to −1.9 V vs. SCE. A mercury pool (130 cm^2) and ultrafine fritted glass were used as a cathode and divided cell, respectively. After the electrolysis was completed (7.5 h, 6.6 F/mol), the reaction mixture was concentrated under vacuum and treated with a usual workup (method A) to give 1.73 g (84%) of **8** as a sole product.

(c) Method C. Electrolysis of 72 mg (0.1 mmol) of **12** was carried out in a mixture of 5 mL of MeOH and 5 mL of DMF containing 0.04 M Et_4NBF_4 for 1 h (11.2 F/mol) at −1.7 V vs. Pt wire. A lead plate (3 cm × 4 cm) and porous cup were used as a cathode and divided cell, respectively. The excess MeOH was removed under vacuum and the residue was treated with a usual workup (method A) and finally chromatographed on silica, eluting with 30:1 CH_2Cl_2/AcOEt, to afford 8 mg (14%) of **14a** and 30 mg (40%) of 2,5-bis[benzyl(*p*-tolylsulfonyl)amino]-4-(1-methyl-2-oxo-4-carbomethoxybutyl)toluene (**17a**) as a colorless solid. Recrystallization of this solid from ether afforded an analytical sample as colorless crystals: mp 107–108 °C; IR (Nujol) 1730, 1710, 1350, 1165 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.24 (d, J = 6.8 Hz, 2 H), 1.1–1.3 (m, 1 H), 1.80 (s, 1.5 H), 1.87 (br t, J = 4.9 Hz, 1.5 H), 2.0–2.9 (m, 10 H), 3.6–3.7 (m, 3 H), 3.8–4.2 (m, 3 H), 4.9–5.2 (m, 2 H), 6.0–6.3 (m, 1 H), 6.4–6.6 (m, 1 H), 6.9–7.8 (m, 18 H); mass spectrum, m/e 721 (M^+ − MeO). Anal. Calcd for $C_{42}H_{44}N_2O_7S_2$: C, 67.00; H, 5.89; N, 3.72; S, 8.52. Found: C, 67.30; H, 6.04; N, 3.77; S, 8.75.

(d) Method D. Electrolysis of 72 mg (0.1 mmol) of **12** was carried out in a mixture of 5 mL of EtOH and 5 mL of DMF containing 0.04 M Et_4NOTs for 7 min (1.2 F/mol) at −1.7 V vs. Pt wire. After the same workup as that described for method C, 3 mg (5%) of **14a** and 48 mg (63%) of 2,5-bis[benzyl(*p*-tolylsulfonyl)amino]-4-(1-methyl-2-oxo-4-carboethoxybutyl)toluene (**17b**) as a colorless solid were obtained. Recrystallization of this solid from ether afforded an analytical sample as colorless crystals: mp 108–110 °C; IR (Nujol) 1725, 1710, 1350, 1165 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.24 (d, J = 6.8 Hz, 2 H), 1.21 (t, J = 7.3 Hz, 3 H), 1.1–1.3 (m, 1 H), 1.80 (s, 1.5 H), 1.87 (br t, J = 4.6 Hz, 1.5 H), 2.0–2.9 (m, 10 H), 4.09 (q, J = 7.3 Hz, 2 H), 3.8–4.2 (m, 3 H), 4.9–5.2 (m, 2 H), 6.0–6.3 (m, 1 H), 6.4–6.6 (m, 1 H), 6.9–7.8 (m, 18 H); mass spectrum m/e 766 (M^+). Anal. Calcd for $C_{43}H_{46}N_2O_7S_2$: C, 67.34; H, 6.05; N, 3.65; S, 8.36. Found: C, 67.51; H, 6.01; N, 3.46; S, 8.32.

Photolysis of 12. A mixture of 1.44 g (2.0 mmol) of **12**, 0.78 g (4.4 mmol) of ascorbic acid, and 0.38 g (2.0 mmol) of 1,5-dimethoxynaphthalene was irradiated with a 500-W, high-pressure mercury lamp through a Pyrex filter in 80% aqueous THF for 8 h under argon atmosphere. The reaction mixture was then neutralized with saturated aqueous $NaHCO_3$ and the solvent was removed under vacuum. The residue was dissolved in AcOEt, and the solution was washed with brine, dried (Na_2SO_4), and evaporated to give the crude mixture. After chromatography on silica, eluting with 5:1 benzene/AcOEt, 0.40 g (48%) of **14b** was obtained as the sole product.

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Registry No. **8**, 88609-66-9; **9c**, 14818-63-4; **10c**, 88589-44-0; **11a**, 72374-10-8; **11b**, 88589-45-1; **12**, 88589-36-0; **14a**, 88589-37-1; **14b**, 88589-38-2; **15**, 88589-39-3; **17a**, 88589-40-6; **17b**, 88589-41-7; **18**, 4703-20-2; **19a**, 72374-00-6; **19b**, 88589-42-8; **19c**, 72374-01-7; **20a**, 88589-43-9; **20b**, 72374-11-9; benzyl bromide, 100-39-0; *p*-toluenesulfonanilide, 68-34-8; anthracene, 120-12-7; ascorbic acid, 50-81-7.

Substituent Electronegativity Parameters

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Values are reported of the atomic electron population on the hydrogen atom in compounds HX as calculated at the ab initio molecular orbital 6-31G* level with geometry optimization. It is shown that these provide a simple and well-defined scale of electronegativity parameters. It is further shown that the one-bond J_{CC} values for C1C2 in monosubstituted benzenes for many but not all substituents are a function of substituent electronegativity.

The concept of electronegativity has been said[1] to be "simultaneously one of the most important and one of the most difficult problems in chemistry". Another recent comment[2] is that "few concepts are as widely used, or as ambiguous ... this situation may be attributed to the fact that the electronegativity of an atom, or functional group, is neither uniquely defined nor directly measurable".

Pauling[3] originally defined electronegativity as "the power of an atom in a molecule to attract electrons to itself". Pauling determined his scale from thermochemical data, but difficulties here have led[4] to alternative bases becoming more common. One approach[1,5–7] is to calculate valence state or orbital electronegativities by using a combination of ground-state ionization energies and electron affinities, together with calculated or spectroscopically determined transition energies. An alternative approach[1,5,8,9] is to consider electronegativity to be some function of the size and charge of an atom, for example, by using covalent boundary potentials. Various refinements have been made to these approaches, but electronegativity scales remain empirical although recently[2] values have been calculated for the first 54 elements on the basis of the electrostatic force between the effective nuclear

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Table I. Atomic Charge Densities on Hydrogen ($1.000 - q_H$) in Compounds HX (6-31G*//6-31G*)

X	$1 - q_H$	X	$1 - q_H$	XX	$1 - q_H$
H	0.000	CH_2F	0.155	NHCHO	0.389
Li	−0.177	CH_2CHO	0.169	$NHNH_2$	0.344
BeH	−0.087	CH_2CN	0.228	NC	0.430
BH_2	−0.041	CN	0.313	NCO	0.419
BMe_2	−0.053	CNO	0.337	NO	0.328
BF_2	−0.089	CHO	0.140	NO_2	0.396
CH_3	0.165	COMe	0.145	OH	0.434
CH_2Me	0.158	CO_2H	0.181	OMe	0.438
$CHMe_2$	0.153	CO_2Me	0.186	OCOMe	0.460
CMe_3	0.155	$CONH_2$	0.144	O^-	0.206
$CHCH_2$	0.176	COF	0.178	F	0.517
CCH	0.276	CF_3	0.174[a]	SiH_3	−0.133[b]
CCMe	0.278	NH_2	0.332	PH_2	−0.031,[b] −0.021[c]
CH_2CCH	0.201	NHMe	0.338	SH	0.109,[b] 0.096[c]
CH_2NH_2	0.155	NMe_2	0.335	SMe	0.090[b]
CH_2OH	0.152	NH_3^+	0.488	Cl	0.245,[b] 0.239[c]

[a] 6-31G*//4-31G. [b] 6-31G*//3G (W. J. Hehre, unreported results). [c] 4-31G//4-31G.

charge and an electron at the relative radius of the atom (calculated from a density contour method).

The determination of substituent or group electronegativity as against atom electronegativities provides further difficulties. Although the substituent electronegativity is primarily determined by the electronegativity of the atom that forms the point of attachment to the rest of the molecule,[5] the electronegativity of this atom is affected both by changes in hybridization (as for example, from $—CH_2CH_3$ to $—CH{=}CH_2$ to $—C{\equiv}CH$) and by the polarity of other atoms in the group. Nevertheless, a clear scale of substituent electronegativity would be highly desirable for use in physical organic chemistry. As was pointed out some years ago,[5] and recently emphasized,[10] the usual mechanism for the transmission of electronic substituent effects in nonconjugated systems is a field effect (F), that is, the through space transmission to the measurement site of the pole or dipole created by the introduction of the substituent. The relevant substituent constant scale σ_F,[11] is identical with the previously designated σ_I. By contrast, the classical idea of transmission via a progressive, but diminishing, relay of charge along a chain of carbon atoms, as represented below, should

$$\overset{\delta-}{X} — \overset{\delta+}{CH_2} — \overset{\delta\delta+}{CH_2} — \overset{\delta\delta\delta+}{CH_2}$$

originate in the electronegativity difference between the substituent X and the attached carbon atom. Such a substituent effect could be designated by a σ_χ[11] scale, if available. A review[10] of a considerable amount of data suggested that electronegativity effects would only be important at measurement sites close to the substituent, possibly, for example, influencing the carbon-13 shifts in methyl derivatives, CH_3X. However, some physical[12,13] or chemical measurements[14] at greater distances seem to be at least partly due to electronegativity effects. For example,[12] the fluorine-19 shifts in 4-substituted bicyclo[2.2.2]octyl fluorides have been suggested to follow a combination of field and electronegativity effects. An independent scale of σ_χ values would allow a statistical examination of such data.

Table II. Ab Initio Molecular Orbital Calculations (STO-3G) of Atomic Charge Densities[a] on Hydrogen in Substituted Alkanes

X	*H*X	*H*CH_2X	*H*CH_2CH_2X[b]
H	0	0	0
Me	64	−7	−1
$CHCH_2$	62		−1
CCH	109		5
CN	149	36	13
NH_2	160	−3	2
OH	186	−2	6
F	209	−1	8

[a] Δq in 10^3 e referred to corresponding hydrocarbon. [b] Trans conformation, OH is average of two planar CCOH conformations.

Table III. Ab Initio Molecular Orbital Calculations (6-31G*//6-31G*) of Atomic Charge Densities in Methyl Derivatives CH_3X (Values in 10^3 e Compared to Methane)

X	$\Delta q(CH_3)$[a]	$\Delta q(H_{av})$[b]	$\Delta q(C)$[c]
H	0	0	0
CH_3	165	−7	184
$CHCH_2$	165	6	149
CHO	177	30	89
CN	318	63	130
CCH	336	66	139
NH_2	340	−10	371
NO	402	35	299
OH	457	−13	497
OCH_3	461	−14	503
F	560	10	597

[a] Change in total electron population in CH_3 group compared to CH_3H. [b] Change in average electron population of hydrogen atoms in CH_3 group compared to CH_3H. [c] Change in electron population of carbon in CH_3 group compared to CH_4.

We recently reported[15] a scale of electronegativity values determined in a simple and clearly defined way by ab initio molecular orbital calculations at the 6-31G* basis on molecules HX. We have now extended our work to produce a σ_χ scale for a considerable number of substituents and here compare these values with various χ scales and the *i* values of Inamoto and co-workers.[16,17] We have also determined $^1J_{CC}$(ortho) coupling constants for additional monosubstituted benzenes in order to further investigate the previously noted[18] relationship of these experimental parameters to the substituent electronegativity.

Calculations and Results

All calculations were performed at the ab initio STO-3G, 4-31G and 6-31G* levels by using the GAUSSIAN-80 program.[19] The calculations involved use of both optimized

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Table IV. Group Electronegativities, Polar (Field) Substituent Constants, and Coupling Constants (Ipso-Ortho in Hertz) in Monosubstituted Benzenes (σ_X, are $1 - q_H$ from Table I)

	Wells[a]	Inamoto,[b] i	σ_X	σ_F	$^1J_{CC}$[c]
H	2.28	2.00	0.00	0.00 (0.00)	0.00
Li	0.97	1.15	−0.18		
CH_3	2.3	2.14	0.17	−0.01 (0.02)	1.07[d]
CH_2Me		2.15	0.16	−0.01	1.09
$CHMe_2$		2.15	0.15	−0.01	1.5
CMe_3		2.16	0.16	−0.01 (0.04)	1.90
$CHCH_2$	(3.0)	2.34	0.17	0.11	1.61
CCH	(3.3)	2.52	0.28	0.29	3.37
CH_2NH_2		2.18	0.16 (0.15)[e]		1.42
CH_2OH		2.22	0.15 (0.17)[e]	0.11	1.65
CH_2F		2.24	0.16 (0.18)[e]		2.0
CH_2CN		2.20	0.23 (0.23)[e]	0.20	3.07
CN	3.3	2.61	0.31	0.57 (0.60)	4.11[d]
CHO		2.39	0.14		2.0[d]
COMe		2.39	0.14	0.30 (0.23)	1.9[d]
CO_2H	(2.85)	2.36	0.18	0.30	
CO_2Me		2.37	0.19	0.32 (0.21)	2.4[d]
$CONH_2$		2.30	0.14	0.28	1.89
COF			0.18		3.3[d]
CF_3	3.35	2.47	0.17 (0.25)[e]	0.40 (0.42)	3.57
NH_2	3.35	2.47	0.33	0.17 (0.14)	5.2[d]
NHMe		2.50	0.34	0.13	5.8[d]
NMe_2	(3.0)	2.48	0.34	0.17 (0.10)	6.89[d]
NHCHO		2.50[f]	0.39	0.33	6.87
$NHNH_2$		2.50	0.34		5.8[d]
NO_2	3.4	2.75	0.40	0.67 (0.65)	11.43[d]
NCO		2.83	0.42		10.0[d]
OH	3.7	2.79	0.43	0.24	9.7[d]
OMe	(3.7)	2.82	0.44	0.30 (0.24)	11.09[d]
OCOMe		2.80	0.46	0.38	12.78
F	3.95	3.10	0.52	0.54 (0.45)	14.84[d]
SiH_3	(2.2)	1.79[g]	−0.13	−0.11[g] (−0.04)[g]	−6.5[d]
SH	(2.8)	2.17	0.12	0.27	4.2[d]
SMe		2.16	0.10	0.30 (0.23)	3.9
Cl	3.03	2.37	0.28	0.47 (0.45)	9.21[d]

[a] Reference 5. [b] Reference 16. [c] Determined as 80% solutions in $(CD_3)_2CO$. [d] From ref 15. [e] Estimated from eq 1 (see text). [f] NHCOMe. [g] $SiMe_3$.

Table V. Coupling Constants $^1J_{CC}$ (Ortho-Ipso)[a] for Some ω-Substituted Phenylalkanes[b]

X	PhX	$PhCH_2X$	$Ph(CH_2)_2X$	$Ph(CH_2)_3X$
H	0.00	0.00	0.00	0.00
Me	1.07	0.02	−0.20	
COMe	1.9	0.49	−0.11	
CN	4.11	2.00	0.05	
OH	9.7	0.58	−0.20	0.02
F	14.84	0.93		

[a] ΔJ referred to corresponding hydrocarbon values in hertz. [b] Determined as 80% solution in $(CD_3)_2CO$.

and standard geometries.[20] Energies and dipole moments for most of the molecules recorded here have been previously published.[21]

Table I lists the atomic charge densities on hydrogen, expressed as $1.000 - q_H$, for a considerable number of compounds HX. These were determined at the 6-31G* basis level with geometry optimization. Table II lists atomic electron populations on hydrogen for some HX, HCH_2X, and HCH_2CH_2X derivatives at the STO-3G level. Table III lists calculations at the 6-31G* level with geometry optimization for methyl derivatives CH_3X.

The $^1J_{C1C2}$ coupling constants for a series of monosubstituted benzenes recorded in Tables IV and V were either taken from the literature[18] or measured on a Brüker WH-400 or a Varian XL-200 spectrometer. Spectra were recorded for solutions containing 80% (by volume) monosubstituted benzene and 20% $(CD_3)_2C{=}O$ in 10-mm tubes. In each case, spectra were recorded for the aromatic region only (typically 1000–1500 Hz spectral width), using 32K data points with resultant data point resolution of 0.06–0.10 Hz. Typically 100 transients were accumulated by using 90° pulses and a combined acquisition time and relaxation delay of 30 s. Coupling constants were measured directly from the AB satellite spectra due to doubly ^{13}C-labeled (ipso and ortho) benzene molecules. In the case of XL-200 spectra, the software peak interpolation routine gives peak positions to 0.01 Hz. In the case of WH-400 spectra, peak positions were measured directly from the oscilloscope with the cursor subroutine. Estimated uncertainty is ±0.05 Hz.

Discussion

What we are seeking is a simple and easily determined measure of substituent electronegativity. The main parameter we have chosen to use for this purpose is the atomic charge density (or fractional ionic charge) on the hydrogen in HX derivatives, as estimated by Mulliken population analysis of the results of ab initio molecular orbital calculations. One major advantage of the H–X systems (as compared to earlier attempts to define substituent electronegativity using semiempirical (MINDO) calculations on CH_3X derivatives[18]) is that the hydrogen has no pseudo-π orbitals that could be involved in hyperconjugative interactions with X. However, the use of atomic charge densities in HX derivatives to define electronegativity involves two fundamental assumptions. The first is that there is a linear relationship between the charge

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Table VI. Electronegativities of Elements

	Pauling[a]	Allred and Rochow[b]	Boyd and Marcus[c]
H	2.2	2.20	1.94
Li	0.98	0.97	1.07
B	1.57	1.47	1.56
B	2.04	2.01	1.95
C	2.55	2.50	2.53
N	3.04	3.07	3.23
O	3.44	3.50	3.53
F	3.98	4.10	4.00
Si	1.90	1.74	1.81
P	2.19	2.06	2.34
S	2.58	2.44	2.65
Cl	3.16	2.83	3.14

[a] Reference 3. [b] Reference 8. [c] Reference 2.

density on hydrogen and the difference in electronegativity between H and X. The second is that substituent-induced changes in hydrogen charge density (or at least trends in these changes[22]) are accurately predicted by Mulliken population analysis.

The actual relationship between fractional ionic charge and electronegativity difference is complex, and both nonlinear[23,24] and linear relationship[24] have been proposed. However, available experimental evidence suggests that the relationship is essentially linear for molecules with partially ionic bonds, but may break down for highly ionic species.[24] The current state of understanding is probably best summarized by the recent comment that "in view of the many approximations and theoretical uncertainties surrounding such relationships, it is questionable whether anything is to be gained by proceeding beyond a simple straight-line fit"[25] with the added cautionary note that this may not apply to highly ionic species.

The weaknesses of Mulliken population analysis are well recognized.[26] In particular, it is likely to be least reliable in highly ionic species.[26] On the other hand, atomic charges determined by Mulliken population analyses are known to predict substituent-induced changes in experimental parameters such as NMR chemical shifts with excellent precision.[27] Consequently, we felt that atomic charge densities from Mulliken population analysis should provide reliable trends that could be used to define a substituent electronegativity scale, again with the cautionary note that results for highly ionic HX derivatives might be unreliable.

We have previously shown[22] that relative atomic populations on hydrogen obtained from ab initio molecular orbital calculations are approximately linear from one basis set to another. We have used the 6-31G* basis to obtain a standard set, although values at this level without geometry optimization should show reasonable agreement.[22]

We are well aware that more sophisticated procedures exist for determining atomic charge densities in simple molecules.[26,28] However, these procedures are all more difficult to carry out and interpret, particularly for the polyatomic molecules we are investigating. In any case, in view of the uncertainty concerning the precise relationship between atomic charge densities and electronegativity differences (particularly for ionic species), it is not clear that the use of such complex procedures is justified. We prefer to use the hydrogen charge densities in HX derivatives as determined by Mulliken population analysis is a simple empirical measure of substituent group electronegativity. The validity of this approach is best judged by comparing our results with those obtained by more complex methods.

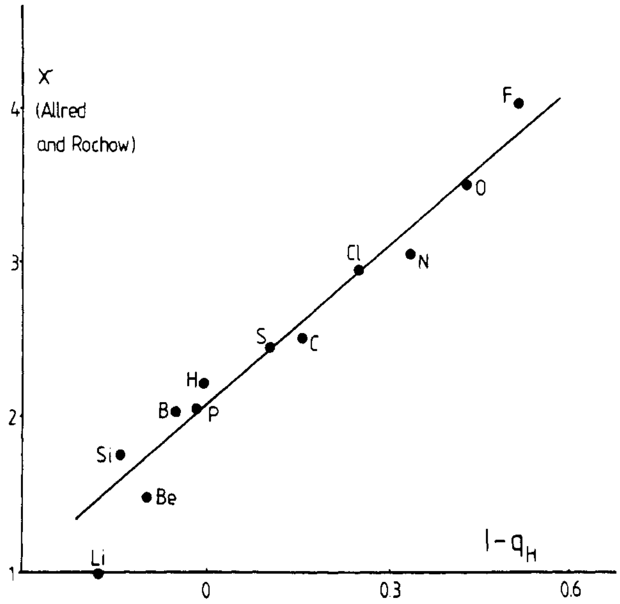

Figure 1. Plot of 1 − q_H values for molecules YH_n vs. χ values for atoms Y.

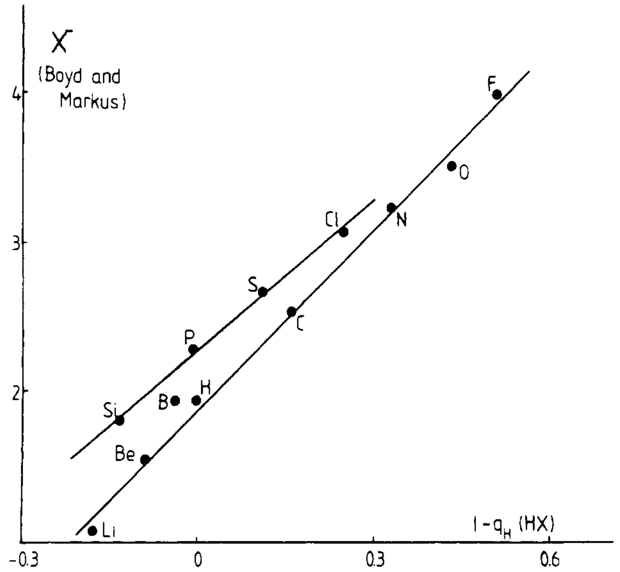

Figure 2. Plot of 1 − q_H values for molecules YH_n vs. χ values for atoms Y.

The 1 − q_H values listed in Table I for compounds HX, show a qualitative pattern in agreement with expectation for an electronegativity scale. Thus, values where X is NH_2 and NO_2 are not too different, similarly for CH_3 and CF_3. The values can be plotted against other scales of electronegativity; for example, those listed for elements in Table VI. In Figure 1, we plot the 1 − q_H values against the χ values, for atoms, of Allred and Rochow[8] and in Figure 2 against the recent values of Boyd and Marcus.[2] Since we

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[22] Since the definition of an electronegativity scale involves an arbitrary scaling factor, one needs only relative hydrogen charge densities in order to define an electronegativity scale.

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[27] (a) Hehre, W. J.; Taft, R. W.; Topsom, R. D. *Prog. Phys. Org. Chem.* **1976**, *12*, 159. (b) Reynolds, W. F.; Gibb, V. G.; Plavac, N. *Can. J. Chem.* **1980**, *58*, 839; (c) Craik, D. J.; Brownlee, R. T. C. *Prog. Phys. Org. Chem.* **1983**, *14*, 1.

[28] (a) Politzev, P.; Harris, R. R. *J. Am. Chem. Soc.* **1970**, *92*, 6451. (b) Bader, R. F. W.; Beddall, P. M. *Ibid.* **1973**, *95*, 305; (c) Grier, D. L.; Steitweiser, A. *Ibid.* **1982**, *104*, 3556.

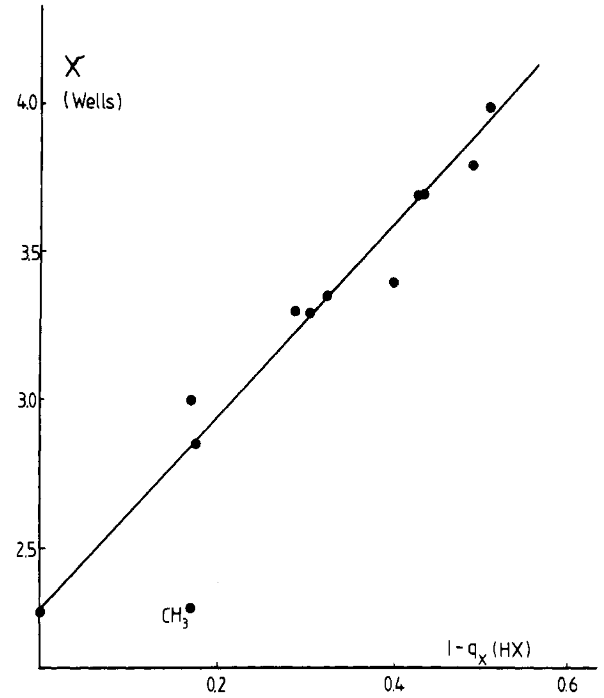

Figure 3. Plot of $1 - q_H$ values for molecules HX vs. χ values for substituents X.

are plotting against elemental values, we use the $1 - q_H$ values for the series HYH_n in each case where Y is the element. Figure 1 shows excellent linearity except for Li and Be, while Figure 2 shows excellent linearity for all of the first major row elements, but with the second major row on a separate line. We conclude that our figures for first row substituents are at least as definitive as those from the references. (The values for second row substituents are not available at the same level of basis set.) The $1 - q_H$ values can also be plotted against group electronegativities although those values are not so well defined as elemental figures. Figure 3 shows a plot of $1 - q_H$ vs. the "mutually consistent" values of Wells,[5] listed in Table IV. Again, the plot is good, except here for the value for the CH_3 substituent. Wells does, however, list values of 2.27–2.63 for this group; the highest end of this range would place the point on the line of best fit of the values for the other substituents.

One feature of the calculations deserves special comment. The calculated hydrogen charge density in LiH (−0.18) is certainly underestimated. The gaseous dipole moment for LiH (5.9 D)[29] indicates that the bond in LiH must be predominantly ionic, even in the gas phase. Clearly, this is a case where Mulliken population analysis fails as suggested above. More sophisticated methods of charge analysis indicate an atomic charge of as large as −0.9 for H in LiH.[28b] However, assuming a linear relationship between hydrogen charges and electronegativity differences, this would in turn indicate an atomic electronegativity for Li of ca. −1.5, well below the values of ca. +1 in other atomic electronegativity scales (see Table VI). Thus, it appears that there is a breakdown in both the Mulliken population analysis and the atomic charge–electronegativity relationship. Interestingly, the two errors approximately cancel out so that our approach gives a value of electronegativity that is in reasonably good agreement with other values (see Figures 1 and 2), far better, in fact, than if we had used a more sophisticated method for determining hydrogen charge density. Thus, due to this fortuitous cancellation of errors, our empirical approach for determining substituent electronegativity works reasonably well even for a substituent where it would have been expected to fail.

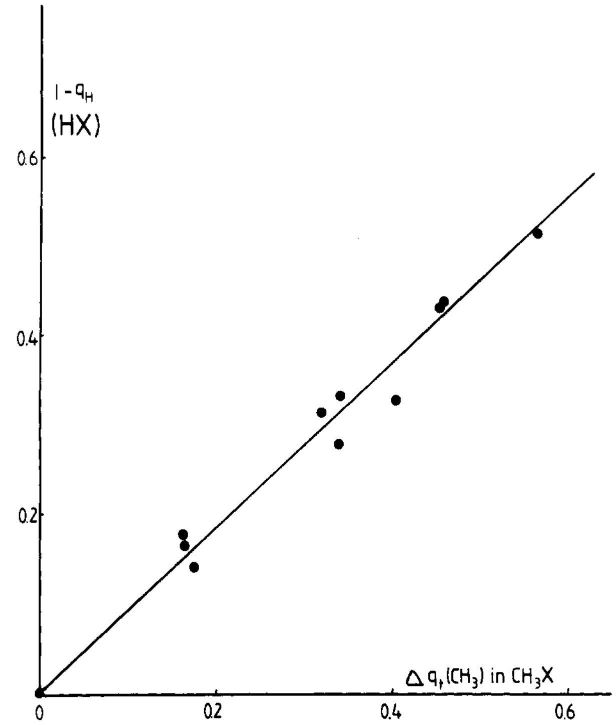

Figure 4. Plot of $1 - q_H$ values for molecules vs. Δq_t values for molecules CH_3X.

Thus, the net charge on the hydrogen in molecules HX seems to provide a well-defined scale of electronegativity and one that is simple to calculate for small substituents. Table II illustrates that the charge on the proton in molecules *H*CH_2X and *H*CH_2CH_2X does not parallel this. Thus, the figures for HCH_2X relative to HCH_2H and HCH_2CH_2X relative to ethane are small and not proportional to the changes in HX. For larger chains, such as *H*$CH_2CH_2CH_2CH_2X$, there is virtually no change in the charge at the H, even if X is changed from H to F. These results indicate that transmission of electronegativity effects through a chain of atoms is almost completely damped out after the first or second atom. Elsewhere, we have shown[30] that changes in atom charge density at more remote atoms are caused by field effects.

As we pointed out above, the total charge transfer from, or to, the methyl group in compounds CH_3X was suggested[18] as a measure of the "group electron-withdrawing power" of X in connection with correlations of J_{CC} values in monosubstituted benzenes. These calculations were done at the semiempirical MINDO level, but we have repeated then for a group of substituents at the ab initio 6-31G* basis level with geometry optimization. These values are listed in Table III and plotted against the $1 - q_H$ values for HX molecules in Figure 4. There is fair linearity here but the possibility of hyperconjugative interaction between the methyl group and substituent in CH_3X and the fact that HX molecules provide for simpler calculation cause us to prefer the later system. The relationship between our $1 - q_H$ values and the charge on the carbon atom in CH_3X is less precise. We also note that

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[29] McClellan, A. "Tables of Experimental Dipole Moments"; W. H. Freeman: San Francisco, 1963.

[30] Topsom, R. D. *J. Am. Chem. Soc.* **1981**, *103*, 39 and references therein. Taagepera, M.; Hehre, W. J.; Topsom, R. D.; Taft, R. W. *Ibid.* **1976**, *98*, 7438.

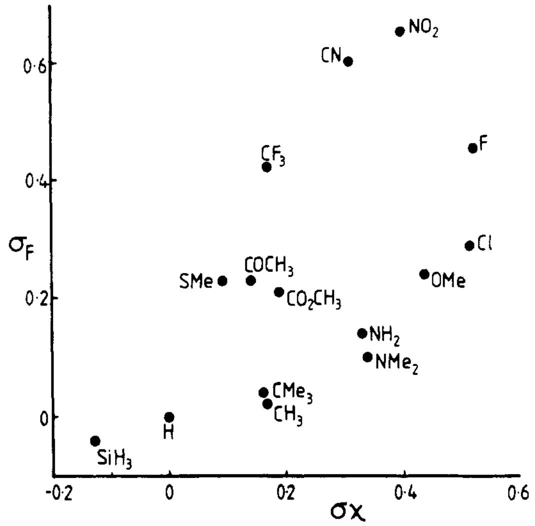

Figure 5. Plot of σ_F values vs. σ_χ values.

values[31] for the σ electron transfer in monosubstituted benzenes are not proportional to the $1 - q_H$ values for HX. This is expected since σ electron populations in benzenes reflect[27a] in part, changes to the π-system which is altered by resonance and field effects of a substituent.

The $1 - q_H$ values are in the range 0–0.52 and are thus the same scale of magnitude as σ_F values. We therefore define a theoretical scale of σ_χ values to be $1 - q_H$ for the proton in molecules HX as obtained at the 6-31G*/6-31G* level. (Values at other levels of ab initio molecular orbital calculations, such as STO-3G, can be corrected[20] to this scale since the various levels give charge values in approximate proportion to one another). We list such σ_χ values to two significant figures in Table IV for most common substituents. We also record there the most recent values[17] of the so-called "inductive substituent parameter" of Inamoto and Masuda. These are derived from electronegativity parameters on the basis of the covalent boundary potential method of Gordy.[9] Slightly different scaling factors are used for each period. These represent an extension and recalculation of earlier values.[16] The authors report[17] a good correlation of their electronegativity values on which the parameters were based with the limited set of $1 - q_H$ values that we earlier reported.[15] Overall, however, there is only a rough proportionality and the values for CHO and COMe on the one hand and for NHX and NR_2 substituents on the other deviate significantly in opposite directions. We prefer our values because of the well-defined method by which they are obtained and the agreement of our NH_2 value with elemental values as discussed above.

Other authors[32,33] have obtained atomic charges by an iterative partial equalization of orbital electronegativities. Such figures are only roughly proportional to the $1 - q_H$ figures reported here.

As mentioned in the introduction, the polar or field substituent constant, σ_F, is not expected to parallel σ_χ (see ref 10 for a detailed discussion of this point). Values of σ_F taken from Charton's recent compilation of substituent constants[34] are listed in Table IV. These values were determined from aqueous acidities. Also listed in Table IV (in parentheses) are σ_F constants that have been determined in aprotic media.[35] The latter constants are plotted against σ_χ in Figure 5. As anticipated,[10] there is a very poor relationship between field, σ_F, and group electronegativity, σ_χ, constants.

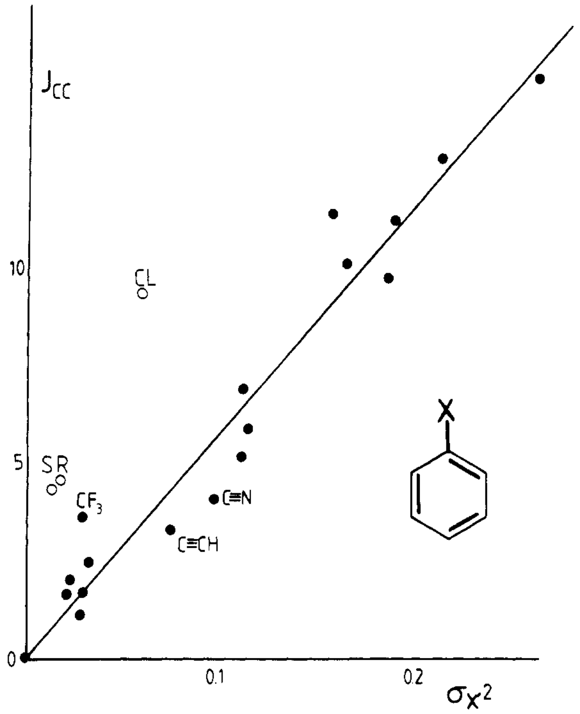

Figure 6. Plot of J_{CC}(ipso–ortho) for C_6H_5X vs. σ_χ^2 values.

It was earlier recognized[15,18] that certain $^1J_{CC}$ coupling constants seemed to be largely a function of electronegativity effects. A check of the literature suggested that $^1J_{CC}$ in CH_2CH_2X, CH_3COX, and C_6H_5X might all be suitable, but we chose to investigate the latter because the coupling constant range is the largest of the three series and because an extensive series of monosubstituted benzenes can readily be obtained. Our results, together with literature values where available, are listed in Table IV. We earlier showed that a plot of $^1J_{CC}$ vs. σ_χ was curved but find empirically that a plot vs. σ_χ^2 is linear as shown for important substituents in Figure 6. For the 28 substituents having a first atom in the first major row less electronegative than hydrogen, the following relationship (eq 1) is found with

$$\Delta J_{CC} = 53.9\sigma_\chi^2 + 0.3 \qquad (1)$$

a correlation coefficient of 0.978. (The empirical relationship fails badly for Cl, SH, SMe, and SiH_3 substituents by using our tentative σ_χ values.) Some substituents such as CF_3, NO_2, C≡CH, and CN show significant deviations. Consequently, while the coupling constants tend to show a strong degree of dependence on substituent electronegativities, there is not a generalized linear correlation.

Table V shows the J_{C1C2} values for some ω-substituted phenylalkanes. It is seen that the coupling constants are small in benzyl derivatives and almost negligible by the time two methylene groups are interposed between the phenyl group and the substituent. This again provides evidence that electronegativity effects are not significant beyond the first intervening carbon atom. Furthermore, the data in Table V provide no support for the idea of a

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[31] Pross, A.; Radom, L. *Prog. Phys. Org. Chem.* **1980**, *13*, 1.

[32] Gasteiger, J.; Marsili, M. *Tetrahedron* **1980**, *36*, 3219.

[33] Gasteiger, J.; Marsili, M. *Org. Magn. Reson.* **1981**, *15*, 353.

[34] Charton, M. *Prog. Phys. Org. Chem.* **1980**, *13*, 1.

[35] Reynolds, W. F.; Gomes, A.; Maron, A.; MacIntyre, D. W.; Tanin, A.; Hamer, G. K.; Peat, I. R. *Can. J. Chem.* **1983**, *61*, 2376.

[36] Just as in the case of the relationship between electronegativity and atomic charge densities, there is no clear theoretical evidence for the functional form of the relationship between electronegativity and $^{13}C-^{13}C$ coupling constants. Therefore, we have chosen the empirical relationship that gives the best fit.

group electronegativity (or σ inductive) effect that alternates in sign along an aliphatic chain, as first suggested by semiempirical molecular orbital calculations on $X-(CH_2)_nCH_3$ derivatives.[37] However, the data for CN and OH derivatives show a reasonable parallel with charge densities for HX and HCH_2X derivatives (Table II) by predicting a surprisingly large effect for $-CH_2CN$ (and also for $-CH_2COCH_3$). It is possible that there is a hyperconjugative contribution to J_{CC} for these derivatives, similar to that suggested for $H{-}CH_2{-}X$ charge densities. It should be noted in this regard that there may be minor errors in calculated σ_X values for CH_nX_{3-n} groups due to this type of hyperconjugative interaction. In particular, σ_X for CF_3 may be too small. It is interesting that if eq 1 is used to estimate σ_X values for these groups, values for CH_2X groups ($X = NH_2$, OH, F, CN) are only slightly altered (although the relative order for $X = NH_2$, OH, and F seems more logical) but σ_X for CF_3 is significantly increased. We suspect that $\sigma_X = 0.25$ is a more reasonable value for CF_3.

Earlier,[38] it was suggested that a series of "inductive" substituent constants could be obtained from olefinic geminal J_{HH} values. The experimental values were taken from several sources, and the derived σ^{J}_{I} values do not seem to follow either σ_F or σ_X values.

Conclusions

In conclusion, hydrogen charge densities in compounds HX as determined by Mulliken population analysis of calculations at the ab initio molecular orbital 6-31G* level provide a straightforward method for estimating substituent group electronegativities. Comparison for simple substituents with previously determined atomic electronegativities indicates that our method is fundamentally sound. An empirical relationship is noted between group electronegativity and $J_{C(ipso)-C(ortho)}$ for many monosubstituted benzenes where the directly bonded atom is a first row element. This provides an alternative method for defining group electronegativities that may be more reliable for CH_nX_{3-n} groups, e.g., CF_3.

Registry No. H_2, 1333-74-0; LiH, 7580-67-8; BeH_2, 7787-52-2; BH_3, 13283-31-3; $HBMe_2$, 7216-97-9; HBF_2, 13709-83-6; CH_4, 74-82-8; C_2H_6, 74-84-0; CH_2Me_2, 74-98-6; $HCMe_3$, 75-28-5; $CH_2{=}CH_2$, 74-85-1; $HC{\equiv}CH$, 74-86-2; $HC{\equiv}CMe$, 74-99-7; H_2NMe, 74-89-5; HOMe, 67-56-1; CH_3F, 593-53-3; CH_3CHO, 75-07-0; CH_3CN, 75-05-8; HCN, 74-90-8; HOCN, 420-05-3; HCHO, 50-00-0; HCO_2H, 64-18-6; HCO_2Me, 107-31-3; $HOCONH_2$, 463-77-4; HCOF, 1493-02-3; HCF_3, 75-46-7; NH_3, 7664-41-7; $NHMe_2$, 124-40-3; NH_4^+, 14798-03-9; H_2NCHO, 75-12-7; H_2NNH_2, 302-01-2; HNC, 6914-07-4; HNCO, 75-13-8; HNO, 14332-28-6; HONO, 7782-77-6; H_2O, 7732-18-5; HOCOMe, 64-19-7; HO^-, 14280-30-9; HF, 7664-39-3; SiH_4, 7803-62-5; PH_3, 7803-51-2; H_2S, 7783-06-4; HSMe, 74-93-1; HCl, 7647-01-0; allene, 463-49-0.

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[37] Pople, J. A.; Gordon, M. S. *J. Am. Chem. Soc.* **1967**, *89*, 4253.
[38] Knorr, R. *Tetrahedron* 1981, *37*, 929.

An Anthrylidenequinodiquinocyclopropane and Related Compounds. Their Structure and Physical Properties

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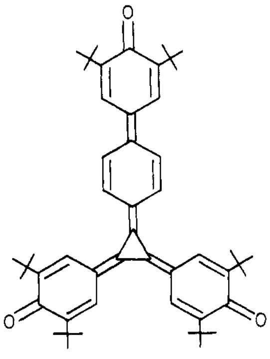
Dihydroquinones **6**, **10**, and **11** have been synthesized and characterized. Oxidation of **6** yields polyquinone **4**, which has its λ_{max} at 672 nm, with $E_1 = 0.09$ V and $E_2 = -0.20$ V. Evidence from cyclic voltammetry and from the ESR of the anion-radical of **4** indicates that steric interactions limit conjugation in this molecule.

The quinocycloalkanes are a family of compounds having intense, low-energy electronic transitions and are potentially useful as dyes, photoconductors, and photographic materials. As a part of our continuing study of these molecules,[1-3] a report from this laboratory several years ago discussed the synthesis and characterization of **1**, an interesting triquinocyclopropane with a remarkable electronic excitation absorption at 1300 nm.[4] This absorption is well into the near-infrared region, an area approaching molecular bond vibrational energy and not often seen for electronic excitation of organic molecules.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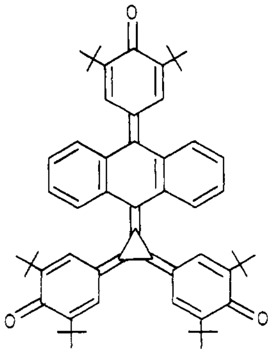
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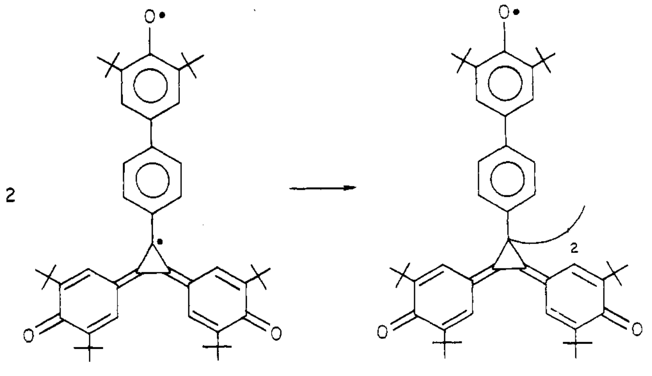
Compound **1** is, however, unstable, decaying by first-order kinetics with a half-life of 92 min at 25 °C. The ESR spectrum of **1** suggests that it exists predominantly in the diradical form **2** which dimerizes to give the diradical dimer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[2] Benham, J. L.; West, R.; Norman, J. A. T. *J. Am. Chem. Soc.* **1980**, *102*, 5047 and references therein cited.
[3] Benham, J. L.; West, R. *J. Am. Chem. Soc.* **1980**, *102*, 5054.
[4] Wendling, L. A.; West, R. *J. Org. Chem.* **1978**, *43*, 1573.

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