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Negative hyperconjugation of some fluorine containing groups†

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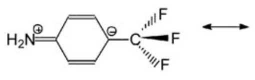
Energies of some aromatic or conjugated aliphatic compounds fluorine containing were calculated within the framework of the density functional theory at the level B3LYP/6-311 + G(d.p)//B3LYP/6-311 + G(d.p). Evaluation proceeded in terms of isodesmic reactions, in which the groups CF_3, SF_5 and SCF_3 acted as substituents. All these groups behave as rather strong resonance acceptors. The pertinent canonical structures must be formulated with one C–F bond broken—no-bond resonance or negative hyperconjugation. In agreement with these formulae, the C–F bond lengths are elongated; they increase particularly strongly if a conjugated donor group is present. The principle of negative hyperconjugation is thus able to predict qualitatively several observable facts (energy, geometry), even when the pertinent formulae much exaggerate the real structural features.

Introduction

The term hyperconjugation has been introduced as an extreme of the resonance theory; it used canonical formulae, in which one bond C–H is lacking and the H atom is positively charged ("no-bond resonance").[1,2] Although alternative explanations of the experimental facts were advanced,[3] hyperconjugation has persisted as a theory discussed from time to time. Recent reinvestigation based on quantum chemical calculations on isolated molecules revealed no effect on energy but some small changes of geometry, which would be consistent with the no-bond formula.[4]

The opposite term "negative hyperconjugation" was connected with the C–F bonds instead of C–H bonds, and the polarity was reversed. Roberts and coworkers[5] measured the basicity of anilines substituted with the substituent CF_3: the strong effect in the position *para* was classified as conjugation and explained by the no-bond resonance formulae **1A** and **1B**.



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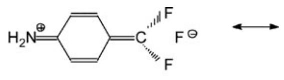
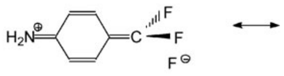
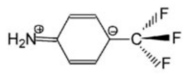


1A



1B



1C

This explanation was accepted against some less probable formulae[6] and is still in use at present.[7–9] Several attempts were made to support or check the no-bond formulae by quantum chemical calculations,[9–12] but they were carried out on rather limited classes of compounds. For the present investigation it is most important that in the theory of substituent effects the group CF_3 was always treated as an acceptor: in all tables of substituent resonance constants it appears with a positive sign. Some such constants are given in Table 1; the most suitable for molecule **1** are those denoted σ_R^-. The group CF_3 appears as a rather strong acceptor, somewhat weaker than for instance CN, for which the conjugation may be expressed by common resonance formulae. When the conjugation of CF_3 is to be pictured by a resonance formula, the no-bond structure is inevitable.

An alternative interpretation of the experimental facts was also advanced[19,20] for conjugated benzene *para* derivatives, for example 4-nitroaniline. Applied to CF_3 derivatives, this explanation does not require the no-bond formula, it assumes that only the donor group is in resonance with the benzene ring, more or less in individual compounds, and the intensity of resonance is controlled by the acceptor group (mainly by its inductive effect). This concept could be represented by the simple formula **1C**. In two cases it was not possible to provide experimental support for this theory, either from bond lengths or from dipole moments.[21,22]

Further groups with possible negative hyperconjugation were investigated much less thoroughly. The substituent SF_5 was introduced in the aliphatic series[23] and its inductive effect was estimated.[13,24] Evaluation of resonance was based on the basicity of substituted *N*,*N*-dimethylanilines in the gas phase[17] and of 4-substituted anilines in water;[6] the no-bond structures were considered together with other less probable possibilities.[6] These formulae, **2A** and **2B**, are pictured here for substituted anilines; in the octahedral configuration on sulfur one must distinguish hyperconjugation of the fluorine atom in the apical position (**2A**) and in the equatorial position (**2B**).[25,26]

Compounds with the substituent SCF_3 were prepared mainly with the intention to study the substituent effects in aromatic derivatives.[26] Its structure did not seem peculiar on

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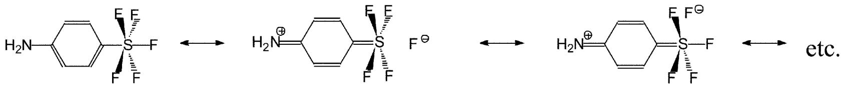
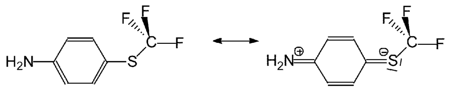
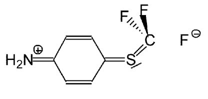


2 **2A** **2B**

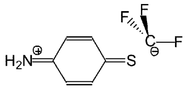
the first sight but its behaviour as a substituent was strange: if one viewed this group as the mercapto group SH substituted by CF_3, it should behave as a donor, although weak. One can attempt to estimate its resonance constant σ_R by the method,[27] in which the more complex substituents are treated as derivatives of the simpler ones. One gets σ_R (SCF_3) = −0.14. However, the group SCF_3 behaves as an acceptor and its values of σ_R or σ_R^- are always positive (Table 1). An explanation could be the formula **3A** with formally ten electrons on sulfur,[25] stabilized by the inductive electron attracting effect of CF_3. This stabilization can be strengthened to reach the no-bond formula **3B**, considered[26] to be less probable, or alternatively **3C**, which is in our opinion still less probable.



3 **3A**



3B



3C

In this article we will deal with the above three groups as with substituents, that is investigate not only their structure but also interaction with other groups, particularly in a conjugated position. This will be done by calculation within the framework of density functional theory (DFT). As in previous work[28–30] we shall restrict the results to observable quantities, energy and geometry. The energy of interaction with an electron donor will be measured by the reaction energies of eqn (1) and (2) under the conditions of increasing electron supply. These equations are both isodesmic[31–33] and homodesmic.[34] Contribution of resonance should be evident mainly according to the difference of reaction energies of eqn (1) and (2), $\Delta_1 E$ and $\Delta_2 E$, respectively.

$$NH_2.C_6H_5 + C_6H_5.X = \underset{\mathbf{1}}{4\text{-}NH_2.C_6H_4.X} + C_6H_6 \qquad (1)$$

$$NH^-.C_6H_5 + C_6H_5.X = 4\text{-}NH^-.C_6H_4.X + C_6H_6 \qquad (2)$$

a $X = CF_3$, **b** $X = SF_5$, **c** $X = SCF_3$, **d** $X = CN$

Contributions of negative hyperconjugation formulae **1A**, **1B**, **2A**, **2B**, **3B** could be estimated according to some geometric parameters, particularly the bond lengths C–F (ref. 10), S–F and the bond angles F–C–F or F–S–F. We were aware that these resonance structures are only oversimplified extreme formulae. The question is not whether these structures are correct, only whether they are able to predict qualitatively some observable facts.

Ultimately we calculated also the inductive constants σ_I and resonance acceptor constants σ_A for isolated molecules; the former on the basis[35] of eqn (3), the latter[30] of eqn (4) as done by us previously.

4

(3)

5

a $X = CF_3$, **b** $X = SF_5$, **c** $X = SCF_3$, **d** $X = CN$

(4)

Calculations

The DFT calculations were carried out at the level B3LYP/6-311+G(d,p)//B3LYP/6-311+G(d,p) with the GAUSSIAN 03 program.[36] Any symmetry was never anticipated, calculations of possibly planar molecules were always started from the structures near to planarity. No correction for the zero-point energy was introduced. All structures were checked by vibrational analysis and behaved as energy minima.

Some important geometric parameters of **1** and **2** are listed in Table 2, the energies are listed in Table 3.

Results and discussion

Agreement of calculations with experiments

In our systematic studies of substituent effects[28–30] we used the quantum chemically calculated energies as source data in place of experimental reactivities. Therefore it was of utmost importance to compare always at least several values of these energies with the available gas-phase reactivities. In our case the pertinent experimental data are extremely scarce but we can show at least one example that agreement with

Table 1 Some constants characterizing resonance of the fluorine containing substituents

Substituent	R^- (ref. 14)	σ_R^- (ref. 15)	σ_R^- (ref. 16)	σ_R (ref. 17)	σ_R (ref. 13)	σ_d (ref. 18)
CF_3	0.27	0.17	0.12	0.07	0.11	0.13
SF_5	0.30	0.20	0.09	0.05	0.03	0.04
SCF_3	0.28	0.14		0.10	−0.01	
CN	0.49	0.33	0.28	0.10	0.08	0.12

Table 2 DFT calculated observable quantities: reaction energies and bond lengths

		CF_3	SF_5	SCF_3	CN
1	Reaction energy eqn (1)/kJ mol^{-1}	−6.83[a]	−9.33	−7.31	−9.36[a]
2	Reaction energy eqn (2)/kJ mol^{-1}	−68.03	−104.64	−74.11	−90.94
3	Reaction energy eqn (3)/kJ mol^{-1}	−26.62[b]	−56.18	−32.38	−37.08[b]
4	Inductive constant σ_I	0.44[b]	0.93[c]	0.53	0.61[b]
5	Reaction energy eqn (4)/J mol^{-1}	−9.68[a]	−15.30	−15.06	−13.50[a]
6	Resonance acceptor constant σ_A	0.25[a]	0.45	0.40	0.38[a]
7	X–F bond length, C_6H_5X/Å	1.358[d]	1.636[e]	1.347	
		1.353	1.645[f]	1.346	
		1.353		1.345	
8	X–F bond length, 4-$NH_2C_6H_4X$/Å	1.363[d]	1.639[e]	1.348	
		1.355	1.648[f]	1.348	
		1.355		1.347	
9	X–F bond length, 4-NH^-–C_6H_4X Å	1.400[d]	1.682[e]	1.364	
		1.373	1.673[f]	1.355	
		1.371		1.354	
10	Average bond angle F–X–F, C_6H_5X	106.6	87.4[e] 89.9[f]	107.4	
11	Average bond angle F–X–F, 4-$NH_2C_6H_4X$	106.3	87.1[e] 89.9[f]	107.3	
12	Average bond angle F–X–F, 4-NH^-–C_6H_4X	104.1	84.7[e] 89.5[f]	106.3	
13	Bond lengths C2–C3 and C5–C6, C_6H_5X/Å	1.392	1.393	1.393	1.376
14	Bond lengths C2–C3 and C5–C6, 4-$NH_2C_6H_4X$/Å	1.387	1.386	1.387	1.384
15	Bond lengths C2–C3 and C5–C6, 4-NH^-–C_6H_4X/Å	1.376	1.373	1.375	1.373
		1.373	1.370	1.372	1.370
16	Reaction energy eqn (6)/kJ mol^{-1}	−33.0	−56.5	−34.2	−43.8
17	Reaction energy eqn (7)/kJ mol^{-1}	−36.0	−57.4	−44.0	−46.7

[a] Ref. 30. [b] Ref. 35. [c] This value is not reliable, see Discussion. [d] The C–F bond in the perpendicular plane to the benzene ring. [e] Apical S–F bond. [f] Equatorial S–F bonds of practically equal length.

Table 3 DFT calculated energies of compounds with substituents containing fluorine[a]

	CF_3[b]	SF_5	SCF_3
C_6H_5X	−569.4608204	−1129.1621944	−967.6630100
4-$NH_2C_6H_4X$	−624.8398135	−1184.5421382	−1023.0421839
4-NH^-·C_6H_4X	−624.2657683	−1183.9810869	−1022.4702712
(*E*)-CH_2═CH–CH═CHX	−493.1878610	−1052.8891357	−891.3905014
(*E*,*E*)-NH_2CH═CHCH═CHX	−548.5715177	−1108.2749347	−946.7728901
4-X-C_8H_{12}-1-COOH	−839.1579047	−1398.8600202	−1237.3551799
4-X-C_8H_{12}-1-COO^-	−838.6101006	−1398.3234754	−1236.8095678
3-X-C_6H_4COOH	−758.0958098	−1317.7960668[c]	−1156.2980510[c]
3-X-$C_6H_4COO^-$	−757.5567767	−1317.266148	−1155.7596246
4-X-C_6H_4COOH	−758.0954459	−1317.7958700	−1156.2949649
4-X-$C_6H_4COO^-$	−757.5576837	−1317.2662598	−1155.7602751

[a] In a.u.; calculated at the level B3LYP/6-311 + G(d,p)//B3LYP/6-311 + G(d,p). [b] Some of these values were already published, usually only the energies, not the geometric parameters, ref. 29,30,42,44. [c] Weighted average from two near values for the two coplanar conformations of the COOH group.

experiments for our particular substituents is not worse that for common substituents. Eqn (5) was derived from eqn (1) and (2); its reaction energies Δ_5E were calculated at the level as used in this work and correlated[37] with the experimental gas-phase basicities $\Delta_5G^\circ(298)$ as shown in Fig. 1. When we add the substituents CF_3 and SCF_3 into this diagram, we observe no deviation.

$$4\text{-}XC_6H_4NH_2 + C_6H_5NH^- = 4\text{-}XC_6H_4NH^- + C_6H_5NH_2 \qquad (5)$$

At the level B3LYP/6-311 + G(d,p) the substituent effects are usually overestimated[38,39] (not always[40]) proportionally for all substituents. Also in Fig. 1 the slope 0.88 is significantly smaller than unity. Of course this is of no consequence for the correlation analysis, which deals only with relative values.

Interaction energy and conjugation

Concerning the substituent effects of the three fluorine containing groups, we can deal separately with two questions: whether the interaction can be classified as resonance and whether this resonance is suitably described by the no-bond formulae (**1A,B**, **2A,B**, **3B**).

Conjugation is characterized by the interaction energy of the reactions eqn (1), (2) and (4). They are given in Table 2, lines 1, 2 and 5, and compared with the well known conjugated acceptor substituent CN (last column). It is evident that all these energies are negative revealing interaction of a donor

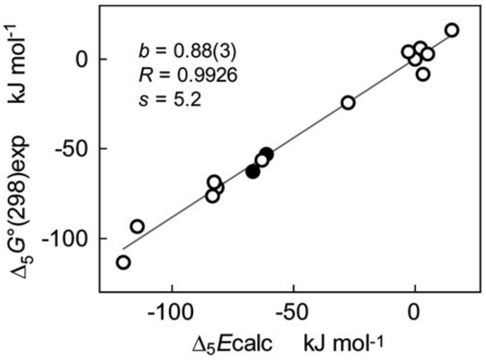


Fig. 1 Plot of the relative acidities of 4-substituted anilines, eqn (5), experimental gas-phase acidities $\Delta_5G°(298)$ *vs.* calculated energies Δ_5E; ● fluorine containing substituents, ○ other substituents.

with an acceptor. Compared with the substituent CN, the group CF_3 appears as somewhat weaker acceptor, SCF_3 almost equal and SF_5 slightly stronger but all groups are of comparable ability as acceptors. Most significant is the dependence on the conjugated donor. With a strong donor the interaction energies increase steeply in the absolute values (Table 2, line 2); even in this point all three groups are comparable with CN and can be classified as resonance acceptors. Note that the term resonance is not given in this connection any more specific meaning; the resonance constants express nothing more than difference of behaviour in the conjugated and unconjugated (or aliphatic) systems.[13]

Resonance can be described more specifically referring to the molecular geometry. In all resonance structures of benzene *para* derivatives the bonds C2–C3 and C5–C6 should be shortened compared to the standard value in benzene. This was also observed for sets of DFT calculated bond lengths.[22,40] For fluorine derivatives, the bond lengths are given in Table 2, items 13 to 15. Shortening in amino derivatives is evident, in the deprotonated amines it is much greater as expected. Note that in the latter compounds, the bonds C2–C3 and C5–C6 are unequal since the NH^- group is coplanar and unsymmetrical (Krygowski AGIBA effect[41]). This fine effect is immaterial compared to that of conjugation.

Negative hyperconjugation

The predicting power of the no-bond formulae can be best observed on the C–F bonds, which should be weakened and lengthened according to the electron supply of the conjugated donor. This was confirmed very clearly (Table 2, items 7 to 9). With the substituent SF_5 there is a difference between the S–F bonds of two kinds: the shorter apical bond is elongated more than the longer equatorial bonds. In terms of canonical structures this means that **2A** is represented more than **2B**. Even in CF_3 the C–F bonds are unequal and that in the symmetrical position is affected more by conjugation (**1A** represented more than **1B**). This all is compatible with the principle of hyperconjugation. With SCF_3 the differences in the C–F bond lengths are minute.

The bond angles F–C–F are also affected by hyperconjugation, little by conjugation with NH_2, much more with NH^- (Table 2, items 10 to 12). When the C–F bonds are weaker, the angle between them is smaller but *a priori* it would not be easy to predict the direction of these changes in an unambiguous way. With the substituent SF_5 there are two different angles: between two equatorial bonds and between one equatorial and one apical bond. The effect of hyperconjugation is observed for each.

In summary, the changes of geometry confirm the prediction of the negative hyperconjugation in all details; the proofs are more convincing than they were in the case of C–H hyperconjugation.[4]

Substituent constants in the gas phase

The resonance effects of our substituents were approximately expressed by the reaction energies of the isodesmic reactions eqn (1)or (2). A more exact determination requires still a correction for the relatively small inductive effect; as the main model the butadiene derivatives were recommended,[30] eqn (4). When we followed this procedure, we obtained the resonance constants of acceptors σ_A as they are given in Table 2, line 6. This more exact procedure confirmed our original estimates: all groups are relatively strong acceptors; SF_5 is stronger than CN, CF_3 is weaker. Of the published values only the constants R^- reveal any resemblance to these values (Table 1). The standard constants[13] σ_R are too small since they were determined on the compounds with an acceptor functional group, they do not describe actual conjugation similarly as with other acceptor substituents.[42]

At this opportunity we determined also the inductive constants σ_I for isolated molecules (or say in the gas phase), which were known only in water solution.[13] To this purpose the calculated reaction energy of the reaction eqn (3) was suggested,[29] which needs only an empirical scaling. The reaction energies are given in Table 2, item 3, the inductive constants in item 4. The latter reveal good agreement with the constants estimated for the gas phase by various not exactly specified methods,[17] except σ_I of SF_5, which is evidently too great, also compared to σ_I in water.[13] We were not able to discover why the well tried model fails for this particular substituent. The non-bonded distance F···H in 4-pentafluorosulfurbicyclo[2.2.2]octane-1-carboxylic acid is 2.28 Å and does not allow any steric interaction. We also repeated calculations at the level MP2/6-311+G(d,p) and obtained $\Delta_3E = -44.7$ kJ mol^{-1}, which would give σ_I of SF_5 0.74, still too great. (Note that the empirical scaling factor was derived for B3LYP calculations and is not *a priori* valid for MP2.)

We calculated as well the effect of the SF_5 substituent on the acidity of benzoic acids, eqn (6) and (7), since it is controlled virtually by the inductive effect.[43] The acidity increase (Table 2, items 16 and 17) is also too great, significantly greater than for the CN group (Table 2), even slightly greater than for the NO_2 group.[44] The probable conclusion is that the inductive effect of this unusual substituent is rather different in the gas phase and in solution but one cannot exclude the possibility that it is not well described by our theoretical model. Note that this shortcoming has nothing in common with the above conclusions concerning the negative hyperconjugation.

$$\text{3-SF}_5\text{C}_6\text{H}_4\text{COOH} + \text{C}_6\text{H}_5\text{COO}^- = \text{3-SF}_5\text{C}_6\text{H}_4\text{COO}^- + \text{C}_6\text{H}_5\text{COOH} \quad (6)$$

$$\text{4-SF}_5\text{C}_6\text{H}_4\text{COOH} + \text{C}_6\text{H}_5\text{COO}^- = \text{4-SF}_5{\cdot}\text{C}_6\text{H}_4\text{COO}^- + \text{C}_6\text{H}_5\text{COOH} \quad (7)$$

Conclusions

When the substituent effects are formally separated into inductive and resonance components, it may happen that the physical meaning is not quite evident; the term resonance means here merely the difference between the behaviour in aromatic and aliphatic (conjugated and unconjugated) systems. The substituents CF_3, SF_5 and SCF_3 appear as strong resonance acceptors. If this may be pictured by any canonical formulae, one must use the no-formulae (negative hyperconjugation) like for instance **1A,B**, **2A,B**, **3B**. It was shown here that this purely formal description has some predicative power. It predicts correctly that the bonds to fluorine are weakened and elongated and that the molecule is stabilized by conjugation with a donor; all these effects increase steeply with the strength (electron supply) of the donor. It was found several times that oversimplified resonance formulae may account correctly for some but not for all observable quantities.

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