Inductive Effects in Isolated Molecules: 4-Substituted Bicyclo[2.2.2]octane-1-carboxylic Acids

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Abstract: Energies of sixteen 4-substituted bicyclo[2.2.2]octane-1-carboxylic acids, their anions, and pertinent 1-substituted bicyclo[2.2.2]octanes were calculated within the framework of density functional theory at the B3LYP/6-311 + G(d,p) level. Substituent effects were evaluated separately in the acid molecule and in the anion in terms of isodesmic homodesmotic reactions. In both cases, the substituent effects are proportional and of opposite sense, that in the anion being eight times greater; in the effect on acidity they are summed. The calculated acidities are in agreement with experimental values with a standard deviation of 1.1 kJ mol^{-1}, and are recommended as a model for evaluating the inductive effect of various substituents, whether they are experimentally accessible or not. The resulting values are closely related to other scales but can be determined more reliably, particularly when compared with the previous quantum chemical method. We also checked electrostatic calculations and confirmed their very approximate character, particularly in the case of unsymmetrical substituents or of substituents with zero dipole moment.

Keywords: ab initio calculations · acidity · carboxylic acids · inductive effect · linear free-energy relationships

Introduction

The classical theory of substituent effects[1] is based on equilibrium and rate constants in solution, mostly in aqueous solvents. In the most important case, the substituent effect may be defined as the Gibbs energy (or enthalpy) of an isodesmic reaction, in which a proton is transferred from a substituted Brønsted acid to the unsubstituted conjugated base, as for instance in Equation (1).

(1)

The substituent effects are further classified into inductive, resonance, steric, and so on, with respect to the structure of compounds in the defining reaction. Of these, the inductive effect has been one of the basic concepts in organic chemistry, although some modern textbooks treat is as something less important.[2] The purpose of the bicyclo[2.2.2]octane skeleton in Equation (1) is to eliminate any conjugation or steric interaction and to guarantee operation of the pure inductive effect.[3] Several simpler or more sophisticated model systems have been advanced with the same intention;[4, 5] some of which have been based on NMR shifts rather than on reactivities.[6]

The above definitions suffer from two defects. In addition to the hardly predictable solvent effect, there is a problem in that only a difference between two species, that is, an acid and the pertinent anion (or a base and the cation), is measured. More recently, acid–base equilibria were also studied in the gas phase,[7] mostly with the result that the substituent effects are nearly proportional to those in water but are much stronger. The second problem mentioned can be solved by means of isodesmic reactions,[8] in which a disubstituted molecule is constructed from two monosubstituted molecules[9, 10] [see Eq. (2) below as an example]. In this way, substituent effects can be investigated independently in the acid molecule and in its anion; they need not be always parallel.[11]

Alternatively, the inductive effect has been evaluated by quantum chemical calculations on an unnatural model system consisting of two molecules kept at a fixed distance.[12] In spite of all of the problems mentioned, it was stated several times that all scales of the inductive effect are closely correlated, their differences only slightly exceeding the experimental errors.[4, 6, 13]

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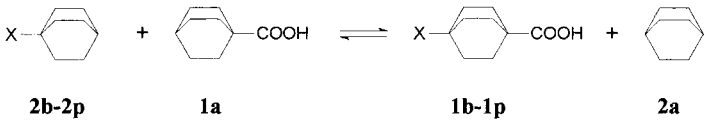
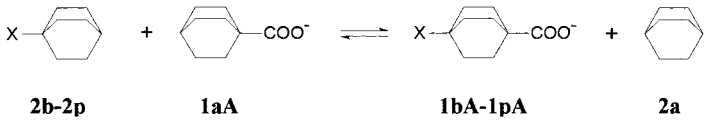
The purpose of this paper is to provide a scale of the inductive effect, free of solvent effects, that is easily reproducible and generally applicable, and is based on quantum chemical calculations but related to real molecules and observable quantities. We turned back to 4-substituted bicyclo[2.2.2]octane-1-carboxylic acids **1**, introduced into correlation analysis by Roberts and Moreland[3] and generally accepted as a model defining the pure inductive effect.[4, 7b] Their acidities have been measured in a variety of solvents,[14] even in the gas phase;[7b,c] their isomers and further derivatives of bicyclo[2.2.2]octane have been investigated to the same end.[15] Some quantum chemical calculations on **1** have been carried out at lower levels.[7c, 16] Previously, we calculated the energies of **1a** and **1f** at the MP2/6-31G(d,p) level.[11] The purpose of that study was to follow the general character of the inductive effect on compounds of different structure.

An additional aim of this study was to compare the acids **1** with substituted benzoic acids. Much discussion was devoted to the relative intensity of transmission of substituent effects through these two systems;[4, 17] this is of importance when the substituent resonance effect is to be estimated as their difference in transmission.[5a, 17]

Energies of compounds **1a**–**1p** were calculated within the framework of density functional theory[18] at the B3LYP/6-311+G(d,p) level. This model is relatively ambitious at present for molecules of this size, but it was chosen in order to obtain results comparable with our previous studies.[19–21] The principle of isodesmic reactions was applied in the same way as in previous studies of the inductive,[11] resonance,[19] and steric[21] effects. The substituent effects in **1** were evaluated as the reaction energy Δ_2E(DFT) of the isodesmic reaction given in Equation (2) and effects in the anions **1A** by the energy Δ_3E(DFT) of the isodesmic reaction Equation (3). The relative acidity is then given by the reaction energy Δ_1E(DFT) of Equation (1) and was obtained as a difference $\Delta_1E(\mathrm{DFT}) = \Delta_3E(\mathrm{DFT}) - \Delta_2E(\mathrm{DFT})$. Equations (1)–(3) are also homodesmotic.[8b]



2b-2p **1a** **1b-1p** **2a** (2)



2b-2p **1aA** **1bA-1pA** **2a** (3)

Results and Discussion

Conformation: According to an older electron diffraction study,[22] the molecule bicyclo[2.2.2]octane (**2a**) is twisted (symmetry D_3) with a dihedral C1-C2-C3-C4 angle of 12°. We have found smaller twisting in **2a** (3.6°); the more symmetrical D_{3h} conformation represents a transition state and the energy barrier is low. We calculated it to be 0.08 kJ mol^{-1}. In the carboxylic acids **1**, the twisting is variable according to the substitution. It is almost zero in the unsubstituted acid **1a** (the C1-C2-C3-C4 angle is 0.2°) and with simple substituents (F, Cl, CN, NH_2), but it becomes evident with unsymmetrical and heavy substituents (OCH_3 12°, NO_2 10°, *t*Bu 19°). In the anions, it is always smaller.

With carboxylic acids **1**, an additional possibility of conformations arises. In the lowest-energy conformer (all Δ_2E values of Table 1) the C=O bond is flanked with one C–H

Table 1. Calculated energies and some geometric parameters of 4-substituted bicyclo[2.2.2]octane-1-carboxylic acids **1a**–**1p**, their anions **1aA**–**1pA** and 1-substituted bicyclo[2.2.2]octanes **2a**–**2p**.[a]

	Substituent	**1**			**1A**			**2**
		E(DFT)	C(1)–C(O)	∢C2C1C6	*E*(DFT)	C(1)–C(O)	∢C2C1C6	*E*(DFT)
a	H	–502.0040490[b]	1.518	121.4	–501.4461049	1.581	128.8	–313.3717029
b	CH_3	–541.3307024	1.519	121.4	–540.7735208	1.581	128.8	–352.6984378
c	$C(CH_3)_3$	–659.2912139	1.516	121.4	–658.7340393	1.578	128.8	–470.6583232
d	CH_2Cl	–1000.9529522	1.519	121.5	–1000.4012316	1.581	129.0	–812.3212816
e	CF_3	–839.1579047	1.519	121.7	–838.6101006	1.581	129.1	–650.5264681
f	$COOCH_3$	–729.9454387	1.519	121.6	–729.3924918	1.581	129.0	–541.3136251
g	CN	–594.2690371	1.521	121.8	–593.7252153	1.583	129.3	–405.6383402
h	NH_2	–557.3746061	1.519	121.4	–556.8191921	1.582	128.9	–368.7426325
i	$N{=}NCH_3{-}(E)$	–650.8110563	1.518	121.5	–650.2571813	1.580	128.9	–462.1790586
j	NO_2	–706.5712585[c]	1.519	121.9	–706.0284317	1.581	129.3	–517.9406034
k	OH	–577.2508001	1.519	121.5	–576.6976473	1.582	129.0	–388.6191211
l	OCH_3	–616.5563777	1.518	121.5	–616.0021383	1.580	128.9	–427.9244130
m	F	–601.2806499	1.519	121.7	–600.7310719	1.582	129.1	–412.6494679
n	Cl	–961.6334543	1.520	121.7	–961.0857345	1.583	129.2	–773.0023372
o	NH_3^+	–557.7422889	1.527	123.5	–557.2914584	1.598	131.6	–369.1160143
p	O^-	–576.6529175	1.512	119.4	–575.9946978	1.578	126.7	–388.0129694

[a] Calculated at the B3LYP/6–31+G(d,p) level, energies in a.u., bond lengths in Å, angles in degrees. [b] The minimum-energy conformation *sp* (the C=O bond eclipsed with one C–C bond); in the conformation *sc* (C–O and C–C bonds eclipsed) there is a secondary minimum with *E*(DFT) –502.0031502 kJ mol^{-1}. [c] Conformation *sp*,*sc* (C=O eclipsed with one C–C bond, N–O with another C–C bond); in *sp*,*sp* conformation (both C=O and N–O eclipsed with the same C–C bond) *E*(DFT) is –706.5711192 kJ mol^{-1}.

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bond, in the second conformer it is the C–OH bond. The energy difference calculated for **1a** is 2.36 kJ mol^{-1}. It could be of some significance in the calculation of absolute acidities, but cannot be observed in the isodesmic reactions [Eqs. (1) and (2)], since it is virtually equal in different acids **1a**–**1p**.

In the nitro acid **1j** and in its anion **1jA** we must still consider the relative position of the two functional groups. The C=O and N–O bonds are both flanked with one C–C bond, but can lie either in different planes (the minimum-energy conformation, Table 1) or in the same plane. However, the calculated energy difference is only 0.37 kJ mol^{-1}. Therefore all conclusions can be based on the least-energy conformation (calculated without any symmetry precondition) and all possible conformations neglected. This is a sufficient approximation for the present purpose and makes the compounds **1** very suitable models as compared, for instance, with the substituted benzoic acids with their numerous conformers.[20]

Comparison with experimental results: The calculated relative acidities Δ_1E can be compared with the experimental acidities $\Delta_1G^\circ(298)$ measured by Fourier transform ion-cyclotron resonance.[7c] The fit (Table 2, entry 1) is the best hitherto achieved;[23, 24] the standard deviation SD is not far from the experimental uncertainty, which is estimated[7c] to be 0.84 kJ mol^{-1} (possibly a little underestimated). In our opinion, our theoretical model is sufficiently precise for the purpose given. Combination of DFT with isodesmic reactions yields a much better precision than the original cautious estimate of Becke himself[18] and is in our opinion more effective than the system of Allinger,[26] which introduces empirical parameters. In any case, it is incomparably better than calculations at STO-3G level with the standard geometry[7c] (Table 2, entry 2). On the other hand, there are no experimental values comparable with Δ_2E, since the necessary enthalpies of formation Δ_fH°(g) are not available. Even when some values were available, their accuracy would not be sufficient according to a recent analysis of Δ_fH°(g) of aromatic derivatives.[27]

Our further conclusions will be based on the calculated values $\Delta_1E - \Delta_3E$, with the presumption that their agreement with experiment has been proven.

Substituent effects in both the acid and anion: These effects are given separately in Table 3 as Δ_2E and Δ_3E. As expected, the effect in the anion Δ_3E is of deciding magnitude; the Δ_2E values are approximately eight times smaller and have opposite sign. A detailed comparison is shown in Figure 1, in which we have omitted the charged substituents whose values are incomparably large. Figure 1 reveals a significant

Table 2. Correlations of the acidities of 4-substituted bicyclo[2.2.2]octane-1-carboxylic acids **1a**–**1n** and of scales of the inductive effect.

Entry	Response function	Explanatory variables	b[a]	R[b]	SD[b] [kJ mol^{-1}]	N[b]
1	Δ_1E this work	Δ_1G° exp[c]	0.96(3)	0.9968	1.13	9
2	Δ_1E ref. [7c]	Δ_1G° exp[c]	0.92(15)	0.929	5.54	8
3	Δ_2E this work	Δ_3E this work	– 0.127(9)	0.975	0.33	13[c]
4	σ_I calcd ref. [12b]	Δ_1E this work	– 0.0136(19)	0.908	0.083[d]	13
5	σ_I calcd ref. [7b]	Δ_1E this work	– 0.0168(11)	0.976	0.050[d]	13
6	^{19}F shifts ref. [6]	Δ_1E this work	7.5(8)	0.949	0.066[d]	13
7	σ_I ref. [4]	Δ_1E this work	– 0.0176(19)	0.943	0.082[d]	13
8	Δ_1G° sol. ref. [14c,d]	Δ_1E this work	0.150(17)	0.963	0.067[d]	8
9	Δ_3E *m*-Bz[e]	Δ_3E this work	1.16(4)	0.9978	1.12	6[e]

[a] Regression coefficient with the standard deviation in parentheses. [b] Correlation coefficient, standard deviation from the regression (in kJ mol^{-1} unless otherwise noted). [c] Only dipolar substituents; *t*Bu omitted as outlier. [d] Recalculated to the σ units scale. [e] Substituent effect in the anions of 3-substituted benzoic acids, ref. [20], only nonconjugated substituents.

Table 3. Calculated and experimental substituent effects in 4-substituted bicyclo[2.2.2]octane-1-carboxylic acids [kJ mol^{-1}, 298 K].

	Substituent	Δ_1E[a]	Δ_1G°[a,b]	Δ_2E[a]	Δ_3E[a]	Δ_2E_{el}[a]	Δ_3E_{el}[a]	σ_I calcd	σ_I calcd[c]
a	H	0	0	0	0	0	0	0	0
b	CH_3	– 1.93	– 4.2	0.21	– 1.72	0	0	0.03	0.00
c	$C(CH_3)_3$	– 1.94		– 1.38	– 3.32	0	0	0.03	0.00
d	CH_2Cl	– 15.72		1.71	– 14.02	~ 0.9	– 6.4	0.26	0.22
e	CF_3	– 25.62	– 27.2	2.30	– 23.32	0.6	– 10.7	0.43	0.44
f	$COOCH_3$	– 12.63		1.35	– 11.28			0.21	0.24
g	CN	– 35.68	– 36.0	4.17	– 31.51	1.3	– 29.3	0.60	0.60
h	NH_2	– 6.39		0.94	– 5.45	~ – 0.3	~ 2.2	0.11	0.14
i	N=NCH$_3$–(*E*)	– 10.28		0.88	– 9.40	0	0	0.17	0.14[e]
j	NO_2	– 38.19	– 36.8	4.27	– 33.92	1.1	– 25.9	0.64	0.63
k	OH	– 12.11		1.69	– 10.42			0.20	0.30
l	OCH_3	– 9.36	– 10.9	0.96	– 8.40			0.16	0.25
m	F	– 21.14[d]	– 23.4	2.94[d]	– 18.20[d]	1.2	– 18.2	0.36	0.44
n	Cl	– 25.83	– 25.9	3.11	– 22.73	1.1	– 17.3	0.43	0.45
o	NH_3^+	– 270.62		15.34	– 255.28	6.8	– 223.3	4.55	2.00[e]
p	O^-	253.35		– 19.21	234.14	– 7.2	222.8	– 4.26	– 1.80[e]

[a] Subscript at Δ corresponds to the number of the isodesmic equation. [b] Experimental gas-phase acidities, ref. [7c]. [c] Ref. [7b]. [d] At the MP2/6–31G(d,p) level, we previously calculated Δ_1E –22.2, Δ_2E 3.5, Δ_3E – 18.7 kJ mol^{-1}, ref. [11]. [e] Calculated by us according to the method of ref. [12].

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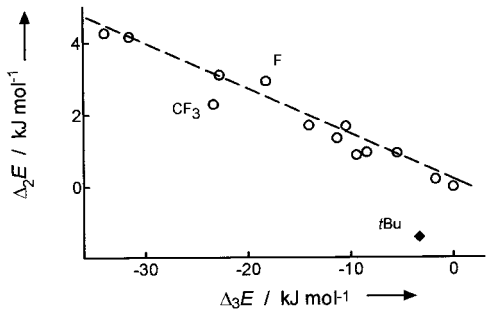

Figure 1. Comparison of substituent effects in the anions, ΔE_3, and in the acid molecules, ΔE_2, of 4-substituted bicyclo[2.2.2]octane-1-carboxylic acids **1**.

deviation of the substituent $C(CH_3)_3$; the negative Δ_2E implies an unexpected stabilization of 4-*tert*-butyl-bicyclo[2.2.2]octane-1-carboxylic acid (**1c**). We have no clear explanation for this deviation, although some deformations of geometry were observed, for instance the C(4)–C bond length of 1.582 or 1.584 Å in **1c** and **1cA**, respectively. Irregular behavior of the substituent $C(CH_3)_3$ has previously been encountered.[21d] When this substituent is eliminated, the substituent effects Δ_2E and Δ_3E are proportional with a good precision (Table 2, entry 3) and both affect the acidity in the same sense. This behavior makes bicyclo[2.2.2]octane-1-carboxylic acids a suitable model for defining and estimating the substituent effect as compared for instance with substituted acetic acids or substituted trimethyl amines, in which the effects in neutral molecules are hardly predictable,[11] or with substituted pyridines[25a] and bicyclo[2.2.2]octane-1-carbonitriles,[11] in which the effects in the base and in the cation are of the same sign and their action on the basicity are partly cancelled.

Note that this approach allows for the determination of substituent effects even if the pertinent compounds do not exist in the proper tautomeric form. The compound **1p** does not exist in the $^-OC_8H_{12}COOH$ structure, but rather as $HOC_8H_{12}COO^-$ (**1kA**), as seen from the energies in Table 1 (difference 117 kJ mol^{-1}). Similarly the anion **1oA** exists as **1h** (energy difference 218 kJ mol^{-1}). The extremely shifted tautomeric equilibria do not prevent calculation of the inductive effect of substituents O^- and NH_3^+.

Our data also allows efficient testing of the classical electrostatic approach.[28] Within the framework of this theory, the inductive effect is expressed by Equation (4) as a Coulombic interaction of the anionic charge and a dipolar substituent; in the case of a charged substituent Equation (5) is appropriate.

$$\Delta E_{el} = eN_A\mu\cos\theta/r^2(4\pi\varepsilon_o\varepsilon_{ef}) \quad (4)$$

$$\Delta E_{el} = e^2N_A/r(4\pi\varepsilon_o\varepsilon_{ef}) \quad (5)$$

In these equations, r is the distance between the substituent and the charge, μ is the dipole of the substituent (considered as a point dipole), and θ is the angle formed by the vectors r and μ. The effective relative permittivity ε_{ef} is usually taken as equal to unity in the gas phase.[28a] Better agreement with experiment was sometimes obtained when interaction in the neutral acid was also taken into account.[29] In the case of dipolar substituents, it is an interaction between two dipoles, μ_1 and μ_2, at the angles θ_1 and θ_2, respectively [Eq. (6)].[28a, 30]

$$\Delta E_{el} = -N_A\mu_1\mu_2(2\cos\theta_1\cos\theta_2 - \sin\theta_1\sin\theta_2)/r^3(4\pi\varepsilon_o\varepsilon_{ef}) \quad (6)$$

We may test Equations (4) and (5) separately by comparing with Δ_3E, and Equation (6) by comparing with Δ_2E. Table 3 reveals that the agreement is merely qualitative in character. The theory correctly predicts the signs and roughly also the relative values; Δ_3E_{el} is much greater than Δ_2E_{el}. Also the relation of charged and dipolar substituents is predicted correctly.[31] However, all values are too small, both for dipolar and charged substituents, as found previously in the comparison with experimental data in many examples.[28a] In contrast to solution data, this disagreement cannot be explained by a particular value of effective permittivity, since $\varepsilon_{ef} < 1$ would be required. Possible correction for the finite dipole length[30] in Equation (4) is irrelevant for these compounds and would not improve the fit. Particular failure was observed for the substituent NH_2, whose dipole is in a reversed position, and for $N{=}NCH_3$ with its zero dipole moment. Incompatibility of such substituents with the electrostatic approach has been previously pointed out,[13] but experimental data have been lacking. Also the substituent CH_2Cl is predicted poorly; Equation (4) generally overestimates the effect of the angle θ.[28a] In conclusion, the electrostatic approach is unacceptable, although it gives a better fit than could be expected from such a rough approximation. The main objection is that there is no reason to use it when much more efficient calculation is possible. Some reasonable results obtained[23, 29] were conditioned by omitting the critical substituents and favorably choosing some disposable parameters, such as the position of the point dipole or position of the charge.[32] When the electrostatic calculations are applied to solution data,[3, 14, 15a] the effective permittivity ε_{ef} becomes the decisive quantity.[33]

Substituent effects on the geometry: Changes of bond lengths or bond angles caused by the inductive effect have not been proven in a convincing way. Data in Table 1 reveal minute changes by dipolar substituents both on the COOH and COO^- groups, perhaps only some widening of the OCO angle in COO^- may be significant. On the other hand, the effect of charged substituents is evident and is similar in the acid molecule and in the anion. It can be described that by being electron-withdrawing, the COOH and COO^- groups become less firmly bound to the rest of the molecule.

Scales of the inductive effect: It was recognized several times that inductive substituent effects are very nearly proportional in reaction series that involve compounds of different structure and particularly with very different measured quantities.[4, 6, 12b, 13, 23] Several suggested scales of constants σ_I have been evaluated mainly according to the attainable accuracy, general applicability, and possible technical difficulties;[4, 6, 12] their mutual compatibility has not been questioned. We recently had the opportunity to compare the most important scales with larger sets of substituents.[12b] All scales

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were closely related, but are not quite identical; the best agreement was between acidities in water;[4, 5c] the ^{19}F NMR shifts were somewhat different.[6]

We used our calculated acidities Δ_1E as reference and correlated the known scales with them (Table 2, entries 4–7). Reasonable fit was observed with σ_I from the ^{19}F shifts[6] or from the acidities of substituted acetic acids;[4] the best fit was obtained with values of inexact origin related to gas-phase acidities.[7b] Even the acidities of the acids **1** in 50% ethanol yielded a good correlation, but the number of data is not sufficient (Table 2, entry 8). Most remarkable is the relatively bad correlation with the quantum chemical calculations of an artificial model,[12b] (Table 2, entry 4). The greatest disagreement was found in the case of charged substituents O^- and NH_3^+ (Table 3, the last two entries); we attribute it to the inconsistency of the artificial model.

We suggest our values of Δ_1E as a new measure of the inductive effect. To convert them to the scale comparable with the standard σ_I, they must by scaled according to Equation (7).

$$\sigma_I = -0.0168\Delta_1E \quad (7)$$

The new values of σ_I are given in Table 3 and compared with the standard values. Compared with the previous quantum chemical calculations,[12] we see two main merits of our approach: it avoids ambiguities in defining the right geometry and it is related to real molecules. The latter property also means that the model is not definitely fixed and can be improved introducing higher-level calculations. On the other hand, we believe that the level applied by us is completely sufficient with respect to the required accuracy of σ_I.

Inductive effect in benzene derivatives: Comparison of the [2.2.2]bicyclooctane and benzene series was of fundamental importance to the general theory of substituent effects. Assuming that the inductive effect is equal, the contribution of resonance was evaluated as a simple difference.[5a]

This procedure has been made more precise[17a] and has been discussed many times.[17] We now have data free of any solvent effect for both the acids **1** and benzoic acids;[20] still more precisely, we can compare only the effects in the anion to avoid some complications in the molecules of benzoic acids.[20] As expected, Figure 2 reveals good linearity for unconjugated substituents without a lone electron pair in the α-position; other substituents deviate according to the degree of their resonance effect. The slope of the linear dependence, 1.16, is with certainty greater than unity (Table 2, entry 9) and is in agreement with an estimate from solution reactivities[17a] (1.10), but at variance with an estimate from the mere geometry.[17c] This value must be applied as a correction before a resonance effect is calculated; it is particularly important for acceptor substituents.

Conclusion

The proposed model has twofold meaning. On the one hand, it can be regarded as a definition of the inductive effect, connecting it with quantum chemical terms. On the other hand, it provides a quantitative scale of inductive constants based on observable quantities of real isolated molecules (as compared with the model of Marriott and Topsom).[12a] Hence it is a method of choice for determining the inductive constant of any new group. It is easier to apply than any experimental determination; in common cases it can be experimentally checked, but can be extended even to inaccessible unstable compounds (for instance the substituent O^-). The properties of isolated molecules can serve as a reference in studying solution reactivity, as there is little difference with many compounds.

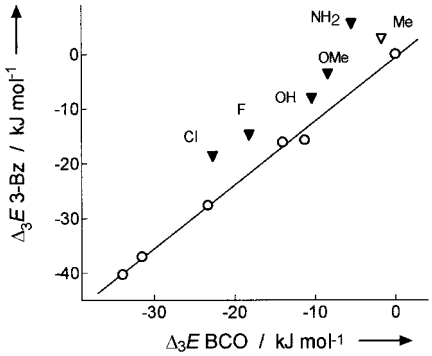

Figure 2. Plot of the substituent effects in the anions of 4-substituted bicyclo[2.2.2]octane-1-carboxylic acids (**1a**–**1p**) and 3-substituted benzoic acids; ○ acceptor substituents without a lone electron pair in the α-position, ▼ donor substituents bearing this electron pair, ▽ methyl substituent; the regression line belongs to the first group.

Scales of the inductive effect are not identical, but are very closely related, despite being obtained from calculations on real molecules or on artificial models, from the gas-phase reactivities, NMR spectra, or from pK values of various acids and bases. Close similarity of the results proves the inductive effect to be a general principle. This has now also been confirmed by its unambiguous proof in neutral molecules. In our opinion, the inductive effect should receive more attention in fundamental textbooks.[2]

Computational Methods

The DFT calculations at a B3LYP/6-311 + G(d,p) level were performed according to the original proposal[18] by using the standard program.[35] All energy-optimized structures were checked by vibrational analysis. No symmetry conditions were presumed except the assumed transition state of **2a**, which was assigned fixed D_{3h} symmetry.

Calculation of the constants σ_I proceeded strictly according to the proposed model,[12] at the level RHF/4-31G.

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[33] We consider here the electrostatic calculations only as a tool for approximate prediction of the acidities. We do not discuss their function in defending the transmission "through space" versus the transmission "through bonds", refs. [17d, 28b,c, 34]. In our opinion (ref. [28a]), the problem is ill formulated.
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