paramagnetic dipolar shifts are calculated for the individual protons of the Phe CD1 ring.[38] Addition of these shifts to the tetrapeptide shift[57] for Phe ring protons yields the predicted resonance positions for the "frozen" Phe CD1 ring. At 25 °C, the calculated chemical shifts are 8.7 and 14.3 ppm (average 11.3 ppm) for the two *m*-H, 8.6 and 7.8 ppm (average 8.2 ppm) for the two *o*-H, and 17.1 ppm for the unique *p*-H, which correspond closely to the observed rotationally averaged shifts at 12.6, 8.7, and 17.3 ppm, respectively. The $\Delta\delta_{m\text{-H}}$ of 2.8 ± 0.6 kHz at 500 MHz leads to a state lifetime for two-site exchange $\tau = 10 \pm 4$ μs at 25 °C through eq 7. Casting $\tau(T) = \tau_0 \exp(-E_a/RT)$, where E_a is the activation barrier to reorientation and assuming that the two individual *m*-H resonances exhibit the same temperature dependence as found for the mean shift (Figure 7) lead to a straight line for the plot $\tau(T)$ versus T^{-1} (Figure 8B) with a slope that yields $E_a = 14 \pm 4$ kcal/mol.

Thus, we have determined the reorientation rate of phenyl ring rotation $\sim 10^5$ Hz at 25 °C and made an estimate of E_a (14 kcal/mol) for Phe CD1 in one state of Mb.[68] This activation energy is well below the reported denaturation enthalpy of 40 kcal/mol[69] for metMb at pH 9 and 25 °C and hence rules out global unfolding. Its value is closer to the range of activation barriers reported for the conformational changes associated with solvent penetration in BPTI (0–15 kcal/mol)[70] and hence is consistent with concerted motions within the folded protein allowing the ring flips.[19] A preliminary survey of Mb genetic variants in the met-cyano state indicates that, while the chemical shift of a resonance with the same NOE connectivities as peak g (averaged *m*-H) is very similar, both its highly variable line width and temperature sensitivity suggest variations in phenyl ring reorientation. It is thus likely that the definitive assignment and detailed elucidation of the exchange properties of such resonances will provide at least one index of the relative flexibility of the C–D corner in Mb and Hb. Detailed studies of such genetic variants, including the use of cryosolvents to freeze out the Phe CD1 motion, are in progress.

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[68] It has been reported that the 2-D NMR assigned *m*-H peaks of sperm whale MbCO are motionally averaged.[34] Assuming the kinetics are the same in both MbCO and MbCN, estimation of $\Delta\delta_{m\text{-H}} = 2.6 \pm 0.3$ ppm based on ring current calculations[39] and the *m*-H coordinates of the "frozen" Phe CD1 in the crystal structure of MbCO,[50] MbO$_2$,[49] and met-Mb[51] leads to $\Delta\nu_{ex} = 12 \pm 4$ Hz at 25 °C and 50 ± 20 Hz at 10 °C for SwMbCO at 500 MHz. Thus exchange broadening should be observable for MbCO at low temperatures unless the reorientation rate of the Phe CD1 side chain is faster in MbCO than in met-MbCN.

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Atomic and Group Electronegativities from the Electron Density Distributions of Molecules

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Abstract: The topological properties of the electron density distributions of molecules are used to define a method for the evaluation of atomic and group electronegativities. According to the bond critical point model, the electronegativity of an atom relative to hydrogen is calculated from properties associated with the bond critical point of the corresponding diatomic hydride. Atomic electronegativities of the 21 main-group elements from lithium to bromine are shown to correlate with atomic electronegativities based on empirical and nonempirical methods. A straightforward extension of the method is used to obtain the electronegativities of 30 groups from the electron density distributions of polyatomic molecules. The group electronegativities are shown to correlate with values from a variety of methods, the exceptions being methods based on total electronegativity equalization. A potential advantage of the bond critical point method is the possibility of direct evaluation of group electronegativities from experimental electron density distributions.

The concept of electronegativity is frequently traced to the work of Pauling[1] in the 1930s. Not only is Pauling's definition of electronegativity as "the power of an atom in a molecule to attract electrons to itself" regarded as the classical definition, but his numerical scale, based on thermochemical data, has been used extensively for qualitative and quantitative discussions. Phillips[2] claims, however, that the concept of relative electronegativity arose in the 18th century in connection with oxidation–reduction potentials. Binary compounds of atoms with large differences in electronegativity were observed by early crystallographers to form rock salt structures while smaller differences in electronegativity lead to more open covalent structures. In any case, electronegativity is very much a part of the vocabulary of contemporary chemistry.

Numerical electronegativity scales have established two general trends: Electronegativity increases from left to right within a given row of the periodic table of the elements and decreases from top to bottom. Moreover, innumerable correlations between electronegativity values and various physical and chemical properties have played a central role in the organization and rationalization of chemical facts and observations.

Electronegativity scales belong to one of two classes. In the empirical methods, thermochemical data, ionization energies and electron affinities, dipole moments, internuclear distances in crystals, atomic spectral data, parameters from magnetic resonance spectra, or other properties are used to assign an electronegativity

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value to an atom or molecular fragment.

In contrast to the empirical methods, there have been relatively few attempts to develop purely theoretical (nonempirical) methods. Of the latter, the first nonempirical scale was derived from the position of bond orbitals in floating spherical Gaussian orbital (FSGO) calculations on hydrides.[3] While the FSGO method is conceptually attractive, it is inherently linked to a particular feature of a specific computational technique. The most extensive theoretical studies of the electronegativity concept have been reported by Parr and his co-workers. When one starts from two fundamental theorems of quantum mechanics, due to Hohenberg and Kohn,[4] electronegativity is identified with the negative of the chemical potential in the density functional theory of the ground state.[5] The density functional approach has been applied extensively.[6] In a related paper, Johnson[7] combined the self-consistent field Xα (SCF-Xα) density functional representation of molecular orbital theory with the orbital electronegativity definition of Hinze, Whitehead, and Jaffe[8] to study the dependence of electronegativity on the electronic structure of a group of atoms in a molecule or cluster. Other theoretical methods include a nonempirical electrostatic model (NEM),[9] which yields electronegativities that correlate well with empirical scales. Furthermore, the results of the nonempirical electrostatic model are consistent with the major conclusions of the density functional approach.

It is remarkable that none of the theoretical approaches relate explicitly the electronegativity concept to electron density distributions in molecules despite the fact that chemical phenomena are often explained in terms of electronegativities and electron density distributions. For instance, the arrow-drawing and electron-pushing mechanisms, which have played a major role in the development of organic chemistry, are based, in part, on electronegativity trends.

Recent observations[10,11] on the topological properties of the electron density distributions of molecules have prompted us to suggest a theoretical method for the evaluation of electronegativities in terms of the electron density. Accordingly, in this paper we introduce an atomic electronegativity scale based on the topological properties of the electron density distributions of molecules, and we show that a natural extension of the method leads to group electronegativities.

Topological Properties of the Electron Density. The topological properties of the electron density $\rho(\mathbf{r})$ have been used by Bader and his co-workers[12-15] to develop a comprehensive theory of molecular structure. In this theory, a molecule may be partitioned into fragments, that is atoms, by zero-flux surfaces that satisfy the condition in eq 1 for every point on the surface of the sub-

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

system, where $\mathbf{n}$ is a unit vector normal to the surface. Points on the zero-flux surfaces at which eq 2 applies are known as critical

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

points. Furthermore, the critical points on bond paths, the paths between bonded atoms along which the electron density is a maximum with respect to a lateral displacement, are known as bond critical points.

Table I. Properties Associated with the Bond Critical Points of Diatomic Hydrides and Atomic Electronegativities

molecule	r_H, au	r_A, au	r_H/r_{AH}, au	$\rho(\mathbf{r}_c)$	F_A	χ_A
LiH	1.676	1.338	0.5561	0.0395	14.08	1.00
BeH	1.495	1.042	0.5893	0.0902	3.267	1.44
BH	1.366	0.970	0.5848	0.1816	1.074	1.90
CH	0.739	1.377	0.3492	0.2823	0.3095	2.60
NH	0.523	1.433	0.2674	0.3411	0.1569	3.08
OH	0.334	1.501	0.1820	0.3696	0.0821	3.62
FH	0.252	1.481	0.1454	0.3766	0.0552	4.00
NaH	1.690	1.876	0.4738	0.0334	14.18	1.00
MgH	1.613	1.656	0.4935	0.0523	4.718	1.32
AlH	1.604	1.510	0.5149	0.0755	2.275	1.58
SiH	1.507	1.365	0.5247	0.1139	1.152	1.87
PH	1.384	1.304	0.5148	0.1626	0.6331	2.17
SH	0.956	1.586	0.3761	0.2160	0.2902	2.64
ClH	0.697	1.712	0.2893	0.2518	0.1641	3.05
KH	1.787	2.446	0.4222	0.0293	14.41	0.99
CaH	1.590	2.195	0.4199	0.0483	4.349	1.34
GaH	1.342	1.801	0.4270	0.0943	1.509	1.75
GeH	1.275	1.726	0.4249	0.1182	0.8985	1.99
AsH	1.220	1.680	0.4207	0.1417	0.5936	2.21
SeH	1.114	1.664	0.4010	0.1733	0.3855	2.46
BrH	0.940	1.734	0.3515	0.2029	0.2474	2.75

Systematic studies of the bond critical points in binary[10] and diatomic[11] hydrides of main-group elements have shown that for each row of the periodic table 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 the electron density suggest the possibility of a relationship between a bond critical point and its associated electronic properties and the electronegativity of the heavy atom relative to that of hydrogen.

Computational Details and Notation. The details of the calculations with large basis sets for most of the binary[10] and diatomic[11] hydrides have been described previously and will not be described herein. The calculations for NaH, MgH, AlH, SiH, and PH have been repeated with two sets of polarization functions in order to be consistent with the results[11] for the other diatomic hydrides. In each case the exponents of a single set of polarization functions were energy optimized, and then the single set was replaced by a double set of polarization functions whose exponents were obtained by a symmetric splitting of the single set. The splitting factors for the exponents of the polarization functions were energy optimized. The additional basis functions have only a small effect on the properties studied in this paper and do not affect our conclusions. For the third-row binary hydrides, the Huzinaga [4s3p1d] basis sets,[16] partially decontracted to (433111/43111/4) and supplemented with two sets of polarization functions, were used for the heavy atoms, while the Dunning [3s] contraction[17] with one set of polarization functions was used for hydrogen. Heavy-atom polarization function exponents were energy optimized as described above.

For molecules containing two or more heavy atoms, Dunning [5s4p/3s] contractions[17] of the Huzinaga[18] basis sets were used for first-row atoms and hydrogen. For second-row atoms the Mclean and Chandler [6s5p] contractions[19] of the Huzinaga[20] basis sets were used. Two sets of polarization functions were added to the basis set of each atom. All calculations were carried out

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at the experimental equilibrium geometries,[21] except where noted otherwise.

The electron density at the bond critical point is denoted by $\rho(\mathbf{r}_c)$ where $\mathbf{r}_c$ denotes the position of the bond critical point. The distance of the bond critical point from the hydrogen atom in AH is denoted by r_H, while r_A denotes the distance from atom A to $\mathbf{r}_c$. Clearly, for a diatomic molecule, the internuclear distance is given by $r_{AH} = r_A + r_H$. The number of valence electrons atom A contributes to the molecule AH is denoted by N_A, and the atomic number of atom A is denoted by Z_A. All quantities in this paper are in atomic units, unless noted otherwise.

Bond Critical Points and Electronegativity. The bond critical points of the diatomic hydrides of the first-row elements move monotonically closer to the hydrogen atom as Z_A increases. Similar monotonic trends are observed for the second- and third-row hydrides (Table I). Thus, within each row, r_H decreases monotonically as a function of Z_A. Given this observation, we might expect that the FSGO orbital multiplier approach of Simons et al.[3] can be generalized to bond critical points. In the FSGO method orbitals float to the location of minimum energy. If a polar single bond between atoms A and B is represented schematically by A···X···B, where X denotes the center of the bond orbital, an orbital multiplier may be defined by eq 3 where R_A

$$f_{AB} = R_A/(R_A + R_B) \tag{3}$$

and R_B are the distances from the nuclei to the orbital center. If $f_{AB} < 0.5$, atom A is said to attract the bonding electrons more strongly than atom B; if $f_{AB} > 0.5$, the converse is true, and if $f_{AB} = 0.5$, the bonding electrons are shared equally between the two atoms. Thus, Simons et al. suggest that the deviation of f_{AB} from 0.5 measures the difference in the electron-attracting power, or electronegativity, of atoms A and B. From the data in Table I, it is readily shown that the FSGO orbital multiplier approach is not generalizable to bond critical points because the monotonic behavior of r_H is not complemented by a corresponding monotonic behavior of r_A. Furthermore, if r_A increases as r_H decreases, r_H/r_{AH} would be expected to vary monotonically within each period. The data in Table I show that this is not the case even though the variation of r_{AH} within each period is monotonic. These and related considerations suggest that r_H values alone are not sufficient to provide a quantitative measure of electronegativity. Consequently, we have examined the behavior of other electronic properties associated with bond critical points. From our earlier calculations[11] on the diatomic hydrides, it is clear that $\rho(\mathbf{r}_c)$ increases monotonically within each period as Z_A increases. Thus, $\rho(\mathbf{r}_c)$ increases while r_H decreases. A key assumption of our approach is to assume that there is an electronegativity factor associated with atom A that is directly proportional to r_H and inversely proportional to $\rho(\mathbf{r}_c)$. This factor fails, however, to allow for the larger size of the heavier atoms. Thus, the r_H value in HCl is much larger than the value in HF (0.697 versus 0.252 au), not only because Cl is less electronegative but also because Cl is larger and leads, therefore, to longer bond lengths. To allow for the size effect, we express r_H as a function of r_{AH}. In addition, we also allow for the number (N_A) of valence electrons atom A contributes to the molecule. Since electronegativity is known to increase from left to right within each period while r_H decreases, we assume that the electronegativity factor varies inversely with N_A. Thus, the electronegativity factor, F_A, associated with atom A in the diatomic hydride AH is given by eq 4. Values of F_A

$$F_A = r_H/N_A\rho(\mathbf{r}_c)r_{AH} \tag{4}$$

for the 21 main-group elements from Li to Br are listed in Table I. The final step is to convert the F_A values into values comparable in magnitude to those of Pauling. To do this, we use the simplest functional form that yields reasonable results. Expressing the electronegativity of atom A as a power curve of F_A (eq 5) and choosing the two parameters ($a = 1.938$ and $b = -0.2502$) to give electronegativities of 1.00 and 4.00 for Li and F, respectively, yields the atomic electronegativities denoted by χ_A in Table I.

$$\chi_A = aF^b \tag{5}$$

Table II. Group Electronegativities

group[a]	χ_A	r_H, au	r_{AH}, au	$\rho(\mathbf{r}_c)$
$-BeH$	1.47	1.449	2.485	0.0956
$-BH_2$	1.93	1.278	2.220	0.1887
$-CH_3$	2.56	0.769	2.052	0.2867
$-CH_2CH_3$	2.56	0.776	2.071	0.2835
$-CHCH_2$	2.61	0.740	2.033	0.2986
$-CCH$	2.66	0.682	2.005	0.3028
$-CN$	2.69	0.659	2.009	0.3023
$-CHO$	2.60	0.739	2.109	0.2852
$-CO$	2.57	0.732	2.126	0.2671
$-CH_2F$	2.61	0.743	2.079	0.2931
$-COOH$	2.66	0.704	2.073	0.3023
$-CH_2OH$	2.59	0.757	2.067	0.2931
$-NH_2$	3.10	0.510	1.912	0.3504
$-NC$	3.30	0.391	1.863	0.3546
$-NO$	3.06	0.533	2.009	0.3309
$-NO_2$	3.25	0.449	1.927	0.3665
$-NCO$	3.22	0.435	1.863	0.3538
$-OH$	3.64	0.329	1.812	0.3767
$-OCN$	3.73	0.296	1.800	0.3748
$-OCH_3$	3.70	0.319	1.786	0.3943
$-OCl$	3.67	0.316	1.827	0.3712
$-OCHO$	3.65	0.316	1.837	0.3617
$-MgH$	1.33	1.585	3.230	0.0545
$-AlH_2$	1.62	1.514	2.986	0.0834
$-SiH_3$	1.91	1.455	2.799	0.1217
$-PH_2$	2.17	1.389	2.683	0.1628
$-SH$	2.63	0.978	2.525	0.2197
$-GeH_3$	2.05	1.217	2.882	0.1327
$-AsH_2$	2.26	1.143	2.855	0.1476
$-SeH$	2.47	1.106	2.759	0.1759

[a] The experimental equilibrium geometries[21] were used for all molecules, except HOCN and HNO_2 for which the 6-31G*-optimized geometries were used. The molecular parameters for HOCN were taken from ref 31. The C_{2v}-optimized parameters for HNO_2 are $r_{NO} = 1.186$ Å, $r_{NH} = 1.020$ Å, and ∠(HNO) = 115.7°.

Although our objective is not to achieve the best fit to other scales, it is interesting to note that the mean deviation between our values and the revised Pauling values due to Allred[22] is less than 0.09 for the elements listed in Table I. Furthermore, Figure 1 shows that the atomic electronegativities based on the bond critical point model correlate well, not only with the empirical values based on Pauling's method but also with the nonempirical values based on the FSGO[3] and electrostatic[9] methods. In Figure 1 the respective correlation coefficients are 0.991, 0.991, and 0.989.

Group Electronegativities. The bond critical point model for atomic electronegativities, whereby the electronegativity of an atom relative to hydrogen is calculated from properties associated with the bond critical point of the corresponding diatomic hydride, is readily extended to group electronegativities. For example, the electronegativity of the methyl group is estimated by determining the position of the bond critical point in methane and substituting the appropriate values into eq 4 and 5. Similarly, the electronegativities of the cyano and methoxy groups are obtained from the electron density distributions of hydrogen cyanide and methanol, respectively. In each case N_A is the number of valence electrons contributed by the atom adjacent to the reference hydrogen atom. The electronegativities of 30 groups calculated by this method, and the associated values of r_H, r_{AH}, and $\rho(\mathbf{r}_c)$, are listed in Table II.

Discussion

Space restrictions preclude an exhaustive discussion of all methods for calculating group electronegativities. Nevertheless, it is appropriate to compare, where possible, our results with the recent tabulation of Mullay.[23] There is a fair correlation (R =

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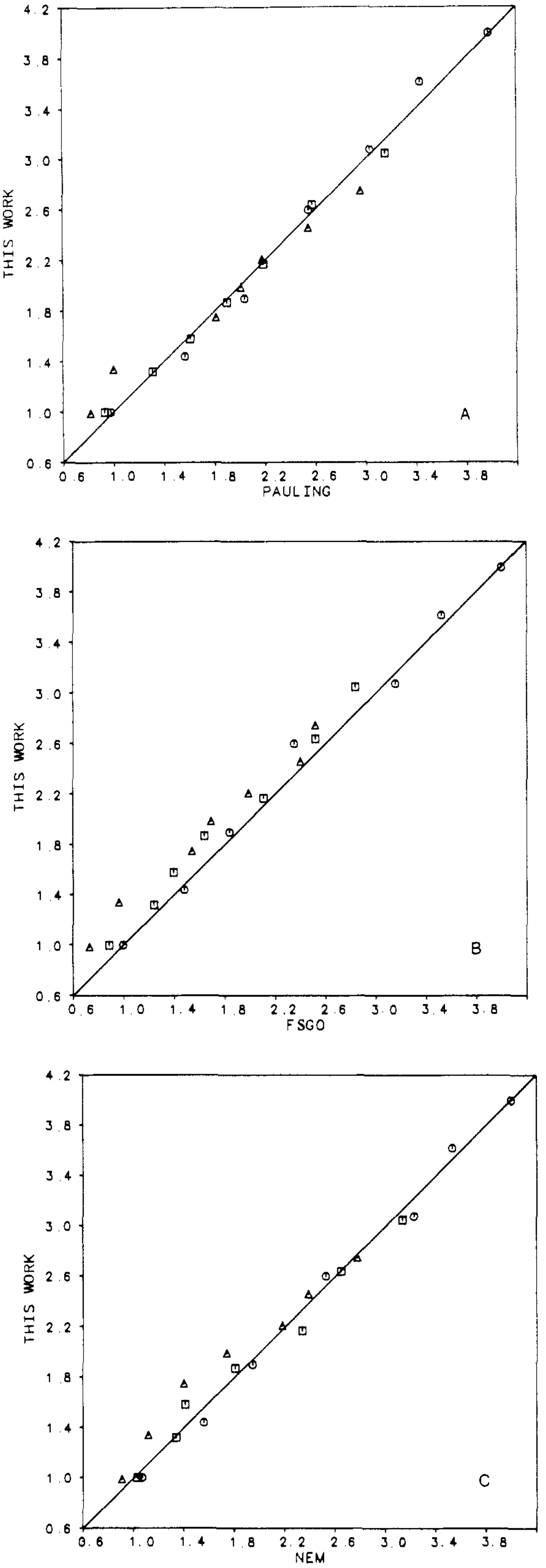

Figure 1. Correlations between atomic electronegativities calculated by means of the bond critical point model and the (A) Pauling, (B) floating spherical Gaussian orbital, and (C) nonempirical electrostatic methods. Data points are indicated by circles, squares, and triangles for first-, second-, and third-row elements, respectively. In each case the line corresponds to a perfect correlation.

0.88) between our values for 11 of the groups listed in Table II and Mullay's group electronegativities. The latter are based on modified Slater effective nuclear charges, effective principal quantum numbers, fractional p characters, and a number of assumptions.[24] Taking the same set of groups, we find stronger correlations with the Inamoto–Masuda[25] and Marriott et al.[26] scales ($R = 0.90$ and 0.92, respectively). The former is based on correlations with NMR data, while the latter is based on Mulliken populations for hydrogen atoms at the 6-31G* level. Furthermore, our values correlate ($R = 0.87$) with the mutually consistent values of Wells.[27] A similar correlation ($R = 0.89$) between the Wells and Mullay values has been used to conclude that the latter reproduce empirical trends better than methods[28,29] based on total electronegativity equalization. For example, a correlation coefficient of only 0.53 is obtained from a plot of the Huheey values versus those of Wells. With group electronegativities calculated by the bond critical point method proposed in this paper, the correlation is even weaker ($R = 0.41$). We conclude, therefore, that the bond critical point method leads to group electronegativities that correlate well with a variety of methods, the exceptions being methods[28,29] based on total electronegativity equalization.

The atomic and group electronegativity values proposed in this paper have been calculated relative to hydrogen. Of course, electronegativities relative to some other atom, such as a halogen, or relative to a group of atoms could be evaluated by the same method. For example, with the methyl group as the reference, calculations for CH_3Li and CH_3F could be used to fix the two parameters in eq 5. Calculations for RCH_3 would then yield the electronegativity of R in the same manner that calculations for RH yield the electronegativity of the R group in this paper.[32] It would be interesting to learn to what extent group electronegativities based on different references would agree with one another.

Since bond critical points, like other properties computed with finite basis sets, are basis set dependent,[30] applications of the bond critical point model for group electronegativities should be carried out at a uniform theoretical level. The large basis sets used in this paper are impractical for applications to larger molecules and, therefore, smaller basis sets are required. In view of our earlier study of the basis set dependence of the bond critical points in the binary hydrides, we expect that the 6-31G* basis set is a reasonable compromise. Substitution of the 6-31G* values[10] into eq 4 and 5 yields 2.55 and 3.10 for the group electronegativities of CH_3 and NH_2, respectively, in close agreement with the larger basis set results (Table II).

In conclusion, we emphasize that there are two major advantages to the bond critical point model for electronegativities. Not only is the method applicable to all groups but also electronegativities can be evaluated from either theoretical or experimental electron density distributions. Thus, at least in principle, the present approach suggests a method for the measurement of group electronegativities.

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Registry No. LiH, 7580-67-8; BeH, 13597-97-2; BH, 13766-26-2; CH, 3315-37-5; NH, 13774-92-0; OH, 3352-57-6; FH, 7646-69-7; NaH, 7646-69-7; MgH, 14332-53-7; AlH, 13967-22-1; SiH, 13774-94-2; PH, 13967-14-1; SH, 13940-21-1; HCl, 7647-01-0; KH, 7693-26-7; CaH,

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(32) Such an extension would yield an electronegativity for H, a quantity unavailable from the present discussion because all electronegativities are relative to H.

14452-75-6; GaH, 13572-92-4; GeH, 13572-99-1; AsH, 12628-08-9; BrH, 10035-10-6; Be, 7440-41-7; B, 7440-42-8; C, 7440-44-0; N, 17778-88-0; O_2, 17778-80-2; Na, 7440-23-5; Mg, 7439-95-4; Al, 7429-90-5; Si, 7440-21-3; P, 7723-14-0; S, 7704-34-9; Cl, 22537-15-1; K, 7440-09-7; Ca, 7440-70-2; Ga, 7440-55-3; Ge, 7440-56-4; As, 7440-38-2; Se, 7782-49-2; Br_2, 10097-32-2; HOCl, 7790-92-3; SeH, 13940-22-2; BeH_2, 7787-52-2; BH_3, 13283-31-3; CH_4, 74-82-8; CH_3CH_3, 74-84-0; $CH_2{=}CH_2$, 74-85-1; $CH{\equiv}CH$, 74-86-2; HCN, 74-90-8; CH_2O, 50-00-0; CHO, 2597-44-6; CH_3F, 593-53-3; CO_2H, 64-18-6; CH_3OH, 67-56-1; NH_3, 7664-41-7; HNC, 6914-07-4; HNO, 14332-28-6; HNO_2, 7782-77-6; HNCO, 75-13-8; H_2O, 7732-18-5; HOCN, 420-05-3; HOCHO, 64-18-6; MgH_2, 7693-27-8; AlH_3, 7784-21-6; SiH_4. 7803-62-5; PH_3, 7803-51-2; SH_2, 7783-06-4; GeH_4, 7782-65-2; AsH_3, 7784-42-1; SeH_2, 7783-07-5.

Molecular Modeling of the Physical Properties of the Alkanes

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Abstract: Eight physical properties (boiling points, molar volumes, molar refractions, heats of vaporization, surface tensions, melting points, critical temperatures, and critical pressures) of 74 normal and branched alkanes were examined by molecular modeling techniques. Structural parameters employed include Wiener indices, connectivity indices, ad hoc descriptors, information indices, and molecular volumes and surface areas. Most of the properties were well modeled ($r^2 > 0.97$) by the Wiener indices, connectivity indices, and ad hoc descriptors. An exception was the melting points, which were not well modeled by any of the available indices. Factor analysis (principal component analysis) was used to examine the intrinsic dimensionalities of the data and parameter sets. A single factor accounts for about 82% of the variance in the eight physical properties, two factors account for 94%, and three factors account for about 99%. The melting points load strongly on a factor independent of the other properties. Of the examined parameter sets, the connectivity indices exhibited the highest dimensionality.

It is obvious that the structure of a compound, both geometric and electronic, determines its properties. Nonetheless, elucidation of the connection between molecular structure and bulk properties has posed a challenge to chemists for more than a century. A central issue has been how to quantify the elusive concept of "structure". In early attempts properties were commonly represented as sums of contributions from atoms, bonds, or larger structural subunits.[1-7] These approaches often required a large number of empirical parameters, and recently attention has turned to the use of more general structural parameters, in particular those derived from chemical graph theory.[8-15] Among the most successful of these general parameters have been Wiener distance indices,[16-19] connectivity indices,[9,13-15,20] information indices,[12,21] and ad hoc descriptors.[15,22] In some cases molecular volumes and surface areas have also been suggested as important variables, most notably for solubility properties.[23-29]

The alkanes represent an especially attractive class of compounds as a starting point for the application of molecular modeling techniques. Many properties of the alkanes vary in a regular manner with molecular mass and extent of branching, and because the alkanes are nonpolar, a number of complexities that arise with more polar compounds are avoided. Our purposes in the present report are threefold. First, we hope to obtain practical structure–property equations for eight representative physical properties of the alkanes, utilizing relatively simple structural parameters. Such equations can be used to predict values for as yet unmeasured properties of compounds and also, in some cases, may aid in the "design" of compounds with properties suitable for special purposes. Second, we wish to evaluate the relative performances of the above descriptor sets in relating the alkane molecular structures to the set of physical properties. Third, we hope to draw inferences from our results concerning the natures of the physical forces responsible for the properties observed. As an aid in this last effort, we have utilized the technique of factor analysis to estimate the inherent dimensionality of the set of physical properties investigated and also the dimensionalities of the parameter sets.

Methods

Data. Eight representative physical properties were selected, based in part on their perceived importances and in part on the availability of a suitable body of data: boiling points (bp), molar volumes at 20 °C (MV), molar refractions at 20 °C (MR), heats of vaporization at 25 °C

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