ORIGINAL RESEARCH

Pushing and pulling electrons: the effect on the heat of formation of trifluoromethyl compounds

John E. Bartmess · Joel Liebman

Abstract The effect on heats of formation, of conjoined or proximate functional groups which can interact via polar or resonance effects, is examined using the –CF$_3$ group as a standard. Two metrics are applied: the difference in heat of formation of G–CF$_3$ and G–CH$_3$, where –G is a wide range of functional groups, and also the deviation of the heat of formation of G–CF$_3$ from the average of the heats of formation of G–G and CF$_3$–CF$_3$. This latter metric reveals both stabilizing and destabilizing effects on the heat of formation, of up to 60 kcal/mol, depending on the polar and resonance nature of the –G structure. The possibility of using such metrics as a correction the group additivity values is examined.

Keywords Negative hyperconjugation · Group additivity values · Electronegativity · Heats of formation

Introduction

It is well established that a difference in electronegativity results in a stronger bond between atoms; the converse of this is the basis of Pauling's definition of electronegativity

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[1]. As an example, the bond dissociation energy (BDE) of 67 kcal/mol (1 kcal/mol = 4.184 kJ/mol) in the interhalogen compound IF is 30 kcal/mol stronger than the average of the BDEs of F_2 at 37 kcal/mol and of I_2 at 36 kcal/mol [2]. This can be attributed to the electrostatic attraction of the atoms strengthening the bond, beyond that expected from its covalent nature alone. This should also be expected to result in a more negative gas phase heat of formation (HOF) of such compounds, though in the case of the halogens, this is partially obscured by the situation of the halogens being elements, with heat of formation defined as zero. Nevertheless, the HOF of gaseous IF at −22.9 kcal/mol [2] is clearly more negative than that of F_2 or I_2.

In a more general sense, such stabilization is not limited to an electronegativity difference, but could be due to any structural effect where electron density is redistributed in a molecule, such as by resonance or polar effects. An example from organic chemistry is *p*-nitroaniline. Were there no interaction between the two functional groups, the first isodesmic reaction in Scheme 1 should be thermoneutral. In fact, in the gas phase, it is exothermic by −4.1 ± 0.9 kcal/mol [3], consistent with quinonoid structure **1b** providing extra stability to that compound. For *m*-nitroaniline, where polar but not through-resonance interactions can occur, only −2.4 kcal/mol of stabilization is seen relative to the additive effects [4]. In contrast, *p*-diaminobenzene is less stable by +1.9 ± 0.8 kcal/mol than predicted by additivity [5], and *p*-dinitrobenzene less stable by +1.2 ± 0.9 kcal/mol [6, 7].

Such through-resonance interactions provide a clear rationale for such effects, and a means to determine where such effects may operate, if not the exact numeric value involved. In the second isodesmic reaction in Scheme 1, without the intervening benzene ring, an exothermicity of −37.8 kcal/mol is found or −18.9 kcal/mol per new bond [8].

Scheme 1 Isodesmic Reactions Affected by "push–pull" Interactions
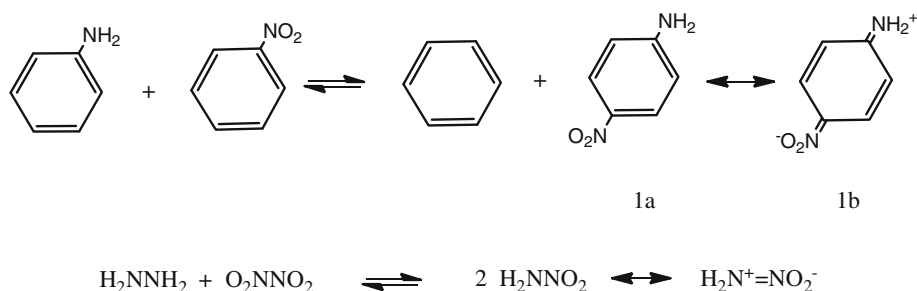
There are additional examples in the literature of this effect. Boyd and coworkers [9, 10] and others [11, 12] showed experimentally that successive replacement of hydrogen by cyano groups in ethylene results in ever-larger increases in the HOF of these nitriles beyond simple additivity, from 32 kcal/mol for the first introduction, to 44 kcal/mol for the fourth. The second carbomethoxy substitution into benzene in the either meta or para positions results in a destabilization enthalpy of ca. 2 kcal/mol [13] greater than expected based on additivity; comparable effects of successive cyano and nitro substitution into benzene are also observed [14]. Computationally, multiple substitutions of the nitro group into cubane yield ever-larger increases in the HOF, beyond $n = 4$, though steric effects likely play a part there as well [15]. Successive substitution of cyano for hydrogen in methane results in ever-larger increases in the HOF of $CH_{4-n}(CN)_n$, $n = 0–4$ [16, 17]. The experimental HOF of $ClCH_2CN$ is 9 kcal/mol more positive than expected from the sum of the effects of substitution into methane of each of those substituents alone [18]. All of these cases are for substituents that are strong electron-withdrawing groups, by both resonance and polar/inductive effects. For fluorine substitution into methane, $CH_{4-n}F_n$, $n = 0–4$, increasingly effective stabilization per fluorine is seen for $n = 0–3$. The fourth substitution is still stabilizing but less so than the third [16, 17]. This effect is likely due to the versatile nature of the fluoro substituent as both a resonance donor and a polar/inductive withdrawing group.

Thus, any molecule A–B, where one moiety is a good electron-donating group (EDG), and the other a good electron-withdrawing group (EWG), would be expected to have a more negative HOF than if A or B was neither of these cases. This is the classic "push–pull" stabilization [1]. Likewise, as noted above for the dinitrobenzene, if both A and B are EWGs, then a "pull–pull" destabilization results, and if both are EDGs as in diaminobenzene, a "push–push" destabilization occurs.

This principle is only minimally taken into consideration in group additivity schemes, such as that of Benson et al. [19], for obtaining HOFs, notably when both groups are on the same atom. The group additivity value (GAV) for the same substructure varies with its attachment to different atom types, but there are relatively few more distant structure corrections in the Tables, notably steric corrections for 1,4-groups, cis, and ortho structures. We contend that this is an oversimplification, because the presence of the "push–pull" or "pull–pull" effects considered here is likely to alter HOFs from the parent cases.

In order to determine whether this concept is operative, two metrics are used here. First, the difference in HOFs of a series of compounds consisting of the trifluoromethyl group, a good EWG, bonded to a number of groups –G ranging from good EDGs to good EWGs, is compared to the same series with –G bonded to the relatively electron-neutral methyl group. We define

$$\gamma = \Delta_f H^o(GCF_3) - \Delta_f H^o(GCH_3) \qquad (1)$$

The –CF_3 group was chosen because it is regarded primarily a polar/inductive withdrawing group, with relatively little resonance interaction [20–22]. The latter assumption will be investigated below. The –CN group has a lower steric demand, but resonance can clearly be large there, so it is not as good a choice for this first examination. We will reserve examination of charged –G groups for future investigation. The approach exemplified by reaction (1) is directed toward the possible use of this concept in corrections to group additivity schemes [19, 23].

A second approach uses the HOFs of the same GCF_3 compounds, compared to the average of the HOFs for the GG and CF_3CF_3 compounds:

$$\varepsilon = \Delta_f H^o(GCF_3) - \left[\Delta_f H^o(CF_3CF_3) + \Delta_f H^o(GG)\right]/2 \qquad (2)$$

This is akin to Pauling's definition of electronegativity. Compared to the first approach, this requires one additional datum in the form of the HOF (GG). Unlike HOF (GCH_3), this is not available as an experimental value for many of the –G groups considered here and must be obtained in many cases from ab initio calculations. As will be seen, however, this second approach yields a cleaner dissection of inductive and resonance effects that the first method does.

In addition to the above GCF$_3$ series of compounds, the σ-insulated GCH$_2$CF$_3$ compounds will be analyzed by both metrics, in order to separate the inductive and resonance effects.

Computational

The Gaussian 03 program [24], implemented on a number of personal computers running Centos Linux, was used to obtain total energies and thermochemical values for the GCF$_3$, GCH$_3$, and GG molecules under consideration, where –G is a wide variety of groups. The G3(MP2)//B3LYP extrapolation method was used, so the geometries, frequencies, and thermal corrections to 298 K are at the DFT B3LYP/6-31G(d) level, and total energies are extrapolated from QCISD(T) and MP2Large calculations, with some empirical corrections [25]. Absolute HOFs were obtained via an automated atomization scheme [26]. As will be seen, these computational HOFs accurately reproduce experimental ones for the cases where the latter are available, as well as the trifluoromethyl for methyl substitution thermochemistry of interest. Experimental HOFs are mostly from the NIST Webbook [2] or the Pedley compilation [3].

Discussion

The group additivity scheme of Benson et al. [19] has only two GAVs for the –CF$_3$ group, attached to an sp^3 carbon (−161 kcal/mol) and to a benzene ring carbon (−162.7 kcal/mol). Relative to the corresponding –CH$_3$ group value (GAV = −10.2 kcal/mol for both attachments), this means that a CF$_3$ for methyl replacement should make the HOF more negative by −150.8 and −152.5 kcal/mol, respectively. Based on literature HOFs [3], the CF$_3$–C$_{sp3}$ value is from the HOF of CF$_3$CF$_3$, not CF$_3$CH$_3$. The latter compound yields a GAV(CF$_3$–C$_{sp3}$) of −168.2 kcal/mol [3], in the direction expected for a push–pull stabilization. This choice of the standard for the GAV indicates that Benson et al. were likely aware of the "push–pull" principle under discussion here.

The first quantity used here to examine push–pull and pull–pull effects is γ, as defined above in Eq. 1. A more negative γ value indicates that the trifluoromethyl structure is stabilized relative to the methyl form; a less negative value indicates destabilization of GCF$_3$ relative to GCH$_3$. It can be shown that

$$\begin{aligned}
&BDE(G - CF_3) - BDE(G - CH_3) \\
&= \Delta_f H^\circ(GCF_3) - \Delta_f H^\circ(GCH_3) - \Delta_f H^\circ(CF_3\cdot) + \Delta_f H^\circ(CH_3\cdot) \\
&= 146.4 \pm 0.6\,\text{kcal/mol} - \gamma
\end{aligned}$$

(3)

so γ is also related to the relative bond strengths of these compounds. Table 1 reveals that for 16 of 17 cases where experimental data for γ are available, it agrees with γ_{calc} to within 2 kcal/mol, and 12 of those 17 are within 1.0 kcal/mol. These groups extend over the entire range of donors to withdrawing groups. Only CF$_3$CH=CH$_2$ is outside the 2.0 kcal/mol range, at −3.7 kcal/mol. Likewise, in absolute values of HOF, 61 of the 68 GCH$_3$ compounds have a calculated atomization HOF within 2.0 kcal/mol of the experimental HOF. We thus accept that the calculated γ values are good enough to allow us to greatly extend the range of –G groups.

An examination of the γ_{calc} values reveals that they vary over a range of 36 kcal/mol, though centered about the expected −152 kcal/mol value indicated above from the GAVs. The experimental γ values, although more limited in number, likewise vary over a 33 kcal/mol range. Inspection of Table 1, presented in γ_{calc} order, reveals that qualitatively the data agree with the premise that EWGs, such as –NO$_2$, –CN, –SO$_2$Y, and –C(=O)Y, increase the HOF (=destabilize) of GCF$_3$ relative to GCH$_3$, being a pull–pull effect. These lie in the first part of the table. In contrast, EDGs like alkyl, –OR, –NR$_2$, and –halo stabilize the compounds in a push–pull effect and are in the latter part of the Table.

Can this be put on a more quantitative basis, perhaps to predict the change in HOF of GCF$_3$ from a simple GAV calculation? The –CF$_3$ group can accept electrons via negative hyperconjugation [20], so both inductive/polar and resonance effects must be considered in any scheme. To separate these effects, it is seen that for the GCH$_2$CF$_3$ structures, where the π-insulating CH$_2$ group prevents any resonance interaction between G and CF$_3$, a reasonably linear ($r = -0.965$) correlation of γ_{calc} with the inductive substituent constant σ_I(–G) is observed, as in Fig. 1, with $\rho_I = 15.9 \pm 1.2$ (in kcal/mol units, not pK$_a$). If –tBu, with the largest deviation of all, at 2.1 kcal/mol less stable than the regression line, is excluded for steric reasons, the new regression line ($r = 0.975$) has an rms deviation of 0.8 kcal/mol and a maximum deviation of 1.8 kcal/mol for the cyano group, over a 15 kcal/mol range in γ. Should such a correlation hold valid over a wider set of XCH$_2$G structures, this would provide a needed source of GAVs for this sparsely populated set.

To obtain the corresponding ρ_I for GCF$_3$, however, one cannot automatically use the normal scaling factor of 2.0 per intervening methylene group [25] on ρ_I. That is for reactions where a full charge is developed, such as in acid/base reactions, clearly not the case here. There are σ_I values, however, for a limited number of –G = –CH$_2$Y groups. The γ_{calc} values correlate well with these ($r = 0.989$ for 5 points), as seen in Fig. 2, with

Table 1 Thermochemical results for GCF$_3$ and GCH$_3$

–G	HOF (GCH$_3$)[a]	HOF (GCF$_3$)[a]	γ_{calc}[c]	HOF (GCH$_3$)[b]	HOF (GCF$_3$)[b]	γ_{expt}[c]	$\gamma_{calc} - \gamma_{expt}$
–SO$_2$CF$_3$		−358.5	−133.8				
–SO$_2$CN	−26.1	−160.2	−134.2				
–SO$_2$F	−134.1	−268.3	−134.2				
–CN	17.6	−120.0	−137.6	17.7 ± 0.1	−118.4 ± 0.4[k]	−136.1	−1.5
–SO$_3$H	−127.0	−265.2	−138.2	−134.4 ± 2.2[d]			
–SOCF$_3$	−179.4	−317.5	−138.2				
–CFO	−105.1	−245.2	−140.1	−105.7 ± 0.8			
–SO$_2$NH$_2$	−80.1	−220.4	−140.2				
–SO$_2$Me	−84.3	−224.7	−140.4	−89.2 ± 0.7			
–COCF$_3$	−199.7	−340.3	−140.6		−334.0 ± 0.0[l]	0.0	
–BF$_2$	−192.3	−333.1	−140.8				
–COCN	−3.3	−144.5	−141.2				
–COCl	−57.7	−199.3	−141.6	−58.0 ± 2.0			
–CF$_3$	−180.0	−322.3	−142.3	−178.0 ± 0.4	−321.3 ± 1.3	−143.3	1.0
–NO$_2$	−17.0	−159.3	−142.3	−17.8 ± 0.2			
–CO$_2$H	−102.6	−245.8	−143.2	−103.4 ± 0.6	−246.5 ± 0.4	−143.1	−0.1
–SCF$_3$	−161.0	−305.2	−144.2				
–CO$_2$Me	−97.8	−242.5	−144.7	−98.8 ± 0.4			
–COSH	−43.0	−187.8	−144.7	−41.8 ± 2.0			
–SiH$_3$	−5.8	−150.6	−144.8	−7.0 ± 2.0[e]			
–SOMe	−34.2	−179.4	−145.2	−36.2 ± 0.2			
–AlH$_2$	18.7	−126.6	−145.3				
–BH$_2$	9.5	−136.2	−145.8				
–C$_6$F$_5$	−203.6	−349.4	−145.8	−201.4 ± 0.4	−303.4 ± 1.9	−102.0	−43.8[n]
–C≡CH	44.0	−102.0	−146.0	44.2 ± 0.2			
–CHO	−39.6	−185.8	−146.2	−39.8 ± 0.1			
–CF$_2$H	−120.3	−267.0	−146.8	−118.8 ± 2.0			
–NC	41.8	−105.1	−146.9				
–COPh	−20.7	−168.4	−147.7	−20.7 ± 0.4			
–CH$_2$SO$_2$CF$_3$	−230.9	−378.7	−147.8				
–CONH$_2$	−54.9	−203.1	−148.2	−57.0 ± 0.2			
–AlMe$_2$	−10.9	−159.2	−148.3				
–NO	17.4	−130.9	−148.3	16.7 ± 0.7			
–CONMe$_2$	−53.4	−201.9	−148.4	−55.6 ± 0.9[f]			
–COMe	−51.2	−199.7	−148.4	−51.9 ± 0.2			
–PH$_2$	−3.8	−152.6	−148.8				
–CH$_2$NO$_2$	−24.1	−173.1	−149.0	−24.5 ± 0.2			
–H	−17.4	−166.5	−149.1	−17.8 ± 0.1	−166.2 ± 0.6	−148.4	−0.7
–CH$_2$SO$_2$Me	−90.3	−239.7	−149.4				
–SiMe$_3$	−50.6	−200.3	−149.7	−55.7 ± 0.8[g]			
–Cl	−19.4	−169.7	−150.3	−19.6 ± 0.1	−168.8 ± 0.5	−149.2	−1.1
–SH	−5.7	−156.1	−150.5	−5.5 ± 0.1			
–BMe$_2$	−24.0	−174.9	−150.9	−29.3 ± 2.5[h]			
–PMe$_2$	−23.3	−174.1	−150.9	−24.2 ± 1.2[h]			
–CH$_2$SOCF$_3$	−185.3	−336.7	−151.4				
–SPh	22.0	−129.7	−151.8	23.3 ± 0.2			
–SMe	−9.0	−161.0	−152.0	−8.9 ± 0.1			
–CH$_2$CF$_3$	−184.9	−337.2	−152.3	−184.0 ± 2.0[i]			

Table 1 continued

–G	HOF (GCH$_3$)[a]	HOF (GCF$_3$)[a]	γ_{calc}[c]	HOF (GCH$_3$)[b]	HOF (GCF$_3$)[b]	γ_{expt}[c]	$\gamma_{calc} - \gamma_{expt}$
–CH$_2$F	−64.8	−217.7	−152.9				
–CH$_2$CN	13.3	−139.8	−153.2	12.4 ± 0.2			
–ONO$_2$	−28.5	−182.1	−153.6				
–CH$_2$Cl	−26.3	−180.0	−153.6	−26.8 ± 0.1			
–CH$_2$CO$_2$H	−107.7	−262.1	−154.3	−108.3 ± 0.1			
–CH=CH$_2$	4.7	−150.6	−155.3	4.8 ± 0.2	−146.8 ± 1.6[m]	−151.6	−3.7
–Ph	11.6	−144.0	−155.6	12.1 ± 0.1	−143.2 ± 0.2	−155.3	−0.3
–CH$_2$CO$_2$Me	−101.9	−257.7	−155.7				
–OCN	0.7	−155.2	−155.9				
–CH$_2$COMe	−56.4	−212.3	−155.9	−57.0 ± 0.2			
–CH$_2$OH	−55.6	−212.5	−156.8	−56.2 ± 0.2	−211.3 ± 0.3	−155.1	−1.7
–OCF$_3$	−212.5	−369.2	−156.8				
–CH$_2$SH	−11.0	−168.5	−157.5	−11.0 ± 0.1			
–CH$_2$NH$_2$	−10.8	−169.0	−158.2	−11.4 ± 0.1			
–CH$_2$tBu	−43.1	−202.2	−159.1				
–CH$_2$Ph	6.6	−152.9	−159.5	7.1 ± 0.3			
–Me	−19.5	−180.0	−160.4	−20.0 ± 0.1	−179.0 ± 0.7[i]	−159.0	−1.4
–tBu	−39.3	−199.8	−160.5	−40.1 ± 0.2			
–Et	−24.4	−184.9	−160.6	−25.0 ± 0.1			
–CH$_2$SiMe$_3$	−52.6	−215.3	−162.7				
–OPh	−17.5	−182.1	−164.6	−16.2 ± 0.2			
–NMe$_2$	−4.9	−169.9	−165.0	−5.4 ± 0.3			
–F	−56.3	−222.9	−166.6	−56.0 ± 2.0[j]	−223.3 ± 0.4	−167.3	0.7
–NH$_2$	−4.1	−171.0	−166.9	−5.6 ± 0.2			
–OMe	−43.6	−212.5	−168.9	−44.0 ± 0.1			
–OtBu	−67.4	−236.7	−169.3	−67.8 ± 0.1			
–OH	−47.7	−217.3	−169.5	−48.2 ± 0.1	−217.3 ± 0.9[o]	−169.1	−0.4
–OSiMe$_3$	−107.1	−280.1	−173.0				

All data in kcal/mol

[a] Calculated from G3(MP2)//B3LYP calculations (Frisch et al. [24]) via heat of atomization; see text

[b] Experimental; from Pedley [3] unless otherwise stated

[c] From Eq. 1

[d] Guthrie and Gallant [32]

[e] Walsh [33]

[f] Beak et al. [34]

[g] Pedley and Rylance [7]

[h] Steele [35]

[i] Kolesov and Papina [36]

[j] Chase [37]

[k] Ruscic et al. [38]

[l] Gordon [39]

[m] Pedley [3]

[n] The experimental HOF of C$_6$F$_5$CF$_3$ disagrees with the computational HOF by +44 kcal/mol, and with that from group additivity by +48 kcal/mol. A redetermination appears to be in order
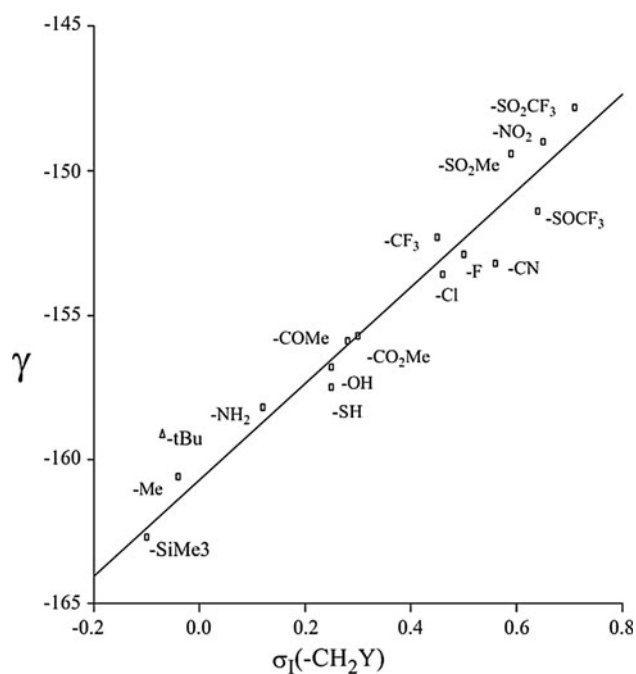
[o] Asher et al. [40]

Fig. 1 γ_{calc}(–G) from Eq. 1 and Table 1 versus σ_I(–CH$_2$Y) from Table 2

Fig. 2 γ_{calc}(–G) from Eq. 1 and Table 1 versus σ_I(–G) from Table 2

$\rho_I = 28.2 \pm 2.3$ and intercept $= -159.2 \pm 0.3$. This line provides a measure of the inductive component of the effect, based on σ_I(–G) values, and the deviation of γ_{calc} for GCF$_3$ from this can thus be taken as the value of the resonance interaction. In Table 2, the first 5 points define the ρ_I line. For the later points, it is seen that many of the groups usually regarded as resonance-withdrawing (carbonyl, cyano, sulfone) show a positive deviation from the inductive line and can be considered destabilized via a pull–pull effect. In contrast, the good resonance donor groups such as –OR, –NR$_2$, and –halo have negative deviations and are thus stabilized via a push–pull effect. However, there are both resonance donor (–SR) and withdrawing groups (–NO$_2$, –NO) that show little deviation, and non-resonance interacting groups that are very destabilized (–H, –SiMe$_3$). At the minimum, the correlation shows that both the polar/inductive and resonance effects are important. Attempts at multiple regressions, using σ_I and various measures of resonance [26] such as σ_R, σ_R+, and σ_R^-, yield poor correlations. This is in part due to a general lack of values for many of the groups here, but also because the substituent parameters mentioned above are largely established based on resonance interaction with the planar sp^2 carbon of a benzene ring, a very different resonance structure than the threefold symmetry of the sp^3 bonding –CF$_3$ group. It is not surprising therefore that the correlation is only semi-quantitative. The best predictor found was σ_{meta}, usually taken as roughly half inductive and half resonance [26]. As shown in Fig. 3, there is
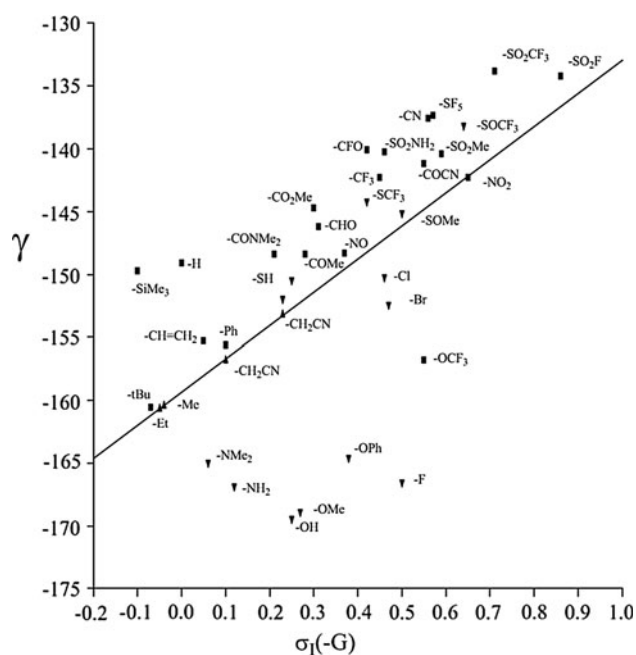
considerable scatter ($r = 0.71$), but if the obvious good lone-pair resonance donor molecules are excluded (–OH, –OR, –NH$_2$, –NR$_2$, –F) plus a few other outliers, a moderate correlation ($r = -0.970$, $\rho = 30.3 \pm 1.3$, intercept $= -157.2 \pm 0.5$) is found. The good donors cited above are more stable than the correlation predicts, by 12–20 kcal/mol for –OR and –F, and by 3–5 kcal/mol for the amines. The –NO and –NO$_2$ groups are more stable than the line, while –SiH$_3$, –SiMe$_3$, –H, –PH$_2$, –PR$_2$, and –BF$_2$ are less stable. The deviations for the silyl and phosphino groups are interesting, in that the thiol and sulfide groups are very close to the line. Interestingly, for the good EDGs –NR$_2$ and –OR, the methylated version is less effective as a donor (less negative γ) than for R = H, while for –BR$_2$, –AlR$_2$, –SiR$_3$, –PR$_2$, and –SR, the methylated versions are better donors than for R = H.

Several subsets of the groups also show good correlations with inductive substituent constants versus γ_{calc}. As above for the –CH$_2$Y groups, the –C(=O)Y, –SO$_2$Y, and –OY structures show linear and parallel ($\rho_I = 17 \pm 3$) correlations with σ_I(–Y), though the data are too sparse to draw strong conclusions from.

What of the charges on the groups? The difference in the Mulliken charges on the –CF$_3$ versus the –CH$_3$ groups shows no correlation ($r < 0.2$) at the B3LYP, QCISD(T), or MP2Large levels involved in the G3(MP2)//B3LYP calculations, when plotted versus γ_{calc}. Use of the CHelpG charges [28] at the B3LYP/6-31G* level is little better with $r = 0.32$ for the same charge difference versus γ_{calc}.

Table 2 σ_I(–G) versus γ_{calc}

–G	σ_I^a	γ^b	Deviation^c
–CH$_2$CN	0.23	−153.2	−0.4
–CH$_2$Cl	0.17	−153.6	0.8
–CH$_2$OH	0.10	−156.8	−0.4
–Me	−0.04	−160.4	−0.0
–Et	−0.05	−160.6	0.0
–SiMe$_3$	−0.10	−149.7	12.3
–H	0.00	−149.1	10.1
–CFO	0.42	−140.1	7.3
–SO$_2$NH$_2$	0.46	−140.2	6.1
–CN	0.56	−137.6	5.8
–SO$_2$CF$_3$	0.71	−133.8	5.4
–CONMe$_2$	0.21	−148.4	4.9
–CHO	0.31	−146.2	4.3
–CF$_3$	0.45	−142.3	4.2
–SCF$_3$	0.42	−144.2	3.2
–COMe	0.28	−148.4	2.9
–COCN	0.55	−141.2	2.5
–CH=CH$_2$	0.05	−155.3	2.5
–SO$_2$Me	0.59	−140.4	2.2
–SH	0.25	−150.5	1.7
–Ph	0.10	−155.6	0.8
–SO$_2$F	0.86	−134.2	0.8
–SMe	0.23	−152.0	0.7
–tBu	−0.07	−160.5	0.7
–NO	0.37	−148.3	0.5
–SOMe	0.50	−145.2	−0.1
–NO$_2$	0.65	−142.3	−1.4
–Cl	0.46	−150.3	−4.0
–NMe$_2$	0.06	−165.0	−7.5
–NH$_2$	0.12	−166.9	−11.0
–OCF$_3$	0.55	−156.8	−13.1
–OPh	0.38	−164.6	−16.1
–OMe	0.27	−168.9	−17.3
–OH	0.25	−169.5	−17.3
–F	0.50	−166.6	−21.6

^{a} From Hine [27]

^{b} From Eq. 1 as derived in Table 1, kcal/mol

^{c} Deviation in kcal/mol from the least squares line of the first 5 points

Table 3 ε values and associated thermochemistry

G	HOF (GG)^a	HOF (GG)^b	ε^c
–SOCF$_3$	−333.8		10.5
–SOMe	−53.4		8.4
–SCF$_3$	−302.7		7.3
–NO	47.1	42.1 ± 1.1^d	6.6
–SO$_2$Me	−138.3		5.6
–CN	72.3	73.3 ± 0.2	5.0
–SO$_2$CF$_3$	−404.5		4.9
–C≡CH	108.8	105.0^e	4.7
–PH$_2$	7.9	5.0^f	4.6
–SO$_2$NH$_2$	−126.7		4.2
–SPh	54.5	58.2 ± 1.0	4.1
–SO$_3$H	−215.8		3.8
–SO$_2$CN	−5.2		3.5
–C$_6$F$_5$	−383.5	−302.2 ± 1.4^g	3.5
–COSH	−59.9		3.3
–SH	3.8	3.7^f	3.1
–SMe	−5.7	−5.9 ± 0.2	3.0
–CO$_2$H	−175.3	−173.0 ± 1.1	3.0
–SO$_2$F	−218.6		2.1
–COCN	29.3		1.9
–COCl	−79.7	−78.5 ± 1.1	1.6
–CH$_2$SO$_2$Me	−160.0		1.5
–CONMe$_2$	−84.3		1.5
–CFO	−171.1		1.4
–CHO	−51.9	−50.7 ± 0.2	1.3
–PMe$_2$	−28.4		1.2
–SiH$_3$	18.8	19.2^f	1.2
–COCF$_3$	−360.1		0.9
–CH$_2$SO$_2$CF$_3$	−436.8		0.8
–COMe	−78.4	−78.2 ± 0.3	0.7
–CH$_2$NO$_2$	−25.0		0.6
–CO$_2$Me	−163.5	−162.7 ± 0.3^h	0.4
–COPh	−15.3	−13.3 ± 0.3	0.4
–NO$_2$	3.2	2.2^f	0.3
–CF$_3$	−322.3	−321.3 ± 1.3^i	0.0
–CF$_2$H	−211.5		−0.2
–AlH$_2$	69.4		−0.2
–CH$_2$SOCF$_3$	−348.2		−1.4
–CONH$_2$	−81.0	−92.5 ± 0.3	−1.5
–BH$_2$	53.2		−1.7
–CH$_2$CF$_3$	−348.3		−1.9
–CH=CH$_2$	25.9	26.3 ± 0.2	−2.4
–BF$_2$	−339.1	−344.2^f	−2.4
–CH$_2$Cl	−31.9	−31.0 ± 0.4	−2.9
–CH$_2$F	−107.3		−2.9
–Ph	40.6	43.1 ± 0.8^j	−3.1
–CH$_2$CN	50.5	50.1 ± 0.1	−3.9
–AlMe$_2$	12.1		−4.1

The one structural parameter which yields even a moderate correlation ($r = 0.92$) with γ_{calc} is the difference in the G–CH$_3$ versus G–CF$_3$ bond lengths, for the B3LYP/6-31G* structures. For the donor groups ($\gamma_{calc} < -155$ kcal/mol), the G–CF$_3$ bond is shorter than the G–CH$_3$ bond, and the opposite holds for the withdrawing groups, as seen in Fig. 4.

The second metric taken here in analyzing these data is based on Eq. 2. The quantity ε is the square of the relative

Table 3 continued

G	HOF (GG)[a]	HOF (GG)[b]	ε^c
–BMe$_2$	−8.7		−4.2
–CH$_2$COMe	−93.7		−4.3
–CH$_2$CO$_2$Me	−184.4		−4.3
–CH$_2$CO$_2$H	−193.2	−196.7 ± 0.8	−4.3
–H	−1.1	0.0[k]	−4.9
–CH$_2$OH	−92.9	−93.7 ± 1.0	−4.9
–SiMe$_3$	−66.3	−73.0 ± 1.8[l]	−6.1
–CH$_2$NH$_2$	−3.1	−4.3 ± 0.2	−6.3
–CH$_2$SH	−1.7	−2.3 ± 0.3	−6.5
–CH$_2$Ph	31.9	34.1 ± 0.3	−7.7
–Cl	0.7	0.0[k]	−8.9
–Me	−19.5	−20.0 ± 0.1	−9.0
–Et	−29.3	−30.0 ± 0.1	−9.2
–CH$_2$SiMe$_3$	−87.8		−10.3
–tBu	−53.6	−54.0 ± 0.3	−11.8
–CH$_2$tBu	−67.0	−68.0[m]	−12.3
–NC	145.0		−16.5
–NMe$_2$	21.6		−19.5
–NH$_2$	24.7	22.8[f]	−22.2
–ONO$_2$	8.8		−25.4
–OCN	76.2		−32.2
–OCF$_3$	−348.4	−360.2 ± 3.2[n]	−33.9
–OtBu	−80.9	−83.4 ± 0.7	−35.1
–OPh	28.7		−35.3
–OMe	−28.3	−30.0 ± 0.3	−37.2
–OH	−31.6	−32.5[o]	−40.3
–OSiMe$_3$	−150.7		−43.6
–F	1.4	0.0[k]	−62.5

All data in kcal/mol

[a] Calculated from G3(MP2)//B3LYP calculations via heat of atomization; see text

[b] Experimental; from Pedley [3] unless otherwise stated

[c] From Eq. 2

[d] Forte and Van den Bergh [41]

[e] Stein and Fahr [42]

[f] Wagman et al. [43]

[g] Pedley et al. [44]. This values seriously disagrees with group additivity (−378 kcal/mol) and with G3(MP2)//B3LYP calculations (−383 kcal/mol), which agree reasonably

[h] Chickos et al. [45]

[i] Chase [37]

[j] Roux et al. [46]

[k] By definition: element

[l] Davalos and Baer [47]

[m] Doering et al. [48]

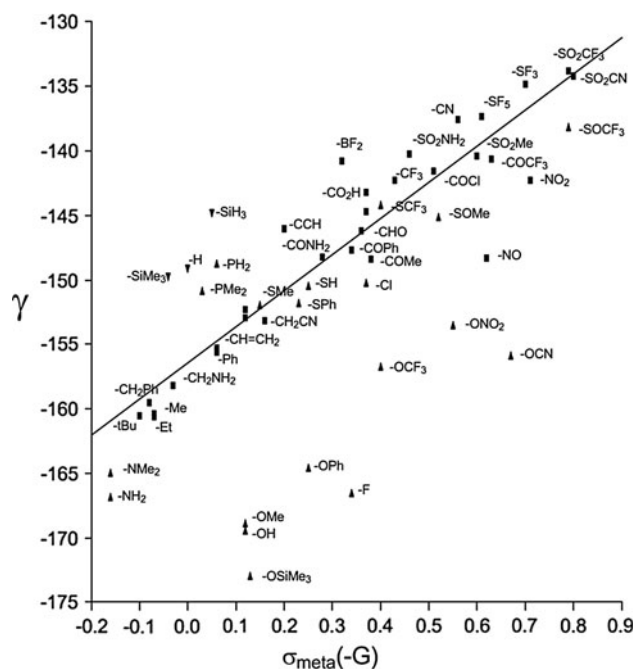[n] Levy and Kennedy [49]

[o] Dorofeeva [50]

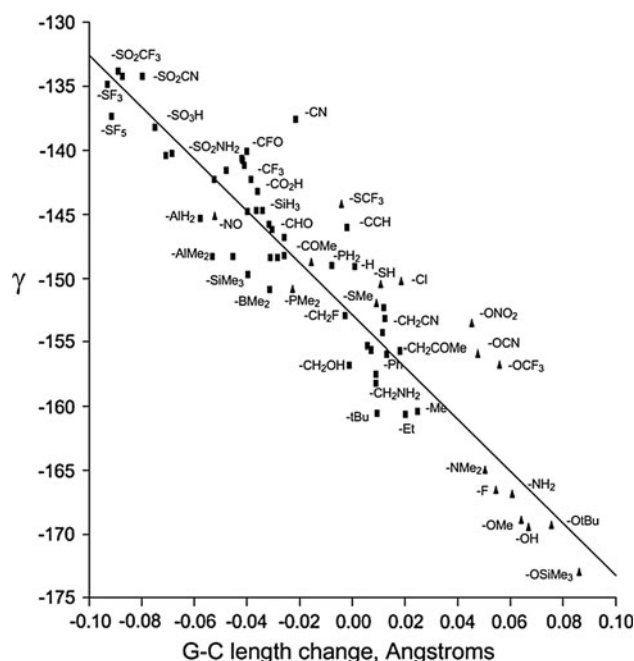**Fig. 3** γ_{calc}(–G) from Eq. 1 and Table 1 versus σ_{meta}(G) from Ref. [26]

Fig. 4 γ_{calc}(–G) from Eq. 1 and Table 1 versus G–C bond length change, of G–CH$_3$ − C–CF$_3$. Some points' labels omitted for clarity

group electronegativity difference, in kcal/mol units, and as given is the stabilization or destabilization of the HOF of the heterofunctional compound GCF$_3$ from the average of the values of the two homofunctional ones, CF$_3$CF$_3$ and
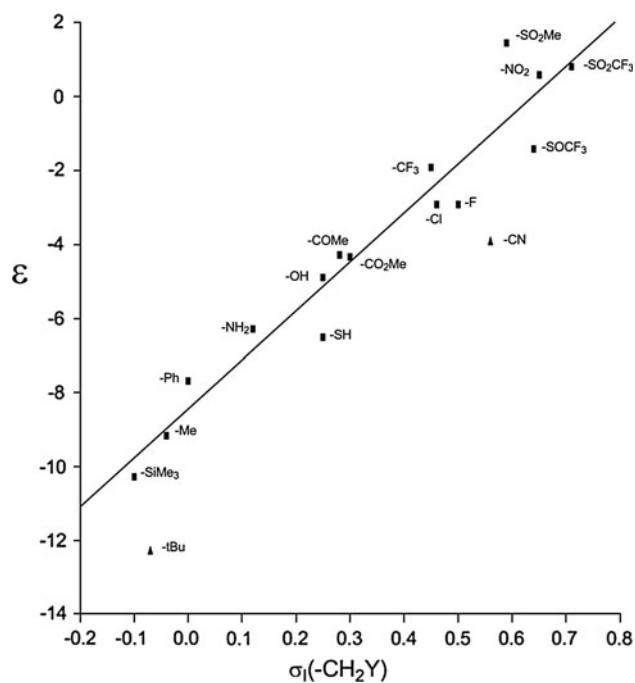
Fig. 5 ε_{calc}(–G) from Eq. 2 and Table 3 versus σ_I(–CH$_2$Y) from Table 2

Fig. 6 ε_{calc}(–G) from Eq. 2 and Table 3 versus σ_I(–G) from Table 2. Some points not labeled for clarity

GG. Pauling's original thermochemical definition of electronegativity is given by Eq. 4:

$$(EN_A - EN_B)^2 = [BDE(A - B) - \tfrac{1}{2}[BDE(A - A) + BDE(B - B)]]/23.06 \quad (4)$$

but because

$$BDE(A - B) = \Delta_f H^o(A\cdot) + \Delta_f H^o(B\cdot) - \Delta_f H^o(AB) \quad (5)$$

it can be shown that

$$(EN_A - EN_B)^2 = -[\Delta_f H^o(AB) - \tfrac{1}{2}[\Delta_f H^o(AA) + \Delta_f H^o(BB)]]/23.06 \quad (6)$$
$$= -\varepsilon/23.06$$

For $A =$ –CF$_3$ and $B =$ –G, all appropriate $\Delta_f H^o$(GG) values have been calculated at the G3(MP2)//B3LYP level, as was done for the GCF$_3$ compounds. Taking the same approach as with γ, for the GCH$_2$CF$_3$ compounds versus σ_I(–G), a good correlation is seen in Fig. 5 with $\rho_I = 13.4 \pm 1.1$, intercept $= -8.9 \pm 0.4$, $r = 0.954$. As with γ, –tBu deviates the most but here in the direction of greater stability. Similar to Fig. 1, the least sterically demanding cyano group is more stable than the line by ca. 2 kcal/mol. Excluding those two groups, the rms deviation is only 0.6 kcal/mol, thus providing a second method for obtaining GAVs of a wide variety of GCH$_2$X structures.

When ε for GCF$_3$ is plotted versus σ_I(–G) as per Fig. 6, it is seen that the great majority of groups follow a roughly linear correlation ($\rho_I = 15.1 \pm 2.0$, intercept $= -5.8 \pm 0.8$,
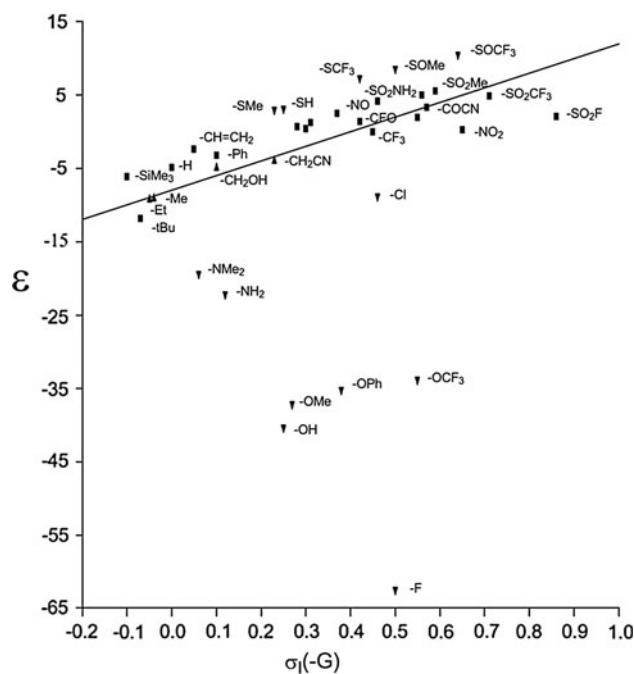
$n = 22$, $r = 0.864$) with a scatter of about ± 4 kcal/mol. Using the –CH$_2$Y groups alone, $\rho_I = 20.0 \pm 3.8$, with $r = 0.92$. The groups that appreciably deviate from this line—and on specific structural grounds were not included in the correlation—are those with lone pairs on the attached atom in –G. These fall on lines roughly parallel to the stated one. Fluorine, with three lone pairs, is 64 kcal/mol more stable than expected; the –OR groups are ca. 36 kcal/mol, and the –NR$_2$ groups are 16 kcal/mol more stable. This pattern can be rationalized as due to negative hyperconjugation [20] where the lone pairs, as available, can overlap with the C–F orbitals to create resonance stabilization. The size of the effect is remarkable, when clearly separated from the polar effect, compared to known negative hyperconjugation effects [20]. The second row group –Cl has only 10 kcal/mol extra stabilization, much less than –F. This is attributable to the poorer overlap of its larger lone pairs with the C–F bonds. The –SR groups are an average of 6 kcal/mol *destabilized* relative to the correlation line, but again in a line fairly parallel to the main line. In light of the result for –Cl, it would not be surprising if the –SR groups were on the main line, but the observed destabilization, though small, is unexpected.

Wells [29] has compiled a set of group electronegativities from a variety of sources. For 19 of these, corresponding to species here, negligible correlation ($r = 0.093$) is seen with the γ_{calc} values. Taking the more likely second approach of Eq. 2, relative EN values are obtained from Eq. 4 and anchored to EN(H) = 2.28. For the non-lone-
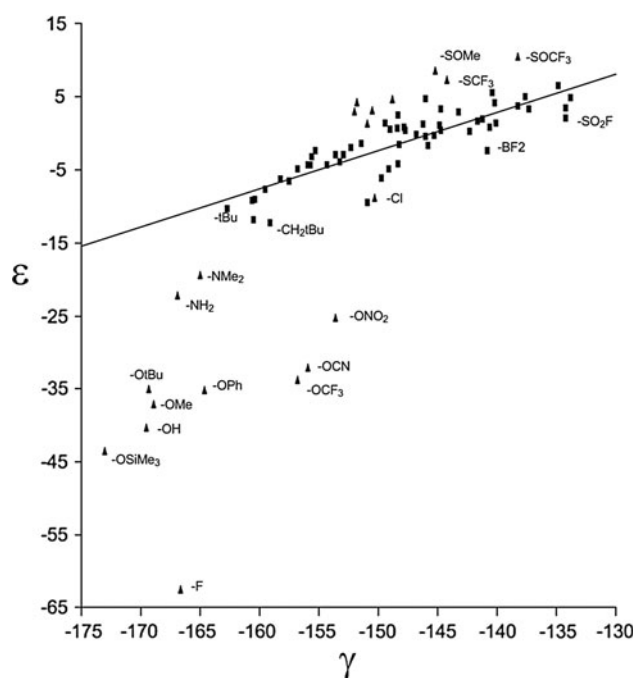
Fig. 7 $\varepsilon_{calc}(-G)$ from Table 3 versus $\gamma_{calc}(-G)$ from Table 1. Only outlying points labeled, for clarity

pair groups (unfortunately only about half of Wells' well-established EN values), an r value of 0.56 is found for the EN values derived here versus Wells' values. This poor correlation does not invalidate this approach to obtaining group EN values, but does imply, however, that a much large data set beyond the common –CF$_3$ group is needed to test this idea.

As with the first method, an examination of bond lengths in the GCF$_3$ molecules shows a correlation with ε of $r = -0.59$ for the non-lone-pair-bearing substituents, with the EDGs having longer bonds, and those with lone pairs having shorter than expected C–C bonds than predicted by the correlation stated.

Finally, is there anything new to be learned from the more computationally intensive ε versus the γ metric? Figure 7 shows these plotted against each other. It is clear that there is considerable correlation, save for the lone-pair donor groups, which show much greater stabilization in the GCF$_3$ compounds by ε than by γ.

Conclusions

Can any of the above be used to predict HOFs, as perhaps a modifier to GAVs? As noted above, the correlations of σ_I with γ and ε provide a means for obtaining GAVs for a range of GCH$_2$CF$_3$ structures. The other correlations do not appear to be good enough to use in this context, although

they do shed light on the quantitative size of negative hyperconjugative interactions. The extension of these ideas to other pairs of functional groups besides –CF$_3$ and –CH$_3$ is being pursued, e.g., we recall that a rough constancy of the differences of heats of formation of G–CF$_3$ and G–COOH was suggested in the literature [30, 31].

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