Group Electronegativities from Benzene Ring Deformations: A Quantum Chemical Study

Anna Rita Campanelli

Department of Chemistry, University of Rome "La Sapienza", I-00185 Rome, Italy

Aldo Domenicano* and Fabio Ramondo

Department of Chemistry, Chemical Engineering and Materials, University of L'Aquila, I-67100 L'Aquila, Italy

István Hargittai

Institute of General and Analytical Chemistry, Budapest University of Technology and Economics and
Structural Chemistry Research Group of the Hungarian Academy of Sciences at Eötvös University,
H-1521 Budapest, P.O. Box 91, Hungary

Received: January 12, 2004; In Final Form: March 19, 2004

We propose a new scale of group electronegativities, derived from benzene ring deformations in Ph−X molecules. A recent analysis of such deformations (Campanelli, A. R.; Domenicano, A.; Ramondo, F. *J. Phys. Chem. A* **2003**, *107*, 6429) has shown that two orthogonal linear combinations of the internal ring angles, termed S_E and S_R, are directly related to the electronegativity and resonance effects of the substituent, respectively. In the present paper, we show that S_E increases linearly with the electronegativity of X within each of the first two rows of the periodic table, acting as a sensitive indicator of the polarity of the Ph−X bond. By using S_E values from ab initio quantum chemical calculations, we have derived the electronegativities of 100 organic and inorganic groups. Nonbonded interactions with the ortho hydrogens and carbons may fictitiously alter the electronegativity of a group; in most cases, however, they are easily eluded by changing the conformation of the substituent with respect to the benzene ring. Although the atom directly linked to the ring tends to dominate the electronegativity of a group, the role of its adjacent atoms is also important. Their effect depends markedly on the nature of chemical bonding and electron density distribution within the group.

1. Introduction

The concept of electronegativity, defined by Pauling as "the power of an atom in a molecule to attract electrons to itself",[1] is one of the most widely used concepts in chemistry and has allowed the correlation and explanation of an impressive number of observations. Although originally considered as an invariant property of atoms,[2−5] electronegativity was soon deemed to depend on hybridization[6] and oxidation state[7]—in other words, on the nature and number of surrounding atoms in the molecule. During the 1960s, Jaffé and co-workers introduced the idea of orbital electronegativity,[8] implying that the electronegativity of an atom depends on the nature of the orbitals involved in bonding and on the partial charge residing on it.

The extension of the concept of electronegativity from atoms to groups of atoms developed naturally from these ideas.[9] Many scales measuring the electronegativity of groups have been proposed, based on a variety of methods, including (i) Huheey's scale,[10] based on complete equalization of electronegativity for all atoms within the group; (ii) Mullay's scale,[11] based on partial electronegativity equalization; (iii) Boyd and Boyd's scale,[12] derived from a topological property of the electron density distribution of the H−X bond (where X is the group for which the electronegativity is determined), namely, the position of its critical point; (iv) Reed and Allen's scale,[13] based on the bond polarity index of the Me−X bond, a quantum-mechanical parameter quantifying the ionicity of the bond;[14] (v) Suresh and Koga's scale,[15] derived from the molecular electrostatic potential at the C−X bond critical point in Me−X molecules, combined with the distance of the critical point from the methyl carbon; (vi) Marriott et al.'s scale,[16] based on the hydrogen charge densities in H−X molecules, as determined by Mulliken population analysis; (vii) the intrinsic group electronegativity scale proposed by De Proft et al.,[17] based on the ionization energies and electron affinities of radicals, as determined by MO calculations at the CISD level; (viii) the empirical ι scale introduced by Inamoto and Masuda,[18] modeled on a method originally developed by Gordy.[4] The agreement between these various scales is far from excellent.

Estimating electronegativities on the basis of geometrical variations has been an attractive approach because molecular geometries could be determined reliably. An early attempt utilized the experimentally determined variations of the S═O bond distances in XSO_2Y sulfones to estimate the electronegativities of the X and Y groups.[19] In general, however, the uncertainties in the experimental results and the fact that some important groups may not be amenable to experimental determination presents limitations in such an approach.

The substituted benzene derivatives are one of those series of substances whose molecular geometry has been extensively investigated. When a hydrogen atom of the benzene molecule is substituted by a different atom or group, changes occur in the ring geometry. In the majority of cases, the deformation conforms to C_{2v} symmetry and is most pronounced in the ipso

---

* Corresponding author. Fax: 39-0862-433753. E-mail: domenica@univaq.it.

10.1021/jp040013p CCC: $27.50

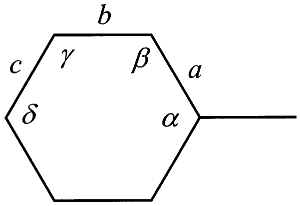

Figure 1. Lettering of the C−C bonds and C−C−C angles in a monosubstituted benzene ring of C_{2v} symmetry.

region; it involves bond distances as well as angles. The overall deformation depends on the nature of the substituent, reflecting its σ electronegativity, and to a lesser extent, its π donor/acceptor ability.[20] The changes of the α angle and of the *a* bond distances (Figure 1) can be explained in terms of hybridization effects at the ipso carbon[20a,21] or valence-shell electron-pair repulsions.[20a]

In 1975, a linear correlation was shown to exist between the α angle and the electronegativity of the substituent,[20b] using many experimental structural results on the phenyl derivatives of second-row elements.[22] Going from Al to Cl causes α to increase by some 5°. From this correlation, the actual electronegativities of phosphorus and sulfur in several classes of related compounds and individual molecules could be evaluated. Extension to first-row substituents proved difficult, however, since the pattern of benzene ring deformations was complicated by resonance effects. These are generally more pronounced with first-row substituents than with second-row ones. Nevertheless, the existence of a correlation between α and the electronegativity of first-row substituents emerged from the experimental data. With third-row substituents, the available structural data were scanty and less reliable, but again, they showed α to be an increasing function of the electronegativity of the substituent.[20b]

Separation of electronegativity and resonance effects acting on the benzene ring geometry was achieved in 1983,[23] through the statistical analysis of a large sample of monosubstituted benzene rings, the structures of which had been determined experimentally with reasonable accuracy. Most of the structures were from X-ray crystallographic studies. By using symmetry distortion coordinates, it was found that the angular variance of monosubstituted benzene rings is described by two orthogonal components of distortion, involving angular changes in different ratios. The component accounting for most of the variance is related to the σ electronegativity of the substituent, while the other component is related to the π donor/acceptor ability. The separation of the two components was not based on chemical considerations but originated directly from the statistical analysis of the data.

A recent analysis of the structures of 74 monosubstituted benzene derivatives, as determined by ab initio MO calculations at the HF/6-31G* level,[24] substantially improved and augmented the results of ref 23. Two orthogonal linear combinations of the internal ring angles, the structural substituent parameters S_E and S_R, were shown to be related to the electronegativity and resonance effects of a substituent, respectively. S_E and S_R values are obtained from the following equations:

$$S_E = 0.706\Delta\alpha - 0.956\Delta\beta + 0.044\Delta\gamma + 0.206\Delta\delta \quad (1)$$

$$S_R = 0.031\Delta\alpha + 0.291\Delta\beta - 0.999\Delta\gamma + 0.677\Delta\delta + 0.28° \quad (2)$$

where $\Delta\alpha = \alpha - 120°$, $\Delta\beta = \beta - 120°$, etc., for a monosubstituted benzene ring of C_{2v} symmetry.[25]

The S_E parameter is a sensitive indicator of the polarity of the Ph−X bond and promises to be particularly well-suited for constructing a group electronegativity scale. Its values span a considerably wide range, more than 16°. Being orthogonal to S_R, it is not affected by resonance interactions, insofar as these are not affecting the electronegativity of the group. It is easily determined by standard geometry optimization, also for experimentally unaccessible species and conformations. In the present paper, we show that S_E is linearly related to Pauling's electronegativity in each of the first two rows of the periodic table. Using these linear relationships, we derive a new scale of group electronegativities from the ring angles of 100 monosubstituted benzene derivatives, as determined by ab initio MO calculations at the HF/6-31G* level.

2. Factors Affecting the S_E Parameter

Although the polarity of the Ph−X bond is the main factor affecting S_E, other factors also play a role. Short contacts between the ortho hydrogens and/or carbons and the substituent cause a decrease of S_E,[24] leading to fictitiously low electronegativity values. Biphenyl is a conspicuous case, where S_E decreases by 2.48° in going from the orthogonal to the coplanar conformation of the molecule, due to strongly repulsive interactions between the hydrogens of the ortho bays. On the other hand, strongly attractive interactions involving the ortho hydrogens may lead to the opposite effect. This occurs, for example, in the benzoate anion, where S_E increases by 0.78° in going from the orthogonal to the coplanar conformation, due to attractive interactions between the ortho hydrogens and the negatively charged oxygen atoms of the carboxylate group.[24] In the majority of cases, repulsive or attractive interactions between the ring and the substituent are easily eluded by changing the conformation of the substituent with respect to the benzene ring.

Two further effects may cause the S_E parameter to vary. They are subtle consequences of resonance interactions; their very existence points to the fact that electronegativity is not unaffected by resonance.

The first effect originates from the transfer of π electrons. Interaction with the benzene ring diminishes the negative charge of a π donor substituent and—as a consequence—such a substituent appears to be more electronegative. The contrary is true of a π acceptor substituent.

The second effect is due to the shortening of the carbon-to-substituent (C−X) bond as its double-bond character increases. This leads to a decrease of α and increase of β (hence to a decrease of S_E, according to eq 1), irrespective of whether the substituent is a π donor or a π acceptor.[20a,24] The enhancement of electron density along the C−X bond—as it becomes shorter—makes X less electronegative. The two effects are generally small since the π charge transferred from the substituent to the benzene ring (or vice versa) seldom exceeds 0.15 electrons, and the shortening of the C−X bond upon conjugation usually amounts to only a few hundredths of an angstrom.[26] With π acceptor groups, the two effects act concurrently and may cause S_E to decrease somewhat, while with π donor groups, they act in a competing fashion and partially cancel each other. For nonlinear groups, the variation of S_E caused by these effects can be substantially reduced by selecting a conformation with minimum resonance interactions.

3. Analogies with Pauling's Procedure

The present procedure for determining the electronegativity of groups has some analogy with that adopted by Pauling[1,2] for determining the electronegativity of atoms. Pauling suggested that the difference between the electronegativities of atoms A and B is proportional to the square root of the difference between the energy of the A−B bond and the mean energy of the A−A and B−B bonds, ΔE_{AB}

$$\chi_A - \chi_B = k\Delta E_{AB}^{1/2} \tag{3}$$

Let us now consider a monosubstituted benzene derivative Ph−X, and let us increase the electronegativity of X in a regular fashion, starting from the point where the electronegativity of X equals that of the phenyl group, $\chi_X = \chi_{Ph}$. As the polarity of the Ph−X bond increases, the geometry of the substituted benzene ring is increasingly distorted along the S_E coordinate. It is in line with Pauling's ideas to assume that the electronegativity difference is proportional to the square root of the deformation energy

$$\chi_X - \chi_{Ph} = k\Delta E_{def}^{1/2} \tag{4}$$

In turn, the deformation energy is proportional to the square of the deformation in the harmonic approximation, as measured by the change in the S_E coordinate

$$\Delta E_{def} = k'\Delta S_E^{2} \tag{5}$$

where k' is a force constant. It follows that

$$\chi_X - \chi_{Ph} = k''\Delta S_E \tag{6}$$

Note that the origin of the deformation scale should not be set at unsubstituted benzene ($S_E = 0$) but rather at the point where the electronegativity of the substituent equals that of the phenyl group. The orthogonal conformation of biphenyl ($S_E = -1.62°$), where the geometry of the benzene ring is not perturbed by steric hindrance, is the obvious origin for first-row groups.

4. Selection of Groups

The substituents considered in the present study are listed in Table 1. They were chosen so as to include most of the common organic functional groups, as well as many inorganic groups. Also included are groups bearing a positive or negative charge or showing interesting chemical effects. Less common groups figuring in other electronegativity scales were included for comparison. Substituents containing atoms heavier than chlorine have not been considered, as they are less amenable to HF/6-31G* calculations. Among the Ph−X species considered are several molecules that we have studied experimentally by gas-phase electron diffraction.[27]

Many Ph−X molecules were studied in more than one conformation, to prove the effect of conformational changes on group electronegativity. To identify the conformation of a nonlinear group with respect to the benzene ring, we make use of the following terms and abbreviations. *Coplanar conformation* (c): this term applies to planar substituents that are coplanar with the benzene ring. It also applies to nonplanar substituents having C_s (or C_{3v}) symmetry, if their symmetry plane (or one of their symmetry planes) coincides with the plane of the ring. *Orthogonal conformation* (o): this term applies to planar substituents when the substituent plane is orthogonal to the plane of the ring and passes through the ipso and para carbons. It also applies to nonplanar substituents having C_s (or C_{3v}) symmetry, if their symmetry plane (or one of their symmetry planes) is orthogonal to the plane of the ring. *Pyramidal conformation* (p and p′): we use this term specifically when the first atom of the substituent has a pyramidal bond configuration with a lone electron pair at the top of the pyramid. A pyramidal conformation is denoted as p when the lone pair axis protrudes from the plane of the benzene ring, as in the equilibrium structure of aniline. It is denoted as p′ when the lone pair axis lies in the ring plane, as in the equilibrium structure of phenylphosphine.

5. Calculations

Ab initio MO calculations were carried out at the Hartree−Fock (HF) level with the 6-31G* basis set[28] and gradient optimization,[29] using the *Gaussian 98* package.[30] The HF level and the 6-31G* basis set were chosen for consistency with our previous work[24] and for their widespread use in the study of molecules of intermediate size. Their suitability to the scope of the present study was checked by HF and MP2(f.c.) level calculations with the 6-311++G** basis set, carried out on a large subset of the molecules investigated. Apart from the symmetry constraints specified in Table 1, geometry optimization was otherwise complete. The molecular geometry of biphenyl in its coplanar, orthogonal, and equilibrium conformation (dihedral angle 46°) was taken from the literature.[31] Natural bond orbital analyses[32] were carried out using the *NBO 3.0* program.[33] Most calculations were run on an Alpha AXP-3000/500 cluster at the University of Rome "La Sapienza".

6. Group Electronegativity Scale

To express our group electronegativities in Pauling units, we must calibrate the scale. The anomalous position of the point for unsubstituted benzene along the S_E axis—close to electronegative groups such as CHO, COOH, and COCl, see Figure 6 of ref 24—strongly suggests that the S_E parameter may depend not only on the electronegativity of the substituent but also on the row of the periodic table to which the first atom of the substituent belongs. Further support to this idea comes from the following observation. The variation of S_E as one goes from Li to F amounts to 10.35°; the corresponding change in atomic electronegativity is $\Delta\chi = 3.00$ Pauling units. Going from Na to Cl causes S_E and χ to vary by 9.18° and 2.10 Pauling units, respectively. Thus, the relative variations of S_E are 3.45 and 4.37° per Pauling unit, respectively—if linearity is assumed. We have therefore made separate calibrations of the electronegativity scale for first- and second-row functional groups.

The dependence of S_E from the row of the periodic table to which the first atom of the substituent belongs is not unexpected since a similar dependence was observed with the experimental values of the α angle.[20b,34] This is easily explained[20b] in the light of the VSEPR model.[35] If X and Y are two atoms of equal electronegativity, belonging to different rows of the periodic table and having, therefore, different covalent radii, the spatial requirements of the σ bonding electron pair will not in general be the same for the C−X and C−Y bonds. This will cause different deformations of the benzene ring.

The calibration for second-row groups was carried out by assigning the atomic electronegativities of Na, Mg, Al, Si, P, S, and Cl, as given by Pauling,[1] to the substituents Na, MgMgH, $Al(AlH_2)_2$, $Si(SiH_3)_3$, $P(PH_2)_2$, SSH, and Cl, respectively. The group electronegativities of MgMgH, $Al(AlH_2)_2$, $Si(SiH_3)_3$, $P(PH_2)_2$, and SSH are expected to match the atomic electronegativities of Mg, Al, Si, P, and S, respectively, because the effect of the terminal H atoms across the X−X bonds (X = Mg, Al, Si, P, S) is presumably quite small. Indeed, the seven data points are well-aligned in the $S_E\chi$ plane (Figure 2; the correlation coefficient is 0.9985), ascertaining the linearity of the present group electronegativity scale.

TABLE 1: Structural Substituent Parameters S_E (deg) and Group Electronegativities χ (Pauling Units), from ab Initio MO Calculations at the HF/6-31G* Level on Monosubstituted Benzene Derivatives[a]

substituent[b]	molecular symmetry[c]	S_E[d]	χ[e]
H	D_{6h}	0.00	
Li	C_{2v}	−7.27	1.03
Be$^+$	C_{2v}	−0.80	2.87
BeH	C_{2v}	−4.32	1.87
BeF	C_{2v}	−4.00	1.96
BeCl	C_{2v}	−4.01	1.96
BeBeH	C_{2v}	−4.59	1.79
BH$_2$(c)	C_{2v}	−2.93	2.26
BH$_2$(o)[f]	C_{2v}	−2.61	2.36
BF$_2$(c)	C_{2v}	−1.70	2.62*
BF$_2$(o)[f]	C_{2v}	−2.00	2.53
BCl$_2$(c)	C_{2v}	−2.60	2.36**
BCl$_2$(o)[f]	C_{2v}	−1.72	2.61
B(BH$_2$)$_2$(c)	C_{2v}	−4.03	1.95
BH$_3^-$(o)	C_s	−6.63	1.21
BH$_3^-$(c)[g]	C_s	−6.64	1.21
BPh$_3^-$ (e)	S_4	−6.30	1.30
CH$_2^+$(c)	C_{2v}	−0.25	3.03
CH$_2^+$(o)[f]	C_{2v}	3.24	4.02
CH$_2^-$(c)	C_{2v}	−7.96	0.83
CH$_2^-$(p′)[f]	C_s	−7.19	1.05
CH$_2^-$(o)[h]	C_{2v}	−8.20	0.76
Me(o)	C_s	−2.27	2.45
Me(c)[f]	C_s	−2.26	2.46
CH$_2$Me(o)	C_s	−2.30	2.44
CH$_2$Me(c)[g]	C_s	−2.68	2.34**
CMe$_3$(c)	C_s	−3.67	2.05**
CMe$_3$(o)[f]	C_s	−3.86	2.00**
CH$_2$NH$_2$(o)	C_s	−2.17	2.48
CH$_2$NH$_2$(c)[g]	C_s	−2.36	2.43
CH$_2$O$^-$(c)	C_s	−2.99	2.25*
CH$_2$O$^-$(o)[f]	C_s	−4.09	1.93
CH$_2$OH(e)	C_1	−1.51	2.67
CH$_2$OH(c)[f]	C_s	−1.30	2.73
CH$_2$OH(o)[f]	C_s	−1.59	2.65
CH$_2$F(e)	C_1	−0.92	2.84*
CH$_2$F(c)[f]	C_s	−0.90	2.84*
CH$_2$F(o)[f]	C_s	−1.40	2.70
CHF$_2$(o)	C_s	−0.22	3.04
CHF$_2$(c)[g]	C_s	−0.19	3.05
CF$_3$(o)	C_s	0.41	3.22
CF$_3$(c)[f]	C_s	0.47	3.23
CH$_2$Cl(o)	C_s	−1.18	2.76
CH$_2$Cl(c)[f]	C_s	−1.42	2.70**
CCl$_3$(c)	C_s	−0.95	2.83**
CCl$_3$(o)[f]	C_s	−1.09	2.79**
CHCH$_2$(e)	C_1	−2.26	2.46**
CHCH$_2$(c)[f]	C_s	−2.42	2.41**
CHCH$_2$(o)[f]	C_s	−1.64	2.63
Ph(e)	D_2	−2.15	2.49
Ph(o)[f]	D_{2d}	−1.62	2.64
Ph(c)[f]	D_{2h}	−4.10	1.93**
CHNH(c)	C_s	−0.83	2.86
CHNH(o)[f]	C_s	−0.88	2.85
CHO(c)	C_s	−0.03	3.09
CHO(o)[f]	C_s	−0.21	3.04
COMe(c)	C_s	−1.06	2.80**
COMe(o)[f]	C_s	−0.48	2.96
COF(c)	C_s	0.52	3.25
COF(o)[f]	C_s	0.65	3.29
COCl(c)	C_s	0.02	3.11**
COCl(o)[f]	C_s	0.94	3.37
CONH$_2$(e)	C_1	−0.64	2.92
COO$^-$(c)	C_{2v}	−2.22	2.47*
COO$^-$(o)[f]	C_{2v}	−3.00	2.25
COOH(c)	C_s	0.16	3.15
COOH(o)[f]	C_s	0.26	3.17
COOMe(c)	C_s	−0.02	3.09
COOMe(o)[f]	C_s	0.10	3.13
CCH	C_{2v}	−0.64	2.92
CN	C_{2v}	0.81	3.33
NH$_2$(p)	C_s	−1.48	2.68
NH$_2$(c)[f]	C_{2v}	−1.64	2.63
NH$_2$(p′)[f]	C_s	−1.29	2.73
NH$_2$(o)[h]	C_{2v}	−1.74	2.60
NMe$_2$(p)	C_s	−3.26	2.17**
NMe$_2$(p′)[f]	C_s	−1.32	2.72
NMe$_2$(c)[f]	C_{2v}	−3.01	2.24**
NF$_2$(p′)	C_s	2.40	3.78
NF$_2$(p)[g]	C_s	1.84	3.62
NCl$_2$(p′)	C_s	1.29	3.47
NCl$_2$(p)[f]	C_s	−0.59	2.93**
NHNH$_2$(e)	C_1	−1.47	2.68
NHNH$_2$(e)[g]	C_1	−1.00	2.82
N(NH$_2$)$_2$(e)	C_1	−1.67	2.62
N(NH$_2$)$_2$(p)[g]	C_s	−1.09	2.79
NHCOMe(c)	C_s	−0.65	2.91**
NHCOMe(o)[h]	C_s	−0.22	3.04
NH$_3^+$(o)[i]	C_s	4.29	4.32
NH$_3^+$(c)[i]	C_s	4.24	4.31
NO$_2$(c)	C_{2v}	3.15	4.00**
NO$_2$(o)[f]	C_{2v}	3.83	4.19
NNH(c)	C_s	0.52	3.25**
NNH(o)[f]	C_s	1.02	3.39
NC	C_{2v}	1.32	3.48
N$_2^+$	C_{2v}	7.26	5.17
O$^-$	C_{2v}	−7.44	0.98
OH(c)	C_s	0.38	3.21
OH(o)[f]	C_s	0.48	3.24
OMe(c)	C_s	−0.13	3.06**
OMe(o)[g]	C_s	0.44	3.23
OF(o)	C_s	2.57	3.83
OF(c)[f]	C_s	2.70	3.87
OCl(o)	C_s	2.08	3.69
OCl(c)[f]	C_s	1.56	3.54**
OOH(e)	C_1	1.57	3.55
OOH(c)[f]	C_s	1.59	3.55
OH$_2^+$(p′)	C_s	8.24	5.45
OH$_2^+$(o)[f]	C_{2v}	8.17	5.43
OH$_2^+$(p)[f]	C_s	8.29	5.46
OH$_2^+$(c)[h]	C_{2v}	8.38	5.49
F	C_{2v}	3.08	3.98
Na	C_{2v}	−7.42	0.83
Mg$^+$	C_{2v}	−0.05	2.53
MgH	C_{2v}	−5.41	1.30
MgF	C_{2v}	−5.04	1.38
MgCl	C_{2v}	−4.91	1.41
MgMgH	C_{2v}	−5.68	1.23
AlH$_2$(c)	C_{2v}	−3.67	1.70
AlH$_2$(o)[f]	C_{2v}	−4.07	1.60
AlF$_2$(c)	C_{2v}	−2.78	1.90*
AlF$_2$(o)[f]	C_{2v}	−3.37	1.76
AlCl$_2$(c)	C_{2v}	−2.84	1.89
AlCl$_2$(o)[f]	C_{2v}	−3.16	1.81
Al(AlH$_2$)$_2$(e)	C_2	−4.54	1.50
SiH$_2^+$(c)	C_{2v}	−0.49	2.43
SiH$_2^+$(o)[f]	C_{2v}	0.33	2.62
SiH$_2^-$(p)	C_s	−6.00	1.16
SiH$_2^-$(p′)[f]	C_s	−5.86	1.19
SiH$_2^-$(c)[f]	C_{2v}	−6.36	1.08
SiH$_2^-$(o)[h]	C_{2v}	−6.04	1.15
SiH$_3$(o)	C_s	−2.70	1.92
SiH$_3$(c)[f]	C_s	−2.73	1.91
SiMe$_3$(c)	C_s	−3.55	1.72
SiMe$_3$(o)[f]	C_s	−3.59	1.71
SiH$_2$F(o)	C_s	−2.44	1.98
SiH$_2$F(c)[f]	C_s	−2.23	2.03
SiHF$_2$(o)	C_s	−1.92	2.10
SiHF$_2$(c)[f]	C_s	−2.05	2.07
SiF$_3$(o)	C_s	−1.55	2.18
SiF$_3$(c)[f]	C_s	−1.63	2.17
SiH$_2$Cl(o)	C_s	−2.19	2.04
SiH$_2$Cl(c)[f]	C_s	−2.24	2.02
SiCl$_3$(o)	C_s	−1.64	2.16
SiCl$_3$(c)[f]	C_s	−1.63	2.17
SiPh$_3$(e)	S_4	−3.31	1.78
Si(SiH$_3$)$_3$(c)	C_s	−3.11	1.82
Si(SiH$_3$)$_3$(o)[f]	C_s	−3.14	1.82
PH$_2$(p′)	C_s	−1.85	2.11
PH$_2$(p)[f]	C_s	−1.80	2.13
PH$_2$(o)[f]	C_{2v}	−1.57	2.18
PH$_2$(c)[h]	C_{2v}	−1.04	2.30
PF$_2$(p′)	C_s	−0.47	2.43
PF$_2$(p)[g]	C_s	−0.66	2.39
PCl$_2$(p′)	C_s	−0.39	2.45
PCl$_2$(p)[f]	C_s	−1.07	2.29**
P(PH$_2$)$_2$(e)	C_1	−1.88	2.11
PH$_3^+$(o)	C_s	1.68	2.93
PH$_3^+$(c)[f]	C_s	1.63	2.91
PPh$_3^+$(e)	S_4	−0.35	2.46
S$^-$	C_{2v}	−5.45	1.29
SH(o)	C_s	−0.36	2.46
SH(c)[f]	C_s	−0.53	2.42
SMe(o)	C_s	−0.73	2.37
SMe(c)[f]	C_s	−1.06	2.30**
SF(o)	C_s	−0.17	2.50
SF(c)[f]	C_s	0.74	2.71
SCl(o)	C_s	0.33	2.62
SCl(c)[f]	C_s	0.37	2.63
SSH(e)	C_1	−0.07	2.52
SSH(o)[f]	C_s	0.14	2.57
SH$_2^+$(p′)	C_s	3.87	3.43
SH$_2^+$(p)[f]	C_s	4.28	3.52
SOMe(e)	C_1	1.34	2.85
SO$_2$Me(o)	C_s	1.80	2.95
SO$_2$Me(c)[f]	C_s	0.97	2.76**
SO$_2$F(o)	C_s	2.62	3.14
SO$_2$F(c)[f]	C_s	2.16	3.04
SO$_2$Cl(o)	C_s	2.95	3.22
SO$_2$Cl(c)[f]	C_s	1.91	2.98**
Cl	C_{2v}	1.76	2.94
ClO(c)	C_s	4.41	3.55*
ClO(o)[f]	C_s	3.04	3.24
ClO$_2$(p)	C_s	5.06	3.70
ClO$_2$(p′)[f]	C_s	5.11	3.72
ClO$_3$(o)	C_s	5.73	3.86
ClO$_3$(c)[f]	C_s	5.74	3.86

[a] Unless otherwise specified, the entries of this table correspond to potential energy minima, as shown by harmonic normal-mode analysis. [b] To identify the conformation of a nonlinear group with respect to the benzene ring, we make use of the terms coplanar (c), orthogonal (o), and pyramidal (p and p′), as defined in section 4. By (e), we denote a conformation that corresponds to a potential energy minimum but is neither coplanar nor orthogonal nor pyramidal. Different conformations of the same group are listed in order of increasing energy. [c] Symmetry constraint imposed in the optimization of molecular geometry. [d] Calculated from eq 1. Whenever necessary, the geometry of the monosubstituted benzene ring has been made consistent with C_{2v} symmetry by using average values of $\Delta\beta$ and $\Delta\gamma$. [e] Calculated from eqs 7 or 8. Starred values are unreliable for the present purpose, as they are either lowered by steric hindrance (double star) or increased by attractive interactions (single star). [f] First-order saddle point. [g] Higher energy minimum. [h] Second-order saddle point. [i] All possible conformations of this group have the same energy at the HF/6-31G* level of calculation.

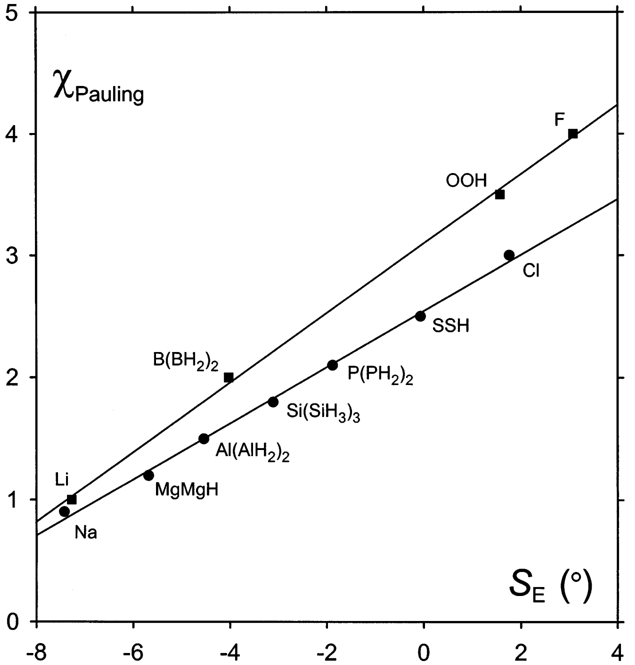

Figure 2. Calibration lines χ vs S_E for first- and second-row groups. The substituents Li, $B(BH_2)_2$, OOH, F, Na, MgMgH, $Al(AlH_2)_2$, $Si(SiH_3)_3$, $P(PH_2)_2$, SSH, and Cl have been assigned electronegativity values equal to the atomic electronegativities of Li, B, O, F, Na, Mg, Al, Si, P, S, and Cl, respectively, as given by Pauling.[1] The groups BeBeH, CMe_3, and $N(NH_2)_2$ have not been included (see text).

A similar procedure was adopted for first-row groups, based on the substituents Li, $B(BH_2)_2$, OOH, and F (Figure 2). The CMe_3 group was not considered since the distortion of the benzene ring occurring in *tert*-butylbenzene is due not only to the electronegativity of the substituent but also to steric effects.[24] The BeBeH and $N(NH_2)_2$ groups had to be excluded because the effect of the terminal H atoms across the X−X bonds was not negligible.

The equations of the two least-squares lines are

$$\chi = 0.285 S_E + 3.10 \tag{7}$$

for first-row groups, and

$$\chi = 0.230 S_E + 2.54 \tag{8}$$

for second-row groups. Eqs 7 and 8 were used to calculate the group electronegativities given in Table 1.

7. Discussion

We start our discussion with a comment on conformational considerations (but see more in section 7.2). For those groups that we have studied in more than one conformation, the electronegativity used in the present discussion is that of the minimum energy conformer. A different conformer has been chosen only for those molecules that are sterically hindered in their minimum energy conformation or show attractive interactions between the ring and the substituent. All such molecules are duly identified in Table 1.

7.1. Chemically Relevant Trends. The group electronegativities obtained by the present procedure show a number of general trends expected from chemical intuition. An impressive trend is the regular increase of χ along the two series of XH_n groups ($0 \leqslant n \leqslant 3$): Li, BeH, BH_2, CH_3, NH_2, OH, F and Na, MgH, AlH_2, SiH_3, PH_2, SH, Cl, see Figure 3. This follows from the monotonic increase in atomic electronegativity that occurs along the first and second rows of the periodic table and from the fact that the electronegativity of an XH_n group is determined primarily by the electronegativity of X. The contribution of the H atoms cannot be ignored, however, and shows up clearly in Figure 3. Note that the electronegativity of a first-row group XH_n is always larger than that of the corresponding second-row group, as expected from the atomic electronegativities of X.

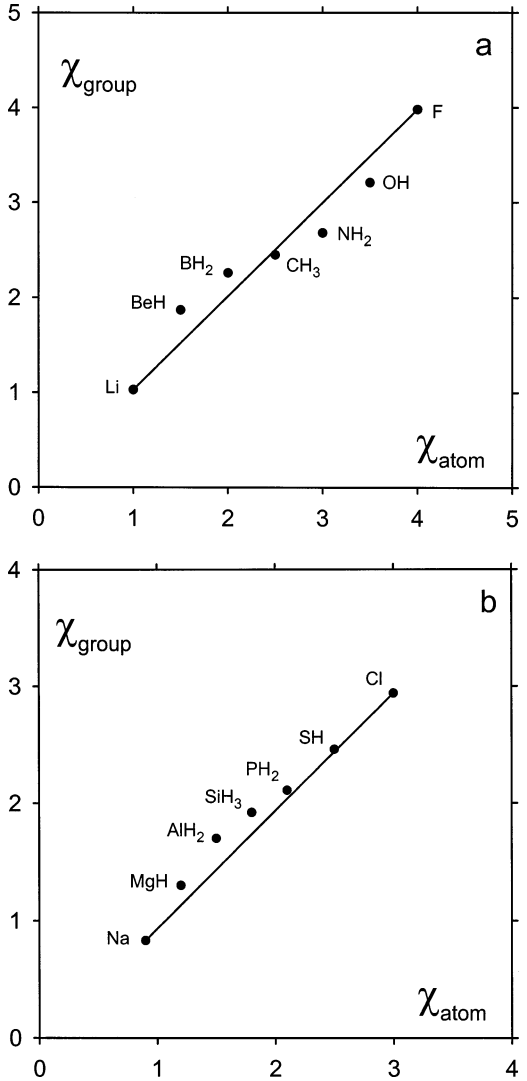

Figure 3. Plots of the electronegativity of XH_n groups ($0 \leq n \leq 3$) vs the atomic electronegativity of X.[1] The groups have been considered in their minimum energy conformation. (a) X = Li through F. (b) X = Na through Cl.

The electronegativity of an XH_n group invariably increases if one or more hydrogen atoms are replaced by more electronegative atoms or groups, such as, for example, NH_2, OH, and F. Note the gradual increase along such series as (i) CH_3 (2.45), CH_2NH_2 (2.48), CH_2OH (2.67), CH_2F (2.70); (ii) CH_3 (2.45), CH_2F (2.70), CHF_2 (3.04), CF_3 (3.22); and (iii) SiH_3 (1.92), SiH_2F (1.98), $SiHF_2$ (2.10), SiF_3 (2.18).

The formation of dative (or double) bonds with oxygen atoms substantially increases the electronegativity of a group, as exemplified by the following two series: SMe (2.37), SOMe (2.85), SO_2Me (2.95) and Cl (2.94), ClO (3.24), ClO_2 (3.70), ClO_3 (3.86).

The electronegativity of a carbon atom is expected to increase as its hybridization state changes from sp^3 to sp^2 and sp, due to the increased s character of the hybrid orbitals.[6,8] The elec-

TABLE 2: Electronegativity Changes (Pauling Units) upon Protonation/ Deprotonation of XH_n Groups[a]

group	$\Delta\chi_{prot}$	$\Delta\chi_{deprot}$
CH_3		−1.62
NH_2	+1.64	
OH	+2.24	−2.23
SiH_3		−0.76
PH_2	+0.82	
SH	+0.97	−1.17

[a] All the groups used for the compilation of this table have been considered in their minimum energy conformations.

TABLE 3: Correlation of Group Electronegativities from Benzene Ring Deformations with Those of Other Scales[a]

scale	number of common groups	correlation coefficient
Huheey[b]	51	0.904
Mullay[c]	24	0.881
Boyd and Boyd[d]	53	0.736
Reed and Allen[e]	23	0.896
Suresh and Koga[f]	40	0.941
Marriott et al.[g]	27	0.788
De Proft et al.[h]	27	0.667
Inamoto and Masuda[i]	47	0.812[j]

[a] For those groups that we have studied in more than one conformation, the electronegativity of the minimum energy conformer has been used in the correlation. A different conformation has been chosen only for species with steric hindrance or in the presence of attractive interactions. The CMe_3 and CCl_3 groups have not been included as the Ph−CMe_3 and Ph−CCl_3 molecules are sterically hindered in all possible conformations. [b] Data from Tables 1−3 of ref 10a and Table 3 of ref 10b. [c] Data from Tables 3 and 4 of ref 11. [d] Data from Table 1 of ref 12. [e] Data from Table 5 of ref 13. [f] Data from Tables 1, 3, and 4 of ref 15. [g] Data from Table 4 of ref 16. [h] Data from Table 2 of ref 17. [i] Data from Table 2 of ref 18. [j] The correlation coefficient increases to 0.932 when the negatively charged groups (COO^-, O^-, and S^-) are not included.

tronegativities of $CH_2{-}CH_3$ (2.44), $CH{=}CH_2$ (2.63), and $C{\equiv}CH$ (2.92), as well as those of $CH_2{-}NH_2$ (2.48), $CH{=}NH$ (2.86), and $C{\equiv}N$ (3.33), are in line with the expected trend. In both series, the electronegativity change is somewhat more pronounced in going from sp^2 to sp hybridization than from sp^3 to sp^2, due to the larger increase in s character of the hybrid orbitals of carbon (sp^3: 25% s character; sp^2: 33.3%; sp: 50%).

The electronegativities of two charged groups, N_2^+ (5.17) and OH_2^+ (5.45), substantially exceed the electronegativity of fluorine. Also high is the value for NH_3^+, 4.32. The electronegativity changes that occur upon addition of a proton to some XH_n groups are given in Table 2. It is seen that adding a proton to a first-row XH_n group may cause χ to increase by as much as 2.2 Pauling units. Opposite changes occur when a proton is removed from the group. The variations occurring with second-row groups are less pronounced, about one-half of those of the corresponding first-row groups, as expected from the increased atomic sizes and screening effects by the core electrons.

7.2. Group Electronegativities and Conformational Changes. The procedure described in the present paper is particularly well-suited for investigating whether the electronegativity of a group attached to the benzene ring is affected by conformational changes. Table 1 shows that the electronegativities of groups having C_{3v} symmetry appear insensitive to such changes. The largest variations, amounting to 0.04−0.05 Pauling units, occur with CMe_3 and CCl_3. The $C_6H_5{-}CMe_3$ and $C_6H_5{-}CCl_3$ molecules are sterically hindered in all possible conformations; this results in fictitiously low electronegativity values. However, the effect of steric hindrance is somewhat less pronounced when one of the C−Me (or C−Cl) bonds lies in the plane of the benzene ring.[36] Thus, the coplanar conformation is the potential energy minimum, while the orthogonal conformation is a first-order saddle point, lying only a few kJ mol^{-1} above the minimum. With both groups, the less hindered coplanar conformation has the highest apparent electronegativity.

When the group has C_{2v} or C_s symmetry, the variation of electronegativity with conformation may not be negligible. In the majority of cases, this is due to steric effects affecting the S_E parameter, as discussed in section 2. Repulsive interactions between the ring and the substituent are responsible for the apparent lowering of the electronegativities of several groups (BCl_2, CH_2Me, CH_2Cl, $CHCH_2$, Ph, COMe, COCl, NHCOMe, NO_2, NNH, OMe, OCl, SMe, SO_2Me, and SO_2Cl), as they go from the orthogonal to the coplanar conformation. Similarly, the pyramidal conformations of NMe_2, NCl_2, and PCl_2 are more sterically hindered and appear less electronegative when the axis of the lone pair lies in a plane orthogonal to the plane of the ring (p) rather than in the plane of the ring (p′). In some cases, the sterically hindered species is still the potential energy minimum, being stabilized by resonance interactions between the ring and the substituent. This occurs with BCl_2, COMe, COCl, NMe_2, NHCOMe, NO_2, and OMe. In other cases ($CHCH_2$, Ph, NCl_2, OCl, PCl_2, SMe, SO_2Me, and SO_2Cl), the coplanar or pyramidal (p) conformations are less strongly stabilized by resonance interactions (or more strongly destabilized by steric hindrance) and become saddle points in the potential energy hypersurface.

The presence of a partial negative charge on one or more atoms of the substituent is expected to result in attractive interactions with the ortho hydrogens. It appears, however, that only in a few instances are such interactions strong enough to cause an apparent increase in the electronegativity of the substituent. The most conspicuous cases are the coplanar conformations of CH_2O^-, COO^-, and ClO.

When a substituent having C_{2v} or C_s symmetry is not involved in strongly repulsive or attractive interactions, the dependence of electronegativity on conformation is small.[37] Suffice it to mention that the four different conformations of aniline considered in the present study yield electronegativity values of the NH_2 group ranging from 2.60 to 2.73.

7.3. Comparison with Other Group Electronegativity Scales. The correlation of our group electronegativity scale with the other scales mentioned in the Introduction is shown in Table 3. The best correlation ($R = 0.941$ on 40 data points) is with Suresh and Koga's scale,[15] derived by combining the molecular electrostatic potential at the C−X bond critical point in Me−X molecules with the distance of the critical point from the methyl carbon. A plot of Suresh and Koga's electronegativities against ours is shown in Figure 4. It appears that opposite deviations from the regression line occur with some π donor and π acceptor functional groups, such as, for example, NH_2 and NO_2.

Of the other group electronegativity scales, we compare only two with ours in some detail, as they show opposite systematic differences. One is Huheey's scale,[10] based on complete equalization of electronegativity for all atoms within the group; the other is Boyd and Boyd's scale,[12] derived from the position of the H−X bond critical point in H−X molecules.

A plot of the group electronegativities calculated by Huheey[10] against those obtained by the present procedure is shown in Figure 5. The agreement between Huheey's values and ours is good for the groups composed of atoms having similar electronegativities. But if the first atom of a group is less electronegative than the others, the data point lies above the

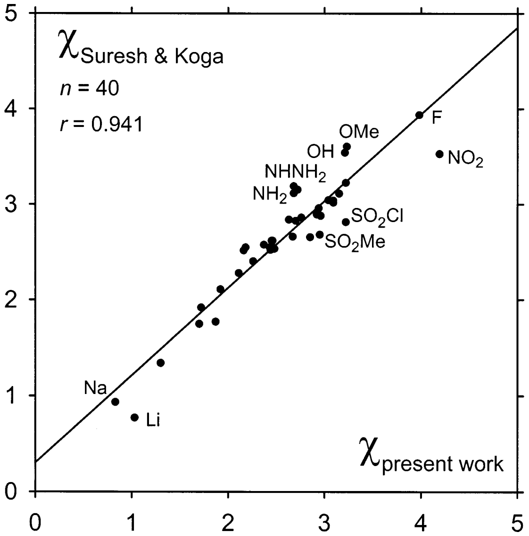

Figure 4. Plot of Suresh and Koga's group electronegativities[15] vs those of the present scale.

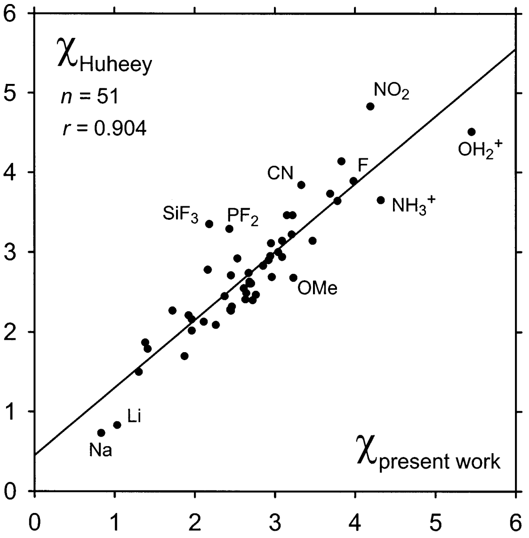

Figure 5. Plot of Huheey's group electronegativities[10] vs those of the present scale.

regression line of Figure 5 (i.e., Huheey electronegativity is larger than ours). This occurs with a number of groups, the most prominent of which are CN, NO_2, SiF_3, and PF_2. The reverse is true when the first atom is more electronegative than the others, as in OMe, NH_3^+, and OH_2^+. These deviations follow from the fact that—in Huheey's procedure—the electronegativities are equalized for all atoms within the group; while, in most cases, the first atom contributes more than the others to the electronegativity of the group.

Huheey was fully aware of the limitations of his model. In his paper on the electronegativity of multiply bonded groups,[10b] he pointed out that the values obtained for the more electronegative groups (such as, e.g., CN and NO_2) were rather high in comparison with previous estimates, as well as with the electronegativities of individual atoms. He concluded that "the assumption of electronegativity equalization is an oversimplified, though useful, description of the polarity within the group".[10b] Introducing partial equalization by means of an appropriate equalization coefficient improves the quality of the results[38] but not without considerable arbitrariness.

A plot of Boyd and Boyd's group electronegativities[12] against those obtained here is shown in Figure 6. The majority of the data points are arranged in nearly horizontal, parallel lines. This is a consequence of the fact that Boyd and Boyd's method greatly underestimates the effect of those atoms of the group that are bonded to the first atom, as well as the effect of positive and negative charges. For instance, groups as different as NH_2, NNH, and NH_3^+ are assigned electronegativity values as close as 3.12, 3.15, and 3.21, respectively.

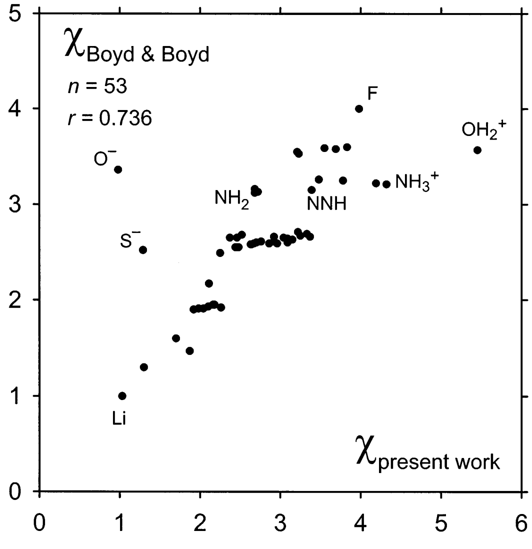

Figure 6. Plot of Boyd and Boyd's group electronegativities[12] vs those of the present scale.

The present group electronegativity scale has some advantages over those proposed by other authors:[10−18]

(1) Electronegativity values from benzene ring deformations can be determined not only from MO calculations but also from experiment. A phenyl group is easily attached as a probe to many groups, including metal complexes and organometallic systems. Moreover, the phenyl group is a fairly rigid system, which helps in deriving accurate experimental values of the internal ring angles, provided enough effort is put in correcting for the various systematic errors inherent to each technique of structure determination.[34]

(2) The procedure described in the present paper can be applied to charged groups. It can also be applied to experimentally inaccessible molecules and different conformations of the same molecule.

(3) Electronegativity values for π donor and π acceptor functional groups are obtained in a straightforward fashion since the ring deformation measured by the structural substituent parameter S_E is orthogonal to that caused by resonance interactions. However, strong resonance interactions might affect the electronegativity of the group.

(4) Group electronegativities determined by measuring a physical property of a probe attached to different groups depend on the nature of the probe−group interaction. Strictly speaking, they are not probe-independent. The position of the phenyl group right in the middle of the electronegativity scale makes it well-suited for acting as a probe.

7.4. Can Group Electronegativities Be Evaluated by Averaging Atomic Electronegativities? Several authors[39] have suggested that the electronegativity of a group be evaluated by averaging the electronegativities of the component atoms. Geometric,[39b] harmonic,[39c] and weighted arithmetic[39d] means have been proposed for this purpose. We find, however, that the BeF and BeCl groups have equal electronegativities (1.96 from Table 1), although fluorine is substantially more electronegative than chlorine. The electronegativities of the magnesium analogues, MgF (1.38) and MgCl (1.41), are also surprising.

Further inspection of Table 1 shows that the electronegativities of many XF_n groups differ only slightly from those of the corresponding XCl_n groups. We attribute this intriguing result to the different lengths of the X−F and X−Cl bonds. The less polar, but longer, X−Cl bond appears to be as effective as the more polar, but much shorter, X−F bond in removing electron density from the valence shell of the X atom;[40] this results in nearly equal electronegativities for the two groups.

Stereoelectronic effects also play an important role in determining the electronic structure of some of these species. Natural bond orbital (NBO) analysis shows that in $Ph-SiY_3$ molecules (Y = F, Cl), electron density is transferred from the lone pair orbitals of the halogens into the larger lobes of the polar σ^*(Si−C) and σ^*(Si−Y) orbitals and also into the d orbitals of silicon. The resulting accumulation of negative charge on the silicon atom lowers the electronegativity of the group, as measured by the deformation of the benzene ring attached to silicon. The shorter Si−Y bonds make the transfer of electron density from the fluorine lone pair orbitals to silicon more effective than from chlorine, which helps in compensating the difference in the electronegativities of the two halogens. The SiF_3 and $SiCl_3$ groups have almost the same electronegativities, 2.18 and 2.16, respectively. In a similar manner, the electronegativity of BF_2, 2.53, is even smaller than that of BCl_2, 2.61. Note, however, that the acceptor ability at the X end of a σ^*-(X−Y) orbital (where X is the first atom of the substituent, varying within a row of the periodic table, and Y = F, Cl, or C_{ipso}) is expected to decrease as the electronegativity of X increases. Thus the electronegativities of NF_2 (3.78) and OF (3.83) are larger than those of NCl_2 (3.47) and OCl (3.69), respectively.

Last, but not least, we mention that a number of groups among those investigated in the present study have electronegativities that exceed those of the component atoms. This is, for example, the case of CN (3.33), NC (3.48), NO_2 (4.19), OCl (3.69), ClO_2 (3.70), and ClO_3 (3.86). This finding is hardly compatible with the idea that group electronegativities are averages of atomic electronegativities.

We conclude that the electronegativity of a group depends markedly on the nature of chemical bonding and electron density distribution within the group. Averaging the electronegativities of the component atoms may work in some cases but leads to unreliable results in many others.

8. Conclusions

(1) The geometry of the carbon skeleton of a monosubstituted benzene ring shows considerable distortion, depending on the electronegativity, resonance, and steric effects of the substituent. A linear combination of the internal ring angles, $S_E = 0.706\Delta\alpha - 0.956\Delta\beta + 0.044\Delta\gamma + 0.206\Delta\delta$, is a sensitive indicator of the polarity of the Ph−X bond. S_E increases linearly with substituent electronegativity within each of the first two rows of the periodic table, examined in this study.

(2) A new scale of group electronegativities has been derived from the S_E values of 100 Ph−X molecules, as obtained by ab initio MO calculations at the HF/6-31G* level. Many groups have been studied in more than one conformation.

(3) The electronegativities of groups having C_{3v} symmetry are virtually insensitive to conformational changes. With groups having C_{2v} or C_s symmetry, apparent electronegativity changes may accompany changes in conformation. These are due to nonbonded interactions involving the ortho hydrogens and carbons. In the majority of cases, repulsive or attractive interactions between the ring and the substituent are easily eluded by changing the conformation of the substituent with respect to the ring.

(4) Although the atom directly linked to the benzene ring usually dominates the electronegativity of a group, the role of its adjacent atoms is also important. Their effect cannot be evaluated by averaging the electronegativities of the component atoms because it depends markedly on the nature of chemical bonding and electron density distribution within the group.

(5) Group electronegativities from benzene ring deformations in Ph−X molecules correlate well with those derived[15] from the molecular electrostatic potential at the C−X bond critical point in Me−X molecules, combined with the distance of the critical point from the methyl carbon.

References and Notes

(1) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960; p 88.

(2) Pauling, L.; Yost, D. M. *Proc. Natl. Acad. Sci. U.S.A.* **1932**, *18*, 414. Pauling, L. *J. Am. Chem. Soc.* **1932**, *54*, 3570.

(3) Mulliken, R. S. *J. Chem. Phys.* **1934**, *2*, 782. Mulliken, R. S. *J. Chem. Phys.* **1935**, *3*, 573.

(4) Gordy, W. *Phys. Rev.* **1946**, *69*, 604.

(5) Allred, A. L.; Rochow, E. G. *J. Inorg. Nucl. Chem.* **1958**, *5*, 264.

(6) Walsh, A. D. *Discuss. Faraday Soc.* **1947**, *2*, 18.

(7) Sanderson, R. T. *J. Chem. Educ.* **1954**, *31*, 2.

(8) Hinze, J.; Jaffé, H. H. *J. Am. Chem. Soc.* **1962**, *84*, 540. Hinze, J.; Whitehead, M. A.; Jaffé, H. H. *J. Am. Chem. Soc.* **1963**, *85*, 148. Hinze, J.; Jaffé, H. H. *Can. J. Chem.* **1963**, *41*, 1315. Hinze, J.; Jaffé, H. H. *J. Phys. Chem.* **1963**, *67*, 1501.

(9) See ref 10a for references to early papers on this subject.

(10) (a) Huheey, J. E. *J. Phys. Chem.* **1965**, *69*, 2384. (b) Huheey, J. E. *J. Phys. Chem.* **1966**, *70*, 2086.

(11) Mullay, J. *J. Am. Chem. Soc.* **1985**, *107*, 7271.

(12) Boyd, R. J.; Boyd, S. L. *J. Am. Chem. Soc.* **1992**, *114*, 1652.

(13) Reed, L. H.; Allen, L. C. *J. Phys. Chem.* **1992**, *96*, 157.

(14) Allen, L. C.; Egolf, D. A.; Knight, E. T.; Liang, C. *J. Phys. Chem.* **1990**, *94*, 5602.

(15) Suresh, C. H.; Koga, N. *J. Am. Chem. Soc.* **2002**, *124*, 1790.

(16) Marriott, S.; Reynolds, W. F.; Taft, R. W.; Topsom, R. D. *J. Org. Chem.* **1984**, *49*, 959.

(17) De Proft, F.; Langenaeker, W.; Geerlings, P. *J. Phys. Chem.* **1993**, *97*, 1826.

(18) Inamoto, N.; Masuda, S. *Chem. Lett.* **1982**, 1007 and references therein.

(19) Hargittai, I. *Z. Naturforsch. A: Phys. Sci.* **1979**, *34*, 755.

(20) (a) Domenicano, A.; Vaciago, A.; Coulson, C. A. *Acta Crystallogr. B* **1975**, *31*, 221. (b) Domenicano, A.; Vaciago, A.; Coulson, C. A. *Acta Crystallogr. B* **1975**, *31*, 1630. (c) Domenicano, A.; Vaciago, A. *Acta Crystallogr. B* **1979**, *35*, 1382.

(21) Carter, O. L.; McPhail, A. T.; Sim G. A. *J. Chem. Soc. A* **1966**, 822. Nygaard, L.; Bojesen, I.; Pedersen, T.; Rastrup-Andersen, J. *J. Mol. Struct.* **1968**, *2*, 209.

(22) Throughout this paper, the terms first-, second-, and third-row are used to denote the elements Li through Ne, Na through Ar, and K through Kr, respectively, which is consistent with our previous work on group electronegativities.[20b] By first-row substituent, we denote a substituent bonded to the benzene ring through a first-row atom, etc.

(23) Domenicano, A.; Murray-Rust, P.; Vaciago, A. *Acta Crystallogr. B* **1983**, *39*, 457.

(24) Campanelli, A. R.; Domenicano, A.; Ramondo, F. *J. Phys. Chem. A* **2003**, *107*, 6429.

(25) For lower ring symmetries, average values for $\Delta\beta$ and $\Delta\gamma$ are used in these equations.

(26) This may not be the case of charged groups. For instance, the π charge transferred by the CH_2^- substituent to the π system of the benzene ring in the coplanar conformation of the benzyl anion amounts to 0.52 electrons, and the decrease of the C−X bond length with respect to the orthogonal conformation amounts to 0.106 Å, from ab initio MO calculations at the HF/6-31G* level. The corresponding figures from HF/6-311++G** calculations are 0.49 electrons and 0.107 Å.

(27) (a) Campanelli, A. R.; Ramondo, F.; Domenicano, A.; Hargittai, I. *J. Phys. Chem.* **1994**, *98*, 11046 and references therein. (b) Portalone, G.; Ramondo, F.; Domenicano, A.; Hargittai, I. *J. Organomet. Chem.* **1998**, *560*, 183 and references therein.

(28) Poirier, R.; Kari, R.; Csizmadia, I. G. *Handbook of Gaussian Basis Sets: A Compendium for ab Initio Molecular Orbital Calculations*; Elsevier: Amsterdam, 1985.

(29) Pulay, P. *Mol. Phys.* **1969**, *17*, 197.

(30) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.6; Gaussian Inc.: Pittsburgh, PA, 1998.

(31) Tsuzuki, S.; Tanabe, K. *J. Phys. Chem.* **1991**, *95*, 139.

(32) Reed, A. E.; Weinhold, F. *J. Chem. Phys.* **1985**, *83*, 1736. Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899.

(33) Glendening, E. D.; Reed, A. E.; Carpenter, J. E.; Weinhold, F. *NBO 3.0 Program*; University of Wisconsin: Madison, WI.

(34) Domenicano, A. In *Accurate Molecular Structures: Their Determination and Importance*; Domenicano, A., Hargittai, I., Eds.; Oxford University Press: Oxford, 1992; Ch. 18.

(35) Gillespie, R. J.; Hargittai, I. *The VSEPR Model of Molecular Geometry*; Allyn and Bacon: Boston, MA, 1991.

(36) A detailed account of the molecular structure and conformation of $C_6H_5-CMe_3$ is given in ref 27a.

(37) When a planar group is a strong π acceptor, the coplanar conformation is found to be less electronegative than the orthogonal. This occurs with CH_2^+, and to a much lesser extent, with SiH_2^+ and BH_2. The decrease of electronegativity is caused by the simultaneous shortening of the C−X bond and transferring of π electrons from the ring to the substituent, as discussed in section 2.

(38) Huheey, J. E. *J. Org. Chem.* **1966**, *31*, 2365.

(39) (a) Clifford, A. F. *J. Phys. Chem.* **1959**, *63*, 1227. (b) Sanderson, R. T. *J. Chem. Educ.* **1988**, *65*, 112 and 227. (c) Bratsch, S. G. *J. Chem. Educ.* **1985**, *62*, 101. (d) Smith, D. W. *J. Chem. Educ.* **1990**, *67*, 559. Smith, D. W. *J. Chem. Soc., Faraday Trans. 2* **1998**, *94*, 201.

(40) Changing the Be−Cl bond length in Ph−BeCl by ±0.20 Å (with the Ph−Be bond length fixed at the equilibrium value) causes the electronegativity of the BeCl group to vary by ±0.09 Pauling units.