Table IX. Calculated Electron Populations[a]

	formamide			formamidic acid		
atom	$\epsilon = 1.0$	$\epsilon = 35.9$	Δ	$\epsilon = 1.0$	$\epsilon = 35.9$	Δ
C	4.037	4.040	0.003	4.214	4.217	0.003
N	8.490	8.494	0.004	8.525	8.528	0.003
O	9.395	9.406	0.011	9.334	9.332	−0.002
H_1	1.023	1.019	−0.004	0.988	0.982	−0.006
H_2	0.520	0.519	−0.001	0.601	0.599	−0.002
H_3	0.535	0.523	−0.012	0.340	0.342	0.002
total	24.000	24.001		24.002	24.000	

	2-pyridone			2-hydroxypyridine		
atom	$\epsilon = 1.0$	$\epsilon = 35.9$	Δ	$\epsilon = 1.0$	$\epsilon = 35.9$	Δ
C_1	4.237	4.258	0.021	4.558	4.575	0.017
C_2	5.950	5.959	0.009	5.911	5.910	−0.001
C_3	5.974	5.968	−0.006	5.963	5.961	−0.002
C_4	5.871	5.851	−0.020	5.952	5.947	−0.005
C_5	5.433	5.450	0.017	5.233	5.239	0.006
N	8.600	8.601	0.001	8.654	8.658	0.004
O	9.414	9.437	0.023	9.335	9.334	−0.001
H_1	0.514	0.518	0.004	0.339	0.343	0.004
H_2	0.992	1.017	0.025	1.001	1.003	0.002
H_3	1.012	0.999	−0.013	1.016	1.007	−0.009
H_4	1.017	0.982	−0.035	1.027	1.016	−0.011
H_5	0.990	0.966	−0.024	1.013	1.011	−0.002
total	50.004	50.006		50.002	50.004	

[a] HF/6-31+G**//HF/6-31G** wavefunctions.

in molecules.[19] As expected, the charge distributions of formamide enol and 2-hydroxypyridine are found to be slightly influenced by a dielectric medium. However, a larger degree of charge separation is predicted for the more polar keto compounds, formamide and 2-pyridone. This difference in reaction field effect on charge distributions is in accord with the changes in dipole moments, molecular geometry, and vibrational frequencies in going from the gas-phase to solution. However, the charge distribution in solution is more delocalized than one would have expected from the dipolar resonance picture. For the keto compounds, the electron populations at the carbonyl oxygens increase in going from vacuo to a polar volume medium, by 0.11 and 0.23 e for formamide and 2-pyridone, respectively (Table IX). Consistent with previous observations for other carbonyl compounds,[27] the change in charge at oxygen does not come from the carbon, but instead comes from the hydrogens. In fact, an increase in electron population is predicted for the carbonyl carbon. It is interesting to note that the electron populations of C_4 and C_5 of 2-pyridone are also perturbed by the reaction field. The changes in electron density in the presence of a solvent reaction field for formamide and 2-pyridone are shown pictorially in Figure 2. It can be seen that the electron density is transferred from the hydrogens to the carbonyl moiety, which leads to a larger degree of charge separation. The SCRF wave functions were obtained using the unrelaxed (gas-phase) geometries in order to make a direct comparison of the effects of solvation.

Conclusions

Several important points emerge from this study:

(1) Geometry optimizations at the correlated level (MP2/6-31G**) are reported for the first time for 2-hydroxypyridine and 2-pyridone. NMR spectroscopy is predicted to offer another means of studying the tautomerization of 2-pyridone in the gas phase.

(2) The solvent effects on the tautomeric equilibrium of 2-pyridone are readily reproduced by ab initio reaction field theory. The calculated tautomerism free energies in the gas phase, cyclohexane, and acetonitrile are in very good agreement with the experimental estimates.

(3) High-level treatment of electron correlation, such as QCISD, is essential for a reliable estimate of the tautomerism energy of 2-pyridone in both the gas phase and solution. However, SCRF calculations at the HF and MP2 levels can provide reasonable estimates of solvation free energy.

(4) The calculated changes in geometry, charge distributions, and infrared spectra of the keto tautomers in going from the gas phase to solution are in accord with the increasing weight of the dipolar resonance structure.

Acknowledgment. This research was supported by a grant from the National Institutes of Health and by Lorentzian, Inc.

Registry No. 2-Pyridone, 142-08-5; 2-pyridinol, 72762-00-6; formamide, 75-12-7; formimidic acid, 60100-09-6.

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(27) Wiberg, K. B.; Wong, M. W. To be published.

Group Electronegativities from the Bond Critical Point Model

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Received August 19, 1991

Abstract: The bond critical point model is used to calculate the electronegativities of over 100 groups from ab initio wave functions. The data show that the electronegativity of a group is largely determined by the connecting atom: atoms that are one bond or more removed have very little effect on the electronegativity of a group. The small effect of atoms one bond or more removed, however, is consistent with qualitative predictions: the higher the electronegativity of B for a given A, the greater the electronegativity of group –AB. Two other trends of note are, firstly, that increasing unsaturation in the vicinal bond increases electronegativity and, secondly, that protonation increases electronegativity of a group while deprotonation decreases it.

Few chemical concepts are as enduring and as widely used as that of electronegativity, "the power of an atom in a molecule to attract electrons to itself".[1] The popularity of the concept is due to its simplicity and to the availability of numerical values for most of the elements. In general, numerical scales indicate that electronegativity increases from left to right within a given row of the periodic table and decreases from top to bottom. Numerous correlations between atomic electronegativities and a variety of

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0002-7863/92/1514-1652$03.00/0

chemical and physical properties have played a key part in the organization and interpretation of chemical facts and observations. (A comprehensive review of atomic electronegativity scales is beyond the scope of this paper. Key references may be found in the recent paper by Allen[2] and in the book edited by Sen and Jørgensen.[3])

Pauling used thermochemical data for diatomic molecules to obtain numerical values for the electronegativities of atoms, and most of the subsequent attempts to develop electronegativity scales continued to regard electronegativity as an atomic property. From Pauling's original definition it can be argued, however, that electronegativity is the power or tendency of a *group* of atoms in a molecule to attract electrons to themselves, i.e. that "electronegativity is not a property of the isolated atom but rather a property of an atom in a molecule, in the environment of and under the influence of surrounding atoms".[4] Relatively few methods have been proposed for the evaluation of group electronegativities; moreover, typically such methods have been used to evaluate relatively small subsets of the chemically interesting groups of atoms.

A recent publication by one of us[5] introduced the bond critical point model for the determination of group electronegativities and presented electronegativities for about 30 groups. Our method, which is based on the topological properties of the electron density distributions of molecules, yields group electronegativities which correlate with values from a variety of methods, the exceptions being methods based on total electronegativity equalization. In view of the continuing interest in electronegativity and a number of requests for the electronegativities of additional groups,[6] we report herein the most complete set, to date, of mutually consistent group electronegativities.

Bond Critical Point Model

The bond critical point model of electronegativity is based on the topological properties of the electron density $\rho(\mathbf{r})$ which for any molecule may be partitioned[7-10] into fragments by zero-flux surfaces that satisfy the condition

$$\nabla\rho(\mathbf{r})\cdot\mathbf{n} = 0 \qquad (1)$$

for every point on the surface of the subsystem where $\mathbf{n}$ is a unit vector normal to the surface. Points on the zero-flux surfaces at which

$$\nabla\rho(\mathbf{r}) = 0 \qquad (2)$$

are known as critical points. Each critical point $\mathrm{r_c}$ can be classified according to its rank and signature (λ,σ). The rank λ of a critical point equals the number of non-zero eigenvalues of the Hessian matrix of $\rho(\mathrm{r_c})$, while the signature is the algebraic sum of the signs of the eigenvalues. A (3,−1) or bond critical point has three curvatures, one positive and two negative, and is therefore a saddle point in $\rho(\mathbf{r})$. In other words at a bond critical point the electron density is at a minimum with respect to a displacement along the bond path joining two bonded atoms, and at a maximum with respect to a lateral displacement from the bond path. A (3,−1) critical point appears between every pair of neighboring bonded atoms. A number of interesting observations relating to bond critical points and related properties have appeared in the literature. In particular, it has been observed that the electron density at the bond critical point is related to the bond type and order.[10-12] More important for the present discussion is the observation that systematic studies[13,14] of main group hydrides have shown that the bond critical point moves monotonically closer to the hydrogen nucleus as the atomic number of the heavier atom increases. This observation, and others relating to the topological properties of $\rho(\mathbf{r})$, led to the definition of a electronegativity factor F_A of atom A in a diatomic hydride:[5]

$$F_A = r_H/N_A(\rho(\mathbf{r}_c))r_{AH} \qquad (3)$$

where r_H is the distance from the bond critical point to the hydrogen nucleus, N_A is the number of valence electrons of atom A, $\rho(\mathbf{r}_c)$ is the electron density at the bond critical point $\mathbf{r}_c$, and r_{AH} is the internuclear distance. The electronegativity factor F_A is converted to an electronegativity for atom A, comparable in magnitude to the Pauling value, by means of a power curve,

$$\chi_A = 1.938F_A^{-0.2502} \qquad (4)$$

where the two parameters were chosen to give electronegativities of 1.00 and 4.00 for Li and F, respectively.[5] The bond critical point model for atomic electronegativities is readily extended to group electronegativities. Thus, the electronegativity of group A is calculated from properties associated with the A–H bond critical point in AH. For example, the electronegativity of the methoxy group, CH_3O–, is obtained by determining the position of the O–H bond critical point in CH_3OH and substituting the appropriate values into eqs 3 and 4, bearing in mind that N_A is the number of valence electrons of oxygen.

Computational Details

The original exposition[5] of the bond critical point model of electronegativity was based on Hartree–Fock calculations with large basis sets at the experimental equilibrium geometries. These basis sets are impractical for the treatment of larger groups and, therefore, smaller basis sets are required. A few test calculations with the 6-31G* basis set yielded results in close agreement with the larger basis set results. Accordingly, we have chosen the 6-31G* basis set as a reasonable compromise between accuracy and applicability. One further change is indicated by the paucity of accurate gas-phase experimental equilibrium geometries. Thus, in order to be able to calculate group electronegativities at a uniform theoretical level, all molecular geometries have been optimized within the Hartree–Fock formalism using the 6-31G* basis set. In standard shorthand notation the group electronegativities have been calculated at the HF/6-31G*//HF/6-31G* level, where "//" means "at the geometry of".

The Hartree–Fock calculations were carried out using the GAUSSIAN 86 and 90 programs,[15,16] and the topological properties were calculated using the PROAIM and modified PROAIM packages.[17,18]

Results and Discussion

Table I lists the bond critical point electronegativities of more than 100 groups, together with the associated properties for their calculation from eqs 4 and 5. (More than one value is listed for groups in which conformationally inequivalent hydrogens can be

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Table I. Group Electronegativities

group		χ^a	$r_H{}^b$	$r_{AH}{}^b$	$\rho(\mathbf{r}_c)^b$
$-BeH$		1.47 (1.48, 1.47)	1.436	3.957	0.095
$-BH_2$		1.92 (1.93, 1.93)	1.271	3.516	0.183
$-CH_3$		2.55 (2.55, 2.56)	0.760	2.048	0.277
$-CH_2CH_3$		2.55 (2.55, 2.56)	0.765	2.052	0.279
$-CH_2CH_2CH_3$	ip[c]	2.55 (2.55, —)	0.766	2.052	0.278
	op[d]	2.55 (2.54, —)	0.767	2.054	0.278
$-CH_2CH(CH_3)_2$	ip	2.54 (2.53, —)	0.768	2.055	0.277
	op	2.55 (2.54, —)	0.767	2.053	0.278
$-CH_2C{\equiv}N$		2.58 (2.56, —)	0.731	2.045	0.282
$-CH_2COH$	ip	2.58 (2.56, —)	0.739	2.044	0.282
	op	2.55 (2.55, —)	0.755	2.053	0.276
$-CH_2COO^-$	ip	2.52 (—, —)	0.777	2.052	0.276
	op	2.52 (—, —)	0.783	2.058	0.272
$-CH_2COOH$	ip	2.58 (—, —)	0.736	2.039	0.284
	op	2.56 (—, —)	0.745	2.048	0.279
$-CH_2COF$	ip	2.59 (2.58, —)	0.732	2.039	0.285
	op	2.57 (2.56, —)	0.741	2.048	0.279
$-CH_2CSH$	ip	2.58 (2.57, —)	0.734	2.040	0.285
	op	2.55 (2.54, —)	0.753	2.056	0.276
$-CH_2COCl$	ip	2.59 (2.57, —)	0.732	2.043	0.284
	op	2.57 (2.56, —)	0.737	2.046	0.280
$-CH(CH_3)_2$		2.55 (2.54, —)	0.769	2.055	0.280
$-CH(CH_2)_2$		2.57 (2.56, —)	0.748	2.033	0.285
$-CH{=}CH_2$		2.58 (2.57, 2.61)	0.741	2.034	0.286
$-CH{=}C{=}CH_2$		2.58 (2.57, —)	0.731	2.033	0.283
$-CH{=}C{=}C{=}O$		2.61 (—, —)	0.718	2.038	0.289
$-CH{=}C{=}O$		2.58 (2.57, —)	0.721	2.025	0.279
$-C(CH_3)_3$		2.55 (2.53, —)	0.771	2.057	0.281
$-C_6H_5$		2.58 (2.58, —)	0.741	2.033	0.288
$-C{\equiv}CH$		2.66 (2.65, 2.66)	0.668	1.997	0.295
$-C{\equiv}CF$		2.66 (2.66, —)	0.662	1.994	0.294
$-C{\equiv}CCl$		2.66 (2.66, —)	0.662	1.996	0.294
$-CH_2NH_2$	ip	2.55 (2.54, —)	0.768	2.052	0.282
	op	2.57 (2.55, —)	0.756	2.053	0.283
$-CH_2NHCH_3$	ip	2.57 (2.57, —)	0.755	2.048	0.284
	op	2.55 (2.55, —)	0.771	2.066	0.277
$-CH_2NO_2$	ip	2.62 (2.61, —)	0.711	2.032	0.294
	op	2.61 (2.60, —)	0.718	2.038	0.289
$-CH{=}NH$		2.59 (2.56, —)	0.742	2.048	0.287
$-CH{=}N{=}N$		2.60 (2.60, —)	0.714	2.018	0.287
$-C{\equiv}N$		2.69 (2.68, 2.69)	0.639	2.001	0.295
$-C{\equiv}NO$		2.69 (2.73, —)	0.621	1.994	0.290
$-CH_2OH$	ip	2.59 (2.58, 2.59)	0.741	2.043	0.291
	op	2.57 (2.57, 2.59)	0.757	2.055	0.285
$-CH_2OOCH_3$	ip	2.61 (2.60, —)	0.731	2.037	0.293
	op	2.61 (2.60, —)	0.729	2.041	0.292
$-COH$		2.60 (2.58, 2.60)	0.735	2.063	0.288
$-COCH_3$		2.59 (2.59, —)	0.741	2.070	0.287
$-CONH_2$		2.61 (2.60, —)	0.732	2.061	0.292
$-CO_2^-$		2.49 (—, —)	0.813	2.130	0.261
$-COOH$		2.63 (2.62, 2.66)	0.704	2.047	0.300
$-COOCH_3$		2.64 (2.62, —)	0.709	2.050	0.299
$-C{\equiv}O$		2.57 (2.54, 2.57)	0.727	2.091	0.267
$-COF$		2.67 (2.65, —)	0.691	2.043	0.302
$-COCl$		2.66 (2.64, —)	0.689	2.046	0.297
$-CFH_2$		2.60 (2.61, 2.61)	0.738	2.045	0.292
$-CF_2H$		2.65 (2.64, —)	0.710	2.037	0.308
$-CF_3$		2.71 (2.68, —)	0.680	2.028	0.321
$-CH_2SH$	ip	2.58 (2.57, —)	0.739	2.044	0.283
	op	2.58 (2.57, —)	0.740	2.043	0.285
$-CSH$		2.62 (2.61, —)	0.708	2.038	0.292
$-CSCH_3$		2.62 (2.62, —)	0.713	2.043	0.293
$-CClH_2$		2.61 (2.60, —)	0.723	2.037	0.290
$-CClFH$		2.66 (2.63, —)	0.700	2.033	0.305
$-CClF_2$		2.71 (2.67, —)	0.674	2.028	0.317
$-CCl_2H$		2.66 (2.66, —)	0.692	2.029	0.301
$-CCl_2F$		2.71 (2.67, —)	0.669	2.026	0.313
$-CCl_3$		2.70 (2.66, —)	0.665	2.025	0.310
$-NH_2$		3.12 (3.10, 3.10)	0.480	1.894	0.342
$-NH_3^+$		3.21 (—, —)	0.418	1.916	0.329
$-NHCH_3$		3.13 (3.11, —)	0.482	1.892	0.346
$-NHCOH$	cis	3.18 (3.16, —)	0.446	1.876	0.345
	trans	3.18 (3.17, —)	0.441	1.881	0.341
$-N(CH_3)_2$		3.13 (3.08, —)	0.483	1.891	0.348
$-N{=}CH_2$		3.13 (3.09, —)	0.482	1.902	0.346
$-N{=}C{=}O$		3.18 (3.20, 3.22)	0.428	1.879	0.330
$-N{=}C{=}S$		3.22 (3.21, —)	0.405	1.870	0.330
$-N{\equiv}C$		3.26 (3.26, 3.30)	0.393	1.862	0.339
$-NHNH_2$	ip[e]	3.16 (3.14, —)	0.470	1.889	0.352
	op	3.13 (3.12, —)	0.485	1.895	0.349
$-N{=}NH$		3.15 (3.12, —)	0.481	1.918	0.350
$-N{=}N{=}N$		3.15 (3.23, —)	0.461	1.901	0.337
$-NHOH$		3.17 (3.14, —)	0.468	1.893	0.354
$-N{=}O$		3.12 (3.05, 3.06)	0.499	1.950	0.343
$-NO_2$		3.22 (—, 3.25)	0.439	1.927	0.349
$-NHF$		3.19 (—, —)	0.462	1.896	0.356
$-NF_2$		3.25 (—, —)	0.442	1.897	0.370
$-O^-$		3.36 (—, —)	0.429	1.827	0.352
$-OH$		3.55 (3.52, 3.64)	0.349	1.790	0.367
$-OH_2^+$		3.57 (—, —)	0.306	1.831	0.322
$-OCH_3$		3.53 (3.51, 3.70)	0.352	1.789	0.370
$-OC{\equiv}N$		3.57 (—, 3.73)	0.332	1.800	0.353
$-OCOH$		3.56 (3.50, 3.65)	0.338	1.801	0.357
$-OCOCH_3$		3.57 (—, —)	0.338	1.799	0.359
$-ONH_2$		3.58 (3.54, —)	0.344	1.788	0.374
$-ON{=}O$		3.55 (3.49, —)	0.342	1.813	0.355
$-OO^\cdot$		3.58 (3.51, —)	0.344	1.802	0.370
$-OOH$		3.59 (—, —)	0.343	1.794	0.373
$-OF$		3.60 (3.56, —)	0.338	1.799	0.371
$-OCl$		3.58 (3.53, 3.67)	0.339	1.797	0.365
$-OPH_2{=}O$		3.54 (—, —)	0.342	1.795	0.354
$-OPH(OH)({=}O)$		3.55 (—, —)	0.335	1.798	0.350
$-MgH$		1.30 (1.31, 1.33)	1.581	3.246	0.049
$-AlH_2$		1.60 (1.61, 1.62)	1.510	2.994	0.079
$-SiH$		1.87 (1.87, —)	1.478	2.852	0.113
$-SiH_3$		1.90 (1.89, 1.91)	1.436	2.787	0.118
$-SiF$		1.88 (—, —)	1.495	2.868	0.115
$-SiFH_2$		1.91 (—, —)	1.433	2.777	0.122
$-SiF_2H$		1.93 (—, —)	1.425	2.762	0.127
$-SiF_3$		1.95 (—, —)	1.408	2.737	0.133
$-SiCl$		1.89 (1.85, —)	1.477	2.884	0.118
$-SiClH_2$		1.91 (1.90, —)	1.428	2.773	0.123
$-SiCl_2H$		1.93 (1.92, —)	1.421	2.760	0.127
$-SiCl_3$		1.95 (1.94, —)	1.413	2.747	0.131
$-PH_2$		2.17 (2.16, 2.17)	1.366	2.653	0.163
$-PH_2{=}O$		2.21 (—, —)	1.372	2.632	0.176
$-PH(OH){=}O$		2.22 (—, —)	1.372	2.626	0.180
$-P(OH)_2{=}O$		2.25 (—, —)	1.354	2.595	0.190
$-S^-$		2.52 (—, —)	1.018	2.537	0.192
$-SH$		2.65 (2.66, 2.63)	0.790	2.515	0.184
$-SCH_3$		2.65 (2.65, —)	0.923	2.506	0.215
$-SCN$		2.70 (—, —)	0.877	2.505	0.219
$-SCF_3$		2.68 (—, —)	0.898	2.505	0.217
$-SH{=}O$		2.72 (—, —)	0.896	2.539	0.227
$-SH({=}O)_2$		2.53 (—, —)	1.318	2.505	0.255
$-SF_5$		2.63 (—, —)	1.262	2.464	0.288
$-SSH$		2.68 (2.67, —)	0.899	2.508	0.217

[a] Electronegativities in column 1 were determined at the HF/6-31G*//HF/6-31G* level using eq 4. Values in parentheses were obtained using the same equation: those in column 2 were determined at level HF/6-31G*//experimental geometry using experimental geometries from ref 21; and those in column 3 are the extended basis set//experimental geometry values from ref 5, included here for easy comparison. [b] Atomic units. [c] In-plane H was used as the reference atom for the electronegativity. [d] Out-of-plane H was used as the reference. [e] The "in-plane" H's for hydrazine are the most nearly planar ones, with the "out-of-plane" H's being approximately perpendicular to the plane.

used as the reference atom. For example, in methanol the reference H may be taken to be either in or out of the COH plane. Typically the electronegativity differences for conformationally inequivalent hydrogens is 0.026 or less.)

The groups are listed in order of increasing priority (Cahn–Ingold–Prelog rules), and as a result it is immediately apparent that the electronegativity of a group is largely determined by the connecting atom. Thus, $-CXYZ$ groups have electronegativities close to 2.6 and $-NXYZ$ groups have electronegativities close to 3.2. Atoms which are one bond (or more) removed from the connecting atom have only a secondary effect on the electronegativity of a group. Thus, the electronegativity of the $-CH_3$

group increases from 2.55 to 2.60 to 2.65 to 2.71 with the substitution of successive F atoms. Not surprisingly the effects of extending a hydrogen residue are very small: χ remains very close to 2.55 in the $-CH_3$, $-CH_2CH_3$, $-CH_2CH_2CH_3$, $-C(CH_3)_3$ series.

Increasing the degree of unsaturation of the vicinal bond increases the electronegativity, as demonstrated by the values of 2.55, 2.58, and 2.66 for $-CH_2CH_3$, $-CH{=}CH_2$, and $-C{\equiv}CH$, respectively; a similar effect is observed for the $-CH_2NH_2$, $-CH{=}NH$, $-C{\equiv}N$ series (χ = 2.55/2.57, 2.59, and 2.69, respectively), also for $-CH_2OH$ and $-CH{=}O$ (χ = 2.59/2.57 vs 2.60). In each of these cases, the change in electronegativity is small between the single- and double-bonded groups, but somewhat greater between the double- and triple-bonded groups. This is even more evident in the series $-NHCH_3$, $-N{=}CH_2$, and $-N{\equiv}C$ (χ = 3.13, 3.13, and 3.26), where the single- and double-bonded groups have the same electronegativity.

Relative to some of the methods[19] that have been proposed for the evaluation of group electronegativities, the bond critical point model electronegativities show a less pronounced dependence on the degree of unsaturation. A similar observation holds for the $-CXYZ$ and $-NXYZ$ series mentioned above.

The fact that atoms which are one bond (or more) removed from the connecting atom have only a secondary effect on the electronegativity of a group is consistent with the contention by many authors[1,2] that electronegativity is primarily an atomic property. Nonetheless, the small variation which does occur between groups with the same connecting atom supports the qualitative prediction that the electronegativity of an atom in a group depends on its environment:[4] the higher the electronegativity of B for a given A, the higher the electronegativity of group -AB. For example $-CH_2NO_2$ has χ = 2.62/2.61 while $-CH_2CH_3$ has χ = 2.55. [The only exception to this generalization comes with S-centered groups. If there are nonbonding pairs on the sulfur atom, such as in $-SSH$ and $-SH{=}O$, the χ is higher (2.68 and 2.72, respectively) than if there are no nonbonding pairs, as in $-SF_5$ and $-SH({=}O)_2$ (χ = 2.63 and 2.53, respectively).]

The fact that the bond critical point electronegativities are largely determined by the connecting atom may be attributed to the recent demonstration by Perrin[20] that the position of the bond critical point depends on the size of the atomic orbitals which make up the bond. Although we do not challenge the validity of Perrin's analysis, we overcome the problem by expressing all group electronegativities in terms of a common reference, the H atom. Even though the position of the bond critical point in the A–H bond of H–AB depends on the sizes of the atomic orbitals of H and A, we also observe a dependence on the nature of B.

Our results for the $-NH_3^+$ and $-OH_2^+$ groups (χ = 3.21 and 3.57, respectively) indicate an increase in electronegativity relative to the $-NH_2$ and $-OH$ groups (χ = 3.12 and 3.55), in agreement with the interpretation proposed for the effect of protonation on the homolytic bond dissociation energies of methyl amine and other molecules.[21] Similarly $-O^-$ and $-S^-$ (χ = 3.36 and 3.52, respectively) are less electronegative than $-OH$ and $-SH$ (χ = 3.55 and 3.65, respectively).

Further comment on the level of the present calculations is needed. In principle, χ should be calculated at the highest possible level, preferably with large basis sets and post-Hartree–Fock methods. In the original paper we used experimental equilibrium geometries[22] and we calculated the electronic properties within the Hartree–Fock formalism with large basis sets. In order to be able to treat an extended set of groups, many of which are computationally more demanding than the original set, we have changed the level of treatment in two ways: we have reduced the basis set to the standard 6-31G* and we have used HF/6-31G* optimized geometries, rather than experimental geometries. To illustrate the consequences of these changes we include in Table I (column 2) the data obtained with the HF/6-31G* calculations at the experimental geometries for those groups for which accurate experimental structures of the parent molecule are available. We also include (column 3), for easy comparison, the data obtained with the extended basis sets described elsewhere[5] at the experimental geometries. The good agreement between the three sets of data justifies the choice of the HF/6-31G*//HF/6-31G* level for the calculation of large groups. With respect to use of the Hartree–Fock method for the calculation of bond critical points, it should be noted that post-Hartree–Fock calculations[18,23] for a few molecules have shown that correlated electron distributions possess the same number and kind of critical points as are found for Hartree–Fock distributions. Moreover, electron correlation leads to only a small shift in the positions of bond critical points and a small change in electron density at bond critical points.

Acknowledgment. The financial support of the Natural Sciences and Engineering Research Council of Canada (to R.J.B.) and the Research Fund of MSVU (to S.L.B.) is gratefully acknowledged. We thank Professors T. T. Tidwell and L. C. Allen, among others, for helpful correspondence.

Note Added in Proof. In their recent application of a bond polarity index to group electronegativity, L. H. Reed and L. C. Allen (*J. Phys. Chem.* **1992**, *96*, 157) have demonstrated that CH_3 is a more appropriate reference than hydrogen. We intend to determine whether or not the same conclusion holds true for the bond critical point model.

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(19) See, for example: Mullay, J. *J. Am. Chem. Soc.* **1985**, *107*, 7271–7275 and references therein.

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