted by rotation around the C2–C3 bond (**4**); the dihedral angle $\tau = \angle C1-C2-C3-C4$ was kept at 90°. While in the planar *ap*-conformer **1** the group X is conjugated with the two double bonds, in **4** only with one double bond; the energy difference $\Delta_4 E$ (Eq. (*4*)) can measure the ability of X to conjugation.

$$(4)$$
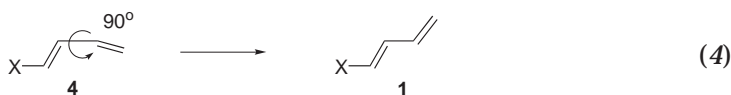
When these energies are presented on a scale, they should be anchored to zero value for X = H as usual. Then the energies are related to the isodesmic reaction, Eq. (*5*), which itself looks somewhat oversophisticated. Equations (*4*) and (*5*) are formally both isodesmic and homodesmotic but do not describe any physical equilibrium since **4** are not stable species.

$$(5)$$
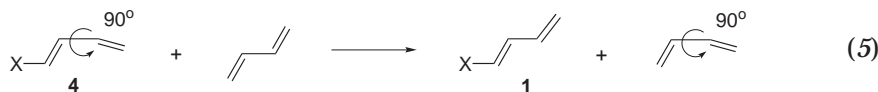
While Eq. (*4*) or (*5*) describe conjugation of a substituent with the hydrocarbon residue, conjugation of two substituents is given by the energy $\Delta_3 E$ of the reaction, Eq. (*3*). The effect of resonance can be separated referring to the twisted conformer **5**. In Eq. (*6*) resonance is inhibited and its contribution should be given by the difference $\Delta_3 E - \Delta_6 E$.

$$(6)$$
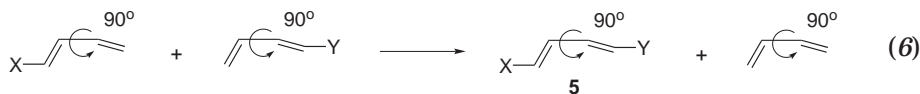
We calculated the energies of **4** and **5** with a variety of substituents, both dipolar and charged (Tables I and II); in **5** the selection was restricted to the combinations acceptor–donor. Calculations were carried out within the framework of the density functional theory[19] as in previous work[10–12]. The resonance effect was evaluated from Eq. (*5*) or from Eqs (*3*) and (*6*). The main problem was whether the fixed conformations give results concordant with those obtained with stable molecules.

CALCULATIONS

DFT calculations were performed at a B3LYP/6-311+G(d,p) level according to the original proposal[19] exploiting the Gaussian 03 program[20]. This level was chosen according to experience with similar compounds[11,12]. Previously we attempted improving the level to B3LYP/AUG-cc-VTZ//B3LYP/6-311+G(d,p) but it was necessary to carry out the calculations at tight convergence: the results were then insignificantly different from the level B3LYP/6-311+G(d,p)[11]. Full energy optimization and vibrational analysis were carried out for stable molecules; the minimum-energy conformations were searched for starting from two or more initial structures.

TABLE I
Calculated energies and bond lengths of monosubstituted nonplanar buta-1,3-dienes **4**

	Substituent X	E(DFT) a.u.	C1=C2 Å	C2–C3 Å	C3–C4 Å	$\Delta_4 E$ kJ mol^{-1}	$\Delta_5 E$ kJ mol^{-1}
4a	H	–156.0300529	1.332	1.484	1.332	–28.25	0
4b	CH$_3$	–195.3596130	1.334	1.484	1.332	–28.99	–0.74
4c	CH$_2$Cl	–654.9818271	1.334	1.483	1.331	–29.16	–0.91
4d	CF$_3$	–493.1824991	1.330	1.482	1.331	–28.41	–0.16
4e	CHO	–269.3897196	1.340	1.479	1.331	–31.93	–3.68
4f	COOH	–344.6686510	1.336	1.479	1.331	–31.66	–3.41
4g	CN	–248.2982256	1.339	1.480	1.331	–31.82	–3.57
4h	NH$_2$	–211.4079127	1.340	1.483	1.331	–33.33	–5.08
4i	N(CH$_3$)$_2$	–290.0404441	1.346	1.484	1.333	–33.95	–5.70
4j	NO$_2$	–360.5946170	1.328	1.479	1.331	–30.82	–2.57
4k	OH	–231.2763770	1.334	1.484	1.332	–29.70	–1.45
4l	OCH$_3$	–270.5866510	1.338	1.485	1.332	–29.75	–1.50
4m	SH	–554.2471026	1.335	1.485	1.332	–15.02	–2.00
4n	F	–255.2978867	1.324	1.484	1.331	–26.37	1.88
4o	Cl	–615.6539481	1.327	1.485	1.331	–27.78	0.47
4p	COO$^-$	–344.1191595	1.335	1.480	1.336	–32.72	–4.47
4q	O$^-$	–230.7084780	1.340	1.467	1.346	–67.85	–39.60
4r	NH$_3{}^+$	–211.7517409	1.325	1.481	1.330	–29.78	–1.53

When calculating energies of the frozen conformations of **4** and **5** with a fixed dihedral angle $\tau = \angle$C1–C2–C3–C4, all remaining geometry parameters were optimized with respect to internal coordinates. Even in this case the possible conformations within the functional group were taken into consideration. For our purpose it was necessary that these conformations

TABLE II
Calculated energies and bond lengths of disubstituted nonplanar buta-1,3-dienes **5**

	Substituent		E(DFT) a.u.	C1=C2 Å	C2–C3 Å	C3=C4 Å	$\Delta_6 E$ kJ mol^{-1}
	X	Y					
5a	CH$_2$Cl	NH$_2$	–710.3602170	1.336	1.481	1.340	–1.39
5b	CF$_3$	NH$_2$	–548.5615248	1.332	1.480	1.341	–3.06
5c	COOH	NH$_2$	–400.0473073	1.338	1.478	1.341	–2.09
5d	CN	NH$_2$	–415.9746352	1.341	1.477	1.342	–4.67
5e	NH$_2$	NH$_2$	–266.7855770	1.340	1.482	1.340	0.51
5f	N(CH$_3$)$_2$	NH$_2$	–345.4176839	1.346	1.484	1.340	1.63
5g	NO$_2$	NH$_2$	–415.9746352	1.331	1.476	1.342	–5.67
5h	OH	NH$_2$	–286.6567005	1.335	1.482	1.341	–6.47
5i	OCH$_3$	NH$_2$	–325.9672950	1.339	1.484	1.340	–7.31
5j	SH	NH$_2$	–609.6257419	1.336	1.483	1.341	–2.05
5k	Cl	NH$_2$	–671.0331303	1.329	1.482	1.341	–3.47
5l	CH$_2$Cl	NO$_2$	–859.5450594	1.333	1.478	1.328	3.50
5m	CF$_3$	NO$_2$	–697.7435589	1.329	1.477	1.327	9.20
5n	COOH	NO$_2$	–549.2307247	1.334	1.473	1.328	6.54
5o	CN	NO$_2$	–452.8583207	1.338	1.476	1.327	11.73
5p	N(CH$_3$)$_2$	NO$_2$	–494.6078073	1.349	1.477	1.331	–7.35
5q	NO$_2$	NO$_2$	–565.1537253	1.327	1.474	1.327	14.32
5r	OH	NO$_2$	–435.8427572	1.336	1.478	1.329	–4.77
5s	OCH$_3$	NO$_2$	–475.1544276	1.339	1.479	1.329	–8.43
5t	SH	NO$_2$	–758.8111073	1.336	1.479	1.329	1.47
5u	Cl	NO$_2$	–820.2162442	1.328	1.479	1.328	5.95

were always the same: in the twisted conformers **4**, in the natural conformers[10] **1** and **2**, in the disubstituted derivatives **3** and **5**. In all but one case these uniform conformations were also those of minimum energy for each compound. The exception is the substituent SH. We have chosen the *sp*-conformations on the C–S bond for all compounds, although in some molecules it is not the minimum-energy form[12]. The consequences for the energy are negligible.

The energies are listed in Tables I and II, together with some geometric parameters. The reaction energies $\Delta_4 E$, $\Delta_5 E$ and $\Delta_6 E$ were calculated according to Eqs (*4*)–(*6*). The reaction energies $\Delta_1 E$ and $\Delta_3 E$ were taken from previous work[10]; $\Delta_1 E$ for X = SH required calculating DFT energies of (*ap*)-CH$_2$=CH–CH=CH–SH –554.2587660 and *n*-C$_4$H$_9$SH –556.7176656 a.u.

RESULTS AND DISCUSSION

The Potential Energy Curve

Conformation of unsubstituted buta-1,3-diene was studied both experimentally and theoretically. The most stable conformer is *ap* ($\tau = 180°$), the second conformer is not planar[21] and is to be classified as *sc* (calculated[22] τ is between 31 and 40°). The energy difference was obtained within the range 10 and 15 kJ mol^{-1} using a variety of theoretical models[22], even more sophisticated than that used here. The experimental values agree merely with the lower limit[22]. Our calculated values, 14.7 kJ mol^{-1} and $\tau = 35°$, are within the given range and our theoretical model is sufficient for the given purpose. The potential energy curve is pictured in Fig. 1 by the heavy line. The transition state lies at $\tau = 100°$ with the energy barrier of 32.6 kJ mol^{-1}, also in reasonable agreement with previous results[22] ($\tau = 100–102°$, barrier 23–31 kJ mol^{-1}). The twisted conformations with the uniform value of $\tau = 90°$ are thus almost identical with the transition state.

The substituent effects are shown on the cyano derivative where they are relatively strong. The shape of potential–energy curve (Fig. 1, broken heavy line) is very little changed by substitution: stable conformers were found at $\tau = 180$ and 29°, the energy difference between them is 12.3 kJ mol^{-1}, transition state at $\tau = 100°$, energy barrier 33.0 kJ mol^{-1}. The whole curve is shifted by the stabilizing resonance effect of the CN group expressed by the reaction energy of Eq. (*1*), $\Delta_1 E = -13.8$ kJ mol^{-1}. When the two potential–energy curves are subtracted, one gets the substituent effect in dependence on τ (Fig. 1, the dash-and-dot line). Its value for $\tau = 90°$ (–3.6 kJ mol^{-1}) is

given by $\Delta_5 E$ of Eq. (5). It may be understood as the difference of resonance energy when the CN group is conjugated with the butadiene chain on the one hand, on the other only with one of its double bonds. The problem is in the relative values: while the steric inhibition of resonance, $\Delta_4 E$, is itself rather great, its dependence on substitution $\Delta_5 E$ is much smaller. The two measures of resonance discussed here are thus unequal: $\Delta_1 E$ is significantly greater than $\Delta_5 E$.

The interpretation of substituent effects by resonance and its steric inhibition might be confirmed from the length of the C2–C3 bond. According to the classical formulas, this bond is shortened either in the presence of an acceptor (**6A** ↔ **6B**) or of a donor (**7A** ↔ **7B**), compared to the unsubstituted butadiene (**8A** ↔ **8B**). In the twisted conformation the resonance is inhibited and the C2–C3 bond should be not shortened. Its dependence on the torsion angle τ is shown in Fig. 1 at the bottom and confirms the predictions only partly. It is shortened by substitution in the stable conformers but it is also somewhat shortened in the twisted form. This could suggest that conjugation is not fully removed by rotation but the changes are only in thousandths of Å. Different effects of resonance on the energies and on the geometry were noted[10,23].
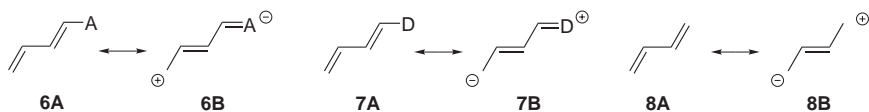
The above picture need not be quite analogous with all substituents. For instance with X = NH_2, the rotation around the C2–C3 bond is accompanied by simultaneous conformation changes of the NH_2 group. The potential–energy curve has then a less smooth shape, although part of this irregularity might be due to the imperfection of the theoretical model. Also the changes in the bond lengths are not proportional with all substituents.

Resonance Effects in Monosubstituted Butadienes

The key question is whether the conjugative energies $\Delta_5 E$, estimated from twisted structures, are proportional to $\Delta_1 E$, estimated[10] by comparison with a saturated molecule (Eq. (1)). Figure 2 reveals that the proportionality is only rough. There is a systematic difference between acceptors and donors, the latter being more sensitive to SIR; even within the two classes the dependence seems to be nonlinear. Charged substituents were omitted in

Fig. 2 because of the substituent O⁻, whose values of Δ_1E and Δ_5E (Table I) are incomparable with the others. This group behaves as an extremely strong donor and its conjugation described in **7B** is not fully suppressed even in the twisted conformation: The C2–C3 bond is shortened significantly (Table I) and even the C3=C4 bond is lengthened by conjugation.

Summarizing, we have found several shortcomings of the model of twisted butadienes. Most important are the small relative values of the resonance effect (Δ_5E); one must also consider that resonance is not completely inhibited and that the conformation of some parts can change with substitution. When the results (Δ_5E) are not proportional to those obtained in the previous model (Δ_1E), we are of the opinion that the latter are better physically founded. Note that in Eqs (*4*) and (*5*) energies of the twisted conformations were related to the minimum-energy *ap*-conformer **1**. They could be related also to the *sp*-conformer **2**, but the results would be almost identical. When we replaced in Eq. (*5*) the conformer **1** by the conformer **2**, we obtained closely correlated results (correlation coefficient $R = 0.994$ for all substituents, 0.966 only for uncharged substituents). Therefore, the pertinent energy values are not explicitly given and are not discussed.
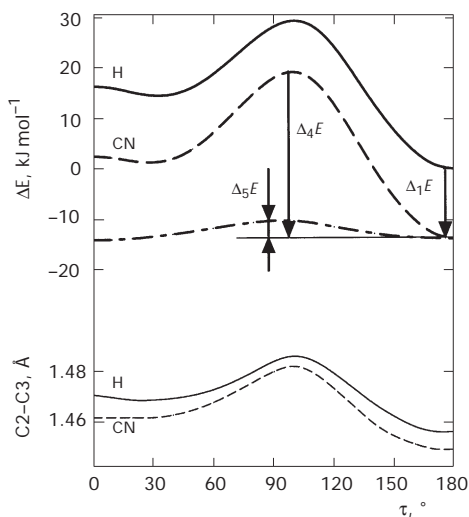

FIG. 1

Potential–energy curves for the rotation around the C2–C3 bond: full heavy line – buta-1,3-diene, broken heavy line – 1-cyanobuta-1,3-diene, dash-and-dot line – difference of these curves, full thin line (at the bottom) – the C2–C3 bond length in buta-1,3-diene, broken thin line – in 1-cyanobuta-1,3-diene. Important energy differences are shown by arrows

Resonance Effects in Disubstituted Butadienes

Effects in 1,4-disubstituted buta-1,3-dienes were investigated[12] on the conformation near to **3**, in order to estimate interaction of the two substituents as defined in Eq. (*3*). It turned out that the minimum-energy conformation is not exactly planar but the energy difference is negligible (Fig. 1). Equation (*3*) is homodesmotic[13] and should express purely the mutual interaction of X and Y. To obtain only the resonance effect, $\Delta_R E$, it was necessary to subtract the assumed inductive effect estimated for instance from 1,4-disubstituted bicyclo[2.2.2]octanes[12]. Reasonable results were obtained when X and Y were an acceptor and a donor; for the combination of two acceptors the values of $\Delta_R E$ were near to zero and little dependable. We attempted to obtain another scale of resonance effects from the twisted conformation **5**; for the reasons given we investigated only the combinations of the typical donor NH_2 with various acceptors (Table II, compounds **5a–5k**) and of the typical acceptor NO_2 with various donors (compounds **5l–5u**).

Interaction in the twisted conformation is expressed by Eq. (*6*). Its reaction energy $\Delta_6 E$ (Table II, last column) should by free of any resonance contribution but – similarly as in the preceding section – the resonance is not completely removed as seen particularly from the bond lengths (Table II,
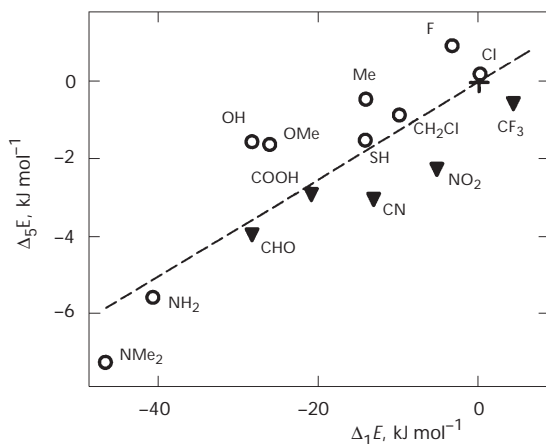

FIG. 2
Comparison of two estimated measures of substituent resonance effect in monosubstituted buta-1,3-dienes: $\Delta_1 E$ determined previously[10] and $\Delta_5 E$ defined here by Eq. (*5*): ○ donor substituents, ▼ acceptor substituents, + hydrogen. The reference line has no mathematical meaning

column 6). The contribution of resonance should be given by the difference of the near-to-planar and twisted forms, i.e. $\Delta_3 E - \Delta_6 E$. Figure 3 reveals that these values are not proportional to the resonance effects $\Delta_R E$ determined previously[12]; in particular there is again a great difference between the behavior of acceptors and donors. A certain relationship exists only in the subset where an acceptor is conjugated with a donor (full points in Fig. 3) but even this correlation would be classified[24] only as "fair". The subsets donor–donor and acceptor–acceptor behave differently; their interaction is evidently controlled by other factors than simple resonance. We can thus only confirm the previous statement[12] that resonance of donors and acceptors is different in character and cannot be brought to a unified scale.

MORE GENERAL CONCLUSIONS

The approach using fixed unstable conformations was investigated here on a typical example in some detail. In our opinion its imperfections were clearly revealed. A conformer created artificially by a purely mathematical intervention has not the properties of a real molecule. The unnatural conformation in one part of the molecule can produce further unnatural
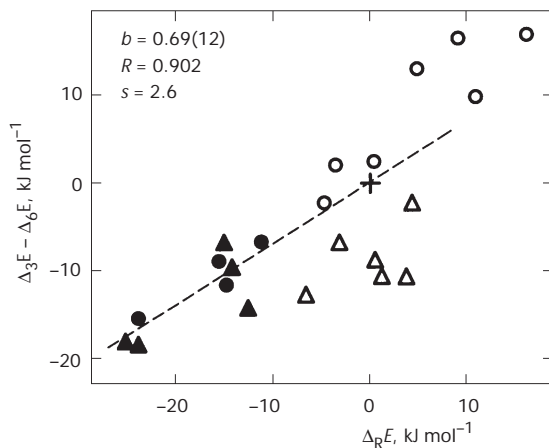

Fig. 3

Comparison of two estimated measures of substituent resonance effect in disubstituted buta-1,3-dienes **3**: $\Delta_R E$ determined previously[12] and the difference $\Delta_3 E - \Delta_6 E$, defined by Eqs (*3*) and (*6*): ● substituents NH_2 together with an acceptor, ○ NH_2 with another substituent, ▲ NO_2 with a donor, △ NO_2 with another substituent, + unsubstituted butadiene. The regression line and the statistics apply to the combined sets ● , ▲ and +, assuming that $\Delta_R E$ is the more accurate quantity

changes in another part; these changes may differ according to the substitution and conformation. It is also evident that conjugation is not always fully removed by rotation. Generally, we consider such models to be inferior to the alternative comparing two molecules, which may be only partly similar but, in any case, are real. The model used in this work had still a shortcoming that the relative effects were rather small. The results obtained in the past with fixed nonplanar conformations must be viewed cautiously. For instance the not coplanar nitro groups represents only a fictive substituent with some interesting properties but with little relation to the real world.

Concerning the classic resonance theory in general, this work confirmed its limitations as observed previously[7,10,12]; particularly the effort was not successful to create a unified scale of resonance ability for all groups. This was probably not caused by the imperfections of the theoretical models: on the contrary, the results with calculated energies were more regular than with experimental quantities. More probably, the problem is in the basic assumption of the common analysis[1,2] that the substituent effect may be represented as an algebraic sum of the inductive and resonance contributions. While the inductive effect can be defined separately with a great accuracy[25], resonance must be obtained by subtraction. In our opinion, the problem is still more fundamental: the resonance cannot be accurately described as an intrinsic property defined for all possible groups and independent of the rest of the molecule. The resonance theory is then a theory, well founded for the typical examples, as for instance resonance in benzene or conjugation of an acceptor with a strong donor (NO_2 with NH_2). However, it can be hardly extended to all possible structures.

REFERENCES

1. a) Ehrenson S., Brownlee R. T. C., Taft R. W.: *Prog. Phys. Org. Chem.* **1973**, *10*, 1; b) Hansch C., Leo A., Taft R. W.: *Chem. Rev. (Washington, D.C.)* **1991**, *91*, 165.
2. Charton M.: *Prog. Phys. Org. Chem.* **1981**, *13*, 119.
3. Exner O.: *Correlation Analysis of Chemical Data*, Chap. 5.2. Plenum Press, New York 1988.
4. Topsom R. D.: *Prog. Phys. Org. Chem.* **1976**, *12*, 1.
5. a) Hehre W. J., Radom L., Pople R. A.: *J. Am. Chem. Soc.* **1972**, *94*, 1496; b) Greenberg A., Stevenson T. A.: *J. Am. Chem. Soc.* **1985**, *107*, 3488; c) Helal M. R.: *J. Mol. Struct. (THEOCHEM)* **2000**, *528*, 255.
6. Exner O., Böhm S.: *J. Chem. Soc., Perkin Trans. 2* **2000**, 1994.

7. Exner O., Böhm S.: *Collect. Czech. Chem. Commun.* **2001**, *66*, 1623.
8. a) Pross A., Radom L., Taft R. W.: *J. Org. Chem.* **1980**, *45*, 818; b) Exner O.: *Org. Reactiv. (Tartu)* **1995**, *29*, 1.
9. Liu L., Fu Y., Liu R., Li R.-Q., Guo Q.-X.: *J. Chem. Inf. Comput. Sci.* **2004**, *44, 652.*
10. Böhm S., Exner O.: *J. Mol. Struct. (THEOCHEM)* **2005**, *722*, 125.
11. a) Exner O., Böhm S.: *J. Comput. Chem.* **2004**, *25*, 1979; b) Böhm S., Exner O.: *Collect. Czech. Chem. Commun.* **2005**, *70, 370.*
12. Exner O., Böhm S.: *J. Phys. Org. Chem.*, in press.
13. George P., Trachtman M., Bock C. W., Brett A. M.: *J. Chem. Soc., Perkin Trans. 2* **1976**, 1222.
14. Baker J. W., Nathan W. S.: *J. Chem. Soc.* **1935**, 1841.
15. Braude E. A., Sondheimer F., Forbes W. F.: *Nature* **1954**, *173*, 117.
16. Kulhánek J., Böhm S., Palát K., Jr., Exner O.: *J. Phys. Org. Chem.* **2004**, *17*, 686.
17. a) Chimichi S., Dell'Erba C., Gruttadauria M., Noto R., Novi M., Petrillo G., Sancassan F., Spinelli D.: *J. Chem. Soc., Perkin Trans. 2* **1995**, 1021; b) Dell'Erba C., Mele A., Novi M., Petrillo G., Sancassan F., Spinelli D.: *J. Chem. Soc., Perkin Trans. 2* **1990**, 2055.
18. a) Wiberg K. B.: *J. Org. Chem.* **2002**, *67*, 4787; b) Wiberg K. B.: *J. Org. Chem.* **2003**, *68*, 9322; c) Lauvergnat D., Hiberty P. C.: *J. Am. Chem. Soc.* **1997**, *119*, 9478.
19. a) Becke A. D.: *Phys. Rev. A: At., Mol., Opt. Phys.* **1988**, *38*, 3098; b) Lee C., Yang W., Parr R. G.: *Phys. Rev. B.: Condens. Matter* **1988**, *37*, 785; c) Miehlich B., Savin A., Stoll H., Preuss H.: *Chem. Phys. Lett.* **1989**, *157*, 200; d) Becke A. D.: *J. Chem. Phys.* **1993**, *98*, 5648.
20. Frisch M. J., Trucks G. W., Schlegel H. B., Scuseria G. E., Robb M. A., Cheeseman J. R., Montgomery J. A., Jr., Vreven T., Kudin K. N., Burant J. C., Millam J. M., Iyengar S. S., Tomasi J., Barone V., Mennucci B., Cossi M., Scalmani G., Rega N., Petersson G. A., Nakatsuji H., Hada M., Ehara M., Toyota K., Fukuda R., Hasegawa J., Ishida M., Nakajima T., Honda Y., Kitao O., Nakai H., Klene M., Li X., Knox J. E., Hratchian H. P., Cross J. B., Adamo C., Jaramillo J., Gomperts R., Stratmann R. E., Yazyev O., Austin A. J., Cammi R., Pomelli C., Ochterski J. W., Ayala P. Y., Morokuma K., Voth G. A., Salvador P., Dannenberg J. J., Zakrzewski V. G., Dapprich S., Daniels A. D., Strain M. C., Farkas O., Malick D. K., Rabuck A. D., Raghavachari K., Foresman J. B., Ortiz J. V., Cui Q., Baboul A. G., Clifford S., Cioslowski J., Stefanov B. B., Liu G., Liashenko A., Piskorz P., Komaromi I., Martin R. L., Fox D. J., Keith T., Al-Laham M. A., Peng C. Y., Nanayakkara A., Challacombe M., Gill P. M. W., Johnson B., Chen W., Wong M. W., Gonzalez C., Pople J. A.: *Gaussian 03*, Revision B.03. Gaussian, Inc., Pittsburgh (PA) 2003.
21. Pincelli U., Cadioli B., Levy B.: *Chem. Phys. Lett.* **1972**, *13*, 249.
22. Karpfen A., Choi C. H., Kertesz M.: *J. Phys. Chem. A* **1997**, *101*, 7426.
23. Böhm S., Exner O.: *Org. Biomol. Chem.* **2003**, *1*, 5147.
24. Jaffé H. H.: *Chem. Rev. (Washington, D.C.)* **1953**, *53*, 191.
25. Exner O., Böhm S.: *J. Phys. Org. Chem.* **2004**, *17*, 124.