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A Molecular Electrostatic Potential Bond Critical Point Model for Atomic and Group Electronegativities

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Received September 20, 2001

Abstract: A consistent set of atomic electronegativities of main block and d-block transition elements has been obtained from the position and value of the molecular electrostatic potential bond critical point of the C−E bond of a methyl-element-hydride system, $H_3C{-}EH_n$ (E is an element and $n = 0$, 1, 2, 3, 4, and 5 depending on the position of E in the periodic table). The new scale shows very good agreement with the popular electronegativity scales such as Pauling, Allen, Allred−Rochow, Mulliken, and Sanderson scales of electronegativity, especially for the main block elements. The present scale of electronegativity for transition elements is expected to be more accurate than the previously derived values because of a more consistent approach. Further, the same approach has led to the evaluation of group electronegativities when the hydrogens of E are replaced by other substituent groups. These group electronegativity values are found to correlate well with Inamoto and Mullay scales.

Introduction

A quantitative knowledge on the electronic effect of an atom or a substituent group on a molecular system is extremely useful to understand the chemical reactivity of that system as well as to design new molecular systems with desired properties. A quantity very often used in chemistry in this regard is electronegativity,[1−14] which is originally defined by Pauling[3] for atoms as “the power of an atom when in a molecule to attract electrons to itself”. Extension of this definition to a substituent group leads to the definition of group electronegativity as the power of a bonded group of atoms, say “G” to attract electrons to itself from another atom or another bonded group of atoms.

One can see several different scales of atomic electronegativity (χ) in the literature,[1−14] which are based on different criteria and methods of computation. Among the various scales of atomic electronegativity, the Pauling scale[3] based on thermochemical data is perhaps the most famous. Other than the Pauling scale, the popular electronegativity scales for atoms are due to Allred−Rochow[4] (based on the electrostatic force of attraction between the nucleus and the valence electrons), Allen[7] (based on the average one-electron energy of the valence shell electrons in the ground-state free atoms), Mulliken[9] (defines χ as the average value of the electron affinity and ionization potential of the atom), Sanderson[10] (a modification of Pauling scale), and Gordy’s electrostatic potential scale of electronegativity.[11a] In density functional theory,[15] electronegativity is identified as the negative of the chemical potential.[16] The applicability of this definition to atoms and diatomic and polyatomic molecules has been explored in the recent literature.[17]

Though there are several different scales of electronegativity, good linear correlations between any two scales can be found only for the main group elements. In fact, there is no conclusive work regarding the electronegativity of transition elements (TEs). Even a precisely defined experimental way to obtain this quantity is lagging. In a very recent article, Murphy et al.[13] argued that Pauling’s χ values are the best for groups 1 and 17 and the second and third rows of the p-blocks and that is largely

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(1) Pritchard, H. O.; Skinner, H. A. *Chem Rev.* **1955**, *55*, 745.
(2) Huheey, J. E.; Keiter, E. A.; Keiter, R. L. *Inorganic Chemistry: Principles of Structure and Reactivity*, 4th ed; HarperCollins: New York, 1993.
(3) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed; Cornell University: Ithaca, NY, 1960.
(4) (a) Allred, A. L.; Rochow, E. G. J. *Inorg. Nucl. Chem.* **1958**, *5*, 264, 269. (b) Allred, A. L. *J. Inorg. Nucl. Chem.* **1961**, *17*, 215.
(5) (a) Porterfield, W. W. *Inorganic chemistry, a unified approach*; Addison-Wesley Publishing Co.: Reading, MA, 1984. (b) *Struct. Bonding Electronegativity*; Sen, K. D., Jorgensen, C. K., Eds.; Springer-Verlag: New York, 1987; p 66.
(6) James, A. M.; Lord, M. P. *Macmillan’s Chemical and Physical Data*; Macmillan: London, 1992.
(7) Allen, L. C. *J. Am. Chem. Soc.* **1989**, *111*, 9003.
(8) (a) Bratsch, S. G. *J. Chem. Educ.* **1988**, *65*, 34. (b) Bratsch, S. G. *J. Chem. Educ.* **1984**, *61*, 588.
(9) (a) Mulliken, R. S. *J. Chem. Phys.* **1934**, *2*, 782. (b) Mulliken, R. S. *J. Chem. Phys.* **1935**, *3*, 573.
(10) (a) Sanderson, R. T. *J. Chem. Educ.* **1988**, *65*, 112. (b) Sanderson, R. T. *Polar Covalence*; Academic Press: New York, 1983.
(11) (a) Gordy, W. *Phys. Rev.* **1946**, *69*, 604. (b) Pasternak, A. *Chem. Phys.* **1977**, *26*, 101.
(12) Boyd, R. J.; Markus, G. E. *J. Chem. Phys.* **1981**, *75*, 5385.
(13) Murphy, L. R.; Meek, T. L.; Allred, A. L.; Allen, L. C. *J. Phys. Chem. A* **2000**, *104*, 5867.
(14) (a) Politzer, P.; Parr, R. G.; Murphy, D. R. *J. Chem. Phys.* **1983**, *79*, 3859. (b) Ray, N. K.; Samuels, L.; Parr, R. G. *J. Chem. Phys.* **1979**, *70*, 3680.
(15) Hohenberg, P.; Kohn, W. *Phys. Rev. B* **1964**, *136*, 864.
(16) Parr, R. G.; Donnelly, R. A.; Levy, M.; Palke, W. E. *J. Chem. Phys.* **1978**, *68*, 3801.
(17) (a) Parr, R. G.; Yang, W. *Density Functional Theory of Atoms and Molecules*; Clarendon Press: Oxford, U.K., 1989. (b) Borkman, R. F. *J. Chem. Phys.* **1969**, *51*, 5596. (c) Borkman, R. F.; Parr, R. G. *J. Chem. Phys.* **1968**, *48*, 1116. (d) Ghosh, S. K.; Parr, R. G. *Theor. Chim. Acta* **1987**, *72*, 379. (e) Bartolotti, L. J.; Gadre, S. R.; Parr, R. G. *J. Am. Chem. Soc.* **1980**, *102*, 2945. (f) Liu, G.-H.; Parr, R. G. *J. Am. Chem. Soc.* **1995**, *117*, 3179. (g) Gazquez, J. L.; Ortiz, E. *J. Chem. Phys.* **1984**, *81*, 2741.

10.1021/ja017122r CCC: $22.00

unrealistic for TEs. They also noted that a very high precision on the electronegativity value (at least three significant figures) is necessary to distinguish 30% of the main group elements and 75% of the TEs. If we include thousands of substituent groups in the electronegativity scale, the accuracy level of χ has to be even higher.

Group electronegativity has been derived by a number of methods including both experimental and computational ones.[1,18−25] Following Gordy's work[11a] on atomic electronegativity, Inamoto and co-workers[21] have calculated the group electronegativities of more than 150 substituents. Using an empirical equation, which incorporates both hybridization and charge on atoms, Mullay[22] proposed a simple way to calculate the atomic as well as group electronegativity. Marriott et al.'s work[23] on group electronegativity is based on the atomic electron population on the hydrogen atom in compounds HX as calculated at the ab initio 6-31G* Hartree−Fock level wave functions. Greelings et al.[24] have used the density functional theory formalism of electronegativity (it is the same as the Mulliken formula[9] for electronegativity, viz., $\chi = (I + A)/2$, where I and A are ionization potential and electron affinity of the system, respectively) for the calculation of the electronegativity of several groups at ab initio level. In a relatively recent work, Boyd and Boyd[25a] have used a bond critical point model based on the topological properties of electron density associated with A−H bond (A is an atom or a group) to obtain atomic as well as group electronegativities. In their method, the electronegativity of A, χ_A, in the Pauling unit is defined using an empirical equation, viz., $\chi_A = 1.938F_A{}^{-0.2502}$. Here, F_A denoted an electronegativity factor assigned for A as equal to $r_H/N_A(\rho(r_c))r_{AH}$, where r_H is the distance of the bond critical point to the hydrogen nucleus, N_A is the number of valence electrons of the atom directly attached to H, and $\rho(r_c)$ is the electron density at the critical point r_c, and r_{AH} is the internuclear distance. This method at Hartree−Fock level provided atomic electronegativities for main group elements, which agreed well with the Pauling scale as well as those from nonempirical electrostatic method.[12] However, in group electronegativity, the values obtained by them were found to be very less sensitive to the nature of the substituents (designated as XYZ) associated with A. For instance, the Boyd−Boyd scale gives a value of 2.60 for the electronegativity of C atom and for most of the −CXYZ groups the value obtained by them can be approximated as 2.60 ± 0.06.

A scalar electronic property of a molecule used in connection with electronegativity as well as atomic radii is molecular electrostatic potential (MESP).[11−12,14,26−27] This quantity generated by a molecule can be calculated rigorously from its electron density, $\rho(\mathrm{r})$, distribution by the equation

$$V(\mathrm{r}) = \sum_{A}^{N} \frac{Z_A}{|\boldsymbol{r} - \boldsymbol{R}_A|} - \int \frac{\rho(\boldsymbol{r}')d^3\boldsymbol{r}'}{|\boldsymbol{r} - \boldsymbol{r}'|} \tag{1}$$

where Z_A is the charge on nucleus A, located at $\boldsymbol{R}_A$.[28−31] It is also defined as the energy required to bring a unit test positive charge from infinity to the point $\boldsymbol{r}$.

The use of this quantity in chemistry is widespread for understanding molecular reactivity, intermolecular interactions, molecular recognition, and a variety of chemical phenomena.[28−35] From a theoretical study of 25 ground-state atoms, Politzer et al.[14a] have established some relationships between atomic chemical potentials, electrostatic potentials, and covalent radii. Recently, Wiener et al.[26] have showed that the minimum of the molecular electrostatic potential (MESP) along an internuclear axis provides a more realistic boundary point between two bonded atoms than the electronic density minimum. Gadre and co-workers[27] reported electrostatic-potential-derived radii for atomic ions as well as sizes and shapes of polyatomic anions on the basis of MESP. Boyd and Markus[12] proposed an electrostatic model to calculate a nonempirical electronegativity scale for the first 54 elements. According to their model, the electronegativity of an atom is identified with the electrostatic force between the effective nuclear charge and an electron at a distance equal to the relative radius of the atom. There are also several other treatments on electronegativity.[36−44] In this paper,

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(18) (a) Wilmshurst, J. K. *J. Chem. Phys.* **1957**, *27*, 1129. (b) Clifford, A. F. *J. Am. Chem. Soc.* **1957**, *79*, 5404. (c) Mcdaniel, D. H.; Yingst, A. *J. Am. Chem. Soc.* **1963**, *86*, 1334.

(19) Bratsch, S. G. *J. Chem. Educ.* **1985**, *62*, 101.

(20) (a) Huheey, J. E. *J. Phys. Chem.* **1965**, *69*, 3284. (b) Huheey, J. E. *J. Phys. Chem.* **1966**, *70*, 2086.

(21) (a) Inamoto, N.; Masuda, S. *Chem. Lett.* **1982**, 1003. (b) Inamoto, N.; Masuda, S. *Chem. Lett.* **1982**, 1007. (c) Inamoto, N.; Masuda, S.; Tori, K.; Yoshimura, Y. *Tetrahedron Lett.* **1978**, 4547. (d) Inamoto, N.; Masuda, S. *Tetrahedron Lett.* **1977**, 3287.

(22) (a) Mullay, J. *J. Am. Chem. Soc.* **1984**, *106*, 5842. (b) Mullay, J. *J. Am. Chem. Soc.* **1985**, *107*, 7271.

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

(24) (a) Proft, F. D.; Langenaeker, W.; Geerlings, P. *J. Phys. Chem.* **1993**, *97*, 1826. (b) Geerlings, P.; Proft, F. D.; Langenaeker, W. *Adv. Quantum Chem.* **1998**, *33*, 303.

(25) (a) Boyd, R. J.; Boyd, S. L. *J. Am. Chem. Soc.* **1992**, *114*, 1652. (b) Boyd, R. J.; Edgecombe, K. E. *J. Am. Chem. Soc.* **1988**, *110*, 4182.

(26) (a) Wiener, J. J. M.; Grice, M. E.; Murray, J. S.; Politzer, P. *J. Chem. Phys.* **1996**, *104*, 5109. (b) Politzer, P.; Weinstein, H. *J. Chem. Phys.* **1979**, *71*, 4218.

(27) (a) Gadre, S. R.; Sen, K. D. *J. Chem. Phys.* **1993**, *99*, 3149. (b) Gadre, S. R.; Shrivastava, I. H. *J. Chem. Phys.* **1991**, *94*, 4384. (c) Pathak, R. K.; Gadre, S. R. *J. Chem. Phys.* **1990**, *93*, 1770.

(28) (a) Scrocco, E.; Tomasi, J. In *Advances in Quantum Chemistry*; Lowdin, P.-O., Ed.; Academic Press: New York, 1978; Vol. 2, (b) Tomasi, J.; Bonaccorsi, R.; Cammi, R. *Theoretical Models of chemical Bonding*; Maksic, Z. B., Ed.; Springer: Berlin, 1990.

(29) Politzer, P. In *Chemical Applications of Atomic and Molecular Electrostatic Potentials*; Politzer, P., Truhlar, D. G., Eds.; Plenum: New York, 1981.

(30) Naray-Szabo, G.; Ferenczy, G. *Chem. Rev.* **1995**, *95*, 829.

(31) Gadre, S. R.; Shirsat, R. N. *Electrostatics of Atoms and Molecules*; Universities Press Ltd.: Hyderabad, India, 2000.

(32) Pullman, B. *Int. J. Quantum Chem. Quantum Biol. Symp.* **1990**, *17*, 81.

(33) Murray, J. N.; Sen, K. D. *Molecular Electrostatic Potential: Concepts and Applications*; Elsevier: New York, 1996.

(34) Politzer, P.; Abrahamsen, L.; Sjoberg, P. *J. Am. Chem. Soc.* **1984**, *106*, 855.

(35) (a) Suresh, C. H. Gadre, S. R. *J. Am. Chem. Soc.* **1998**, *120*, 7049. (b) Gejji, S. P.; Suresh, C. H.; Babu, K.; Gadre, S. R. *J. Phys. Chem. A* **1999**, *103*, 7474.

(36) (a) Cioslowski, J.; Mixon, S. T. *J. Am. Chem. Soc.* **1993**, *115*, 1084. (b) Cioslowski, J.; Stefanov, B. *J. Chem. Phys.* **1993**, *99*, 5151.

(37) (a) Hinze, J.; Whitehead, M. A.; Jaffe, H. H. *J. Am. Chem. Soc.* **1963**, *85*, 148. (b) Hinze, J.; Jaffe, H. H. *J. Am. Chem. Soc.* **1962**, *84*, 540. (c) Bergman, D.; Hinze, J. *Struct. Bonding* **1987**, *66*, 145 and references therein.

(38) (a) Politzer, P.; Huheey, J. E.; Murray, J. S.; Grodzicki, M. *J. Mol. Struct. (THEOCHEM)* **1992**, *259*, 99. (b) Politzer, P.; Parr, R. G.; Murphy, D. R. *Phys. Rev.* **1985**, *B31*, 6809.

(39) (a) Pearson, R. G. *J. Mol. Struct. (THEOCHEM)* **1992**, *87*, 261. (b) Parr, R. G.; Pearson, R. G. *J. Am. Chem. Soc.* **1983**, *105*, 7512.

(40) Graham, J. E.; Ripley, D. C.; Smith, J. T.; Smith, V. H.; Weaver, D. F. *J. Mol. Struct. (THEOCHEM)* **1995**, *343*, 105.

(41) (a) Allen, L. C. Electronegativity and the Periodic Table. In *Encyclopedia of Computational Chemistry*; Schleyer, P. v. R., Ed.; John Wiley: New York, 1998. (b) Reed, L. H.; Allen, L. C. *J. Phys. Chem.* **1992**, *96*, 157.

(42) Nalewajski, R. F.; Korchowiec, J. *Charge Sensitivity Approach to Electronic Structure and Chemical Reactivity*; World-Scientific: Singapore, 1997. (b) Nalewajski, R. F.; Sikora, O. *J. Phys. Chem.* **2000**, *104*, 5638.

(43) Ghanty, T. K.; Ghosh, S. K. *J. Phys. Chem.* **1996**, *100*, 17429.

(44) (a) Mortier, W. J.; Ghosh, S. K.; Shankar, S. *J. Am. Chem. Soc.* **1986**, *108*, 4315. (b) Mortier, W. J.; Genechten, K. V.; Gasteiger, J. *J. Am. Chem. Soc.* **1985**, *107*, 829. (c) Toufar, H.; Nulens, K.; Janssens, G. O. A.; Mortier, W. J.; Schoonheydt, R. A.; De Proft, F.; Geerlings, P. *J. Phys. Chem.* **1996**, *100*, 15383. (d) Baekelandt, B. G.; Mortier, W. J.; Lievens, J. L.; Schoonheydt, R. A. *J. Am. Chem. Soc.* **1991**, *113*, 6730.

we report a new method based on the MESP topography of substituted methanes for the calculation of atomic and group electronegativities.

Method

In a very recent work,[45] we have showed that the atomic radii (R_A) of an element can be obtained from the methyl group substituted elemental hydrides (MEH systems) of the form H_3C-EH_n (E is any main block or d-block transition elements and n is 0, 1, 2, 3, or 4 depending on the position of E in the periodic table) as the C−E bond distance minus one-half the C−C bond distance of ethane. For instance, for atoms H, Li, Be, B, C, N, O, and F, the H_3C-EH_n systems used were H_3C-H, H_3C-Li, H_3C-BeH, H_3C-BH_2, H_3C-NH_2, H_3C-OH, and H_3C-F, respectively. Basically, the idea used in that work was to connect an element with a methyl group and then saturate its remaining normal valencies with hydrogen atoms. Because both C and E atoms were saturated, C has no lone pair electrons or no vacant p or d orbitals and C is not a high electronegative atom, there was little chance for electrons of other atoms to interact with the C−E bond electrons. As a result, the inherent nature of the atomic size of E was retained in their C−E bond distances. It is expected that a periodic property such as electronegativity can also be studied systematically using such a model by monitoring the electronic property of the C−E bond. To do this, we consider the MESP bond critical point (CP) of the C−E bond of MEH systems and evaluate the deviation in the position and values of it with respect to the position of E in the periodic table. The model MEH systems used for the main block elements are the same as that used for our previous work[45] on atomic radii. For group 3, 4, 5, and 6 transition elements, 2, 3, 4, and 5 metal−hydrogen bonds will be used. For example, in Sc, Ti, V, and Cr, the corresponding MEH systems are H_3C-ScH_2, H_3C-TiH_3, H_3C-VH_4, and H_3C-CrH_5, respectively. In other words, all these systems are d^0 systems. It means that all their outermost electrons are used for bonding (maximum six electrons in Cr from six outermost orbitals), and therefore they are similar to the main block MEH systems, particularly the early half. For group 7, 8, 9, 10, and 11, the number of metal−hydrogen bonds used in this work is 4, 3, 2, 1, and 0, respectively. It means that the number of bonds around the metal is equal to the number of unpaired outermost electrons in its atomic state. The other electrons of the metal occupy lone pair orbitals. This construction can also be compared with the main block MEH systems. For example, H_3C-NiH and H_3C-Cu can be considered as similar to H_3C-OH and H_3C-F, respectively. In Zn, Cd, and Hg, the corresponding MEH systems are H_3C-ZnH, H_3C-CdH, H_3C-HgH, respectively. It is expected that the C−E bond will show comparable behavior whether E is a main block element or a TE because of the pairing of all outermost electrons of E.

On the basis of the above strategy, the geometry optimization of closed-shell MEH systems containing elements up to bismuth (except Ce to Lu and noble gases) has been done at density functional theory level using B3LYP functional[46] in Gaussian 98 set of programs.[47] For molecules containing elements up to bromine, 6-31++G(d,p) basis set[48] is used in the calculations. For other molecules, a general basis set is used, which contains 6-31++G(d,p) for C and H, and LanL2DZ+pol for the other elements[49−51] (here, "pol" indicates an extra polarization function). This method is expected to give reliable geometries. Further, vibrational analysis of all the MEH systems are done to ensure that all of them are minima on the potential-energy surface. Moreover, stability of all the closed-shell "wave functions" for the TE systems are checked.

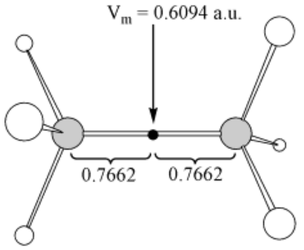

Figure 1. MESP bond critical point (V_m) of ethane. The distances are in Å.

Calculation of molecular electrostatic potential (MESP) is based on eq 1. Between two bonded atoms, one can always find an axial minimum (a critical point) in the MESP. Because at this point $\nabla V(r)$ is zero and the Hessian matrix of $V(r)$ has two negative eigen values, this point is called as a (3, −1) bond CP (following Bader[52]) in the MESP topography. For all the MEH systems, V_m that exists between C and E of a C−E bond will be located at the DFT level of theories mentioned in the previous paragraph.

Results and Discussion

1. Atomic Electronegativity. (a) Main Block Elements. Let us first consider the MESP bond CP of ethane (cf. Figure 1). It is a (3, −1) CP and located exactly at the midpoint of the C−C bond. The MESP value at this point suggests that the energy required to bring a unit test positive charge from infinity to this point is 0.6094 au. What other chemically meaningful information can be obtained from this point? Does this point say anything about the electronegativity of the carbon atom? The answer to this question is perhaps no because of the homogeneous nature of the C−C bond. However, if we change one of the CH_3 group by another atom, say in general −E, with single valency or an atom having all but one valency is satisfied with other atom or group of atoms, say −EXYZ, the C−E bond will show a V_m closer to either C or E. This behavior as well as the value of V_m is expected to change depending on the electronegativity of −E or −EXYZ. To further understand this and to make a systematic approach, first we consider the substituents directly attached to E to be equal to H.

In Table 1, the values of the C−E bond distance, the MESP minimum located along the C−E internuclear axis (V_m), the distance of V_m from methyl carbon (d_1), the distance of V_m from E atom (d_2), and various electronegativity scales for main block MEH systems are depicted. The values of d_1 and d_2 clearly indicate that the location of V_m along the C−E bond changes considerably depending on the position of E in the periodic table. According to Wiener et al.,[26] d_1 is an indicator of the covalent

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(45) Suresh, C. H.; Koga, N. *J. Phys. Chem. A* **2001**, *105*, 5940.

(46) (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 1372. (b) Becke, A. D. *J. Chem. Phys.* **1993**, *96*, 5648.

(47) 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.3; Gaussian, Inc.: Pittsburgh, PA, 1998.

(48) Hariharan, P. C.; Pople, J. A. *Mol. Phys.* **1974**, *27*, 209.

(49) (a) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 275. (b) Wadt, W. R.; Hay, P. J. *J. Chem. Phys.* **1985**, *82*, 284. (c) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 299. (c) LANL2DZ basis set for fourth-raw (Rb−Ag) and fifth-raw elements (Cs−Au) are relativistic.

(50) *Gaussian basis sets for molecular calculations*; Huzinaga, S., Ed.; Elsevier: New York, 1984.

(51) f-Polarization functions are taken from Ehlers, A. W.; Bohme, M.; Dapprich, S.; Gobbi, A.; Hollwarth, A.; Jonas, V.; Kohler, K. F.; Stegmann, R.; Veldkamp, A.; Frenking, G. *Chem. Phys. Lett.* **1993**, *208*, 111.

(52) (a) Bader, R. F. W. *Chem. Rev.* **1991**, *91*, 893. (b) Bader, R. F. W. *Atoms in Molecules: A Quantum Theory*; Oxford: New York, 1990. (c) Bader, R. F. W.; Nguyen-Dang, T. T. *Adv. Quantum Chem.* **1981**, *14*, 63.

Table 1. MESP Minimum (V_m) on the C−E Bond of $CH_3{-}EH_n$ Systems and the Distance of V_m from Carbon (d_1) and E Atom (d_2)[a]

atom	d_1	d_2	V_m	χ_A	$\chi_{Pauling}$	$\chi_{Sanderson}$	$\chi_{Allred-Rochow}$	$\chi_{Mulliken}$	χ_{Allen}
H	0.6954	0.3973	0.8142	3.382[b]	2.20	2.59	2.20	2.25	2.300
Li	0.9856	0.9998	0.1009	0.771	0.98	0.89	0.97	0.97	0.912
Be	0.8351	0.8420	0.4133	1.770	1.57	1.81	1.47	1.54	1.576
B	0.7726	0.7848	0.5782	2.402	2.04	2.28	2.01	2.04	2.051
C	0.7662	0.7662	0.6094	2.555	2.55	2.75	2.50	2.48	2.544
N	0.7407	0.7241	0.7260	3.117	3.04	3.19	3.07	2.90	3.066
O	0.7288	0.6957	0.8068	3.542	3.44	3.65	3.50	3.41	3.610
F	0.7253	0.6739	0.8745	3.938	3.98	4.00	4.10	3.91	4.193
Na	1.0648	1.2461	0.0481	0.934	0.93	0.56	1.01	0.91	0.869
Mg	0.9443	1.1545	0.2347	1.342	1.31	1.32	1.23	1.37	1.293
Al	0.8741	1.0911	0.3707	1.748	1.61	1.71	1.47	1.83	1.613
Si	0.8385	1.0503	0.4648	2.109	1.90	2.14	1.74	2.28	1.916
P	0.8362	1.0401	0.4947	2.279	2.19	2.52	2.06	2.30	2.253
S	0.8281	1.0089	0.5580	2.620	2.58	2.96	2.44	2.69	2.589
Cl	0.8244	0.9807	0.6169	2.960	3.16	3.48	2.83	3.10	2.869
K	1.1197	1.6244	−0.035 0	0.760	0.82	0.45	0.91	0.73	0.734
Ca	1.0154	1.4953	0.1068	0.991	1.00	0.95	1.04	1.08	1.034
Ga	0.8702	1.0949	0.4029	1.922	1.81	2.42	1.82	2.01	1.756
Ge	0.8510	1.0941	0.4616	2.166	2.01	2.62	2.02	2.33	1.994
As	0.8581	1.1168	0.4582	2.189	2.18	2.82	2.20	2.26	2.211
Se	0.8617	1.1177	0.5004	2.472	2.55	3.01	2.48	2.6	2.424
Br	0.8637	1.1035	0.5332	2.686	2.96	3.22	2.74	2.95	2.685
Rb	1.1600	1.8229	−0.048	0.930	0.82	0.31	0.89	0.69	0.706
Sr	1.0334	1.6607	0.0932	1.018	0.95	0.72	0.99	1.00	0.963
In	0.9247	1.2268	0.3070	1.667	1.78	2.14	1.49	1.76	1.656
Sn	0.9013	1.2446	0.3710	1.918	1.96	1.49	1.72	2.21	1.824
Sb	0.9055	1.2814	0.3713	1.945	2.05	2.46	1.82	2.12	1.984
Te	0.8969	1.2694	0.4244	2.22	2.10	2.62	2.01	2.41	2.158
I	0.8993	1.2637	0.4652	2.487	2.66	2.78	2.21	2.74	2.359
Cs	1.1750	2.0329	−0.069 0	0.894	0.79	0.22	0.86	0.62	
Ba	1.0565	1.8584	0.0477	0.88	0.89	0.68	0.97	0.88	
Tl	0.9568	1.3406	0.2711	1.644	1.62	2.25	1.44	1.96	
Pb	0.9246	1.2751	0.3415	1.879	2.33	2.29	1.55	2.41	
Bi	0.9298	1.3324	0.3274	1.824	2.02	2.34	1.67	2.15	

[a] The distances are in Å and V_m is in A.U. [b] In the present model, the χ_A value of H is considered as an exception. See text for details.

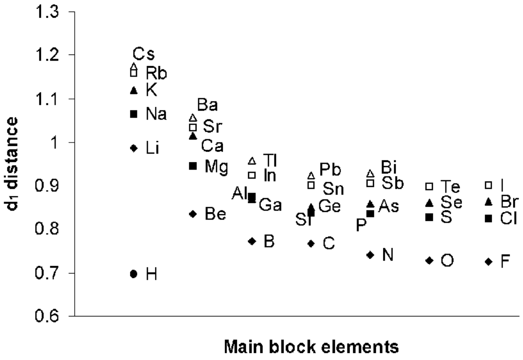

Figure 2. Variation of d_1 distances along the periodic table.

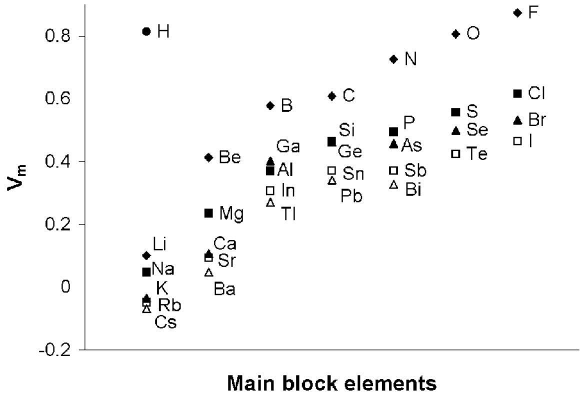

Figure 3. Variation of V_m values along the periodic table.

radii of carbon atom and d_2 is that of the element E. However, the d_1 value changes as the atomic number of E changes. In fact, the d_1 distance of only ethane (0.7662 Å) can be used as a meaningful measure of the covalent radii of the carbon atom, which is nothing but half the C−C bond distance. In our previous work,[45] we have showed that the MEH system-based covalent radii can be obtained by simply subtracting the d_1 distance of ethane from each of the C−E bond distances, d_{C-E}, that is, $R_{covalent} = d_{C-E} - 0.7662$. These values were found to correlate very well with other atomic radii values. The smallest value of d_1 equal to 0.6954 Å is observed when E = H (i.e., for $H_3C{-}H$ system). In Figure 2, a chart showing the variation of the d_1 distance along the main block elements is given. This chart shows that along the second and third period, the d_1 value gradually decreases from left to right. The same observation is valid for the periods of 3, 4, and 5 when the elements are in group 1, 2, and 13 and after that up to group 17, the d_1 value is almost a constant. On the other hand, on moving from top to bottom of a group, the d_1 value shows a gradual increase. An exception is the slightly larger value of Al as compared to Ga. In general, the d_1 values show good similarities to the periodic nature of the atomic sizes.

The V_m value at the C−E bond shows almost an opposite trend as compared to the trends of the d_1 value as one goes from left to right along a period and top to bottom along a group (cf. Figure 3). In periods 2−6, V_m values increase when one goes from left to right. Two exceptions to this observation are the slight decrease in the V_m value of As and Bi as compared to Ge and Pb, respectively. Along any group, the V_m value shows a gradual decrease when moving from top to bottom. An

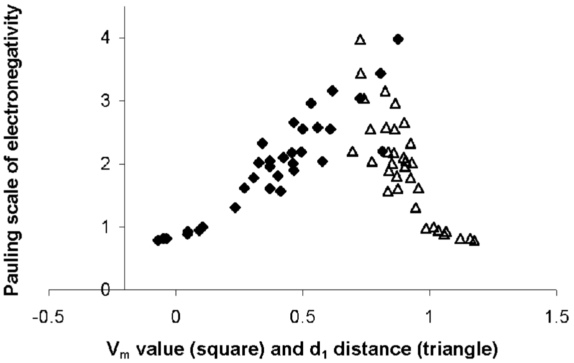

Figure 4. Relation between V_m or d_1 distance with Pauling electronegativity.

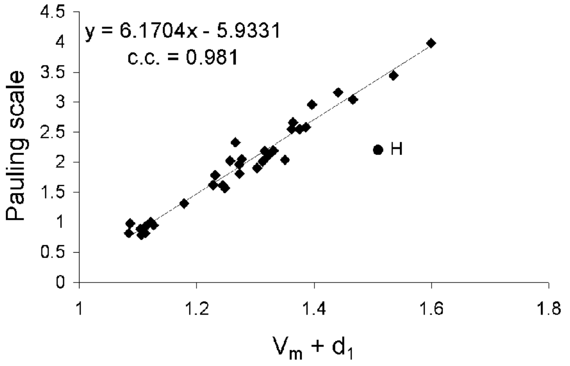

Figure 5. Correlation between ($V_m + d_1$) and Pauling electronegativity.

exception is the cases of Al and Ga where the V_m value of Ga is 0.0322 au larger than that of Al.

One can immediately notice the change in V_m with respect to electronegativity of E. Generally, an E with high electronegativity gives a high positive value for V_m and a less electronegative E makes it less positive. V_m is even negative when E is a very weak electronegative atom such as Cs, Rb, and Ba. However, in the case of hydrogen, the V_m value is more positive than that of oxygen. A probable reason for this is the very small atomic radii of the hydrogen atom, which causes an overestimation of the MESP because of the larger contribution of the nuclear term in eq 1. The d_1 value showed a periodic nature somewhat parallel to the size of the E atom in the CH_3-EH_n systems. Because the electron accepting and releasing power of an atom depends on its size as well, the d_1 values could also be related with the electronegativity of the E atoms. Figure 4 depicts the relationship between the V_m and d_1 values to the Pauling electronegativity scale. It is expected that an appropriate combination of V_m and d_1 could yield the electronegativity of an atom E. We have found that this appropriate combination is just the sum of V_m and d_1! Let us define this sum as an atomic electronegativity factor a^f of the element E., that is,

$$a^f = V_m(CH_{3-}EH_n) + d_1(CH_{3-}EH_n) \qquad (2)$$

Except hydrogen, all the a^f values show a very good linear correlation with the Pauling electronegativity (cf. Figure 5). The correlation does not change if we write a^f in the following way.

$$a^f = [V_m(CH_3-EH_n) - V_m(CH_3-CH_3)] + [d_1(CH_3-EH_n) - d_1(CH_3-CH_3)] \qquad (3)$$

This is because the values of $V_m(CH_3-CH_3)$ and $d_1(CH_3-CH_3)$ are constants. Now it can be seen that with a larger value of the MESP bond CP, V_m in CH_3-EH_n as compared to that in CH_3-CH_3 is a measure of the higher electronegativity of E atom as compared to electronegativity of C atom and vice versa. Moreover, if V_m is located away from C in CH_3-EH_n as

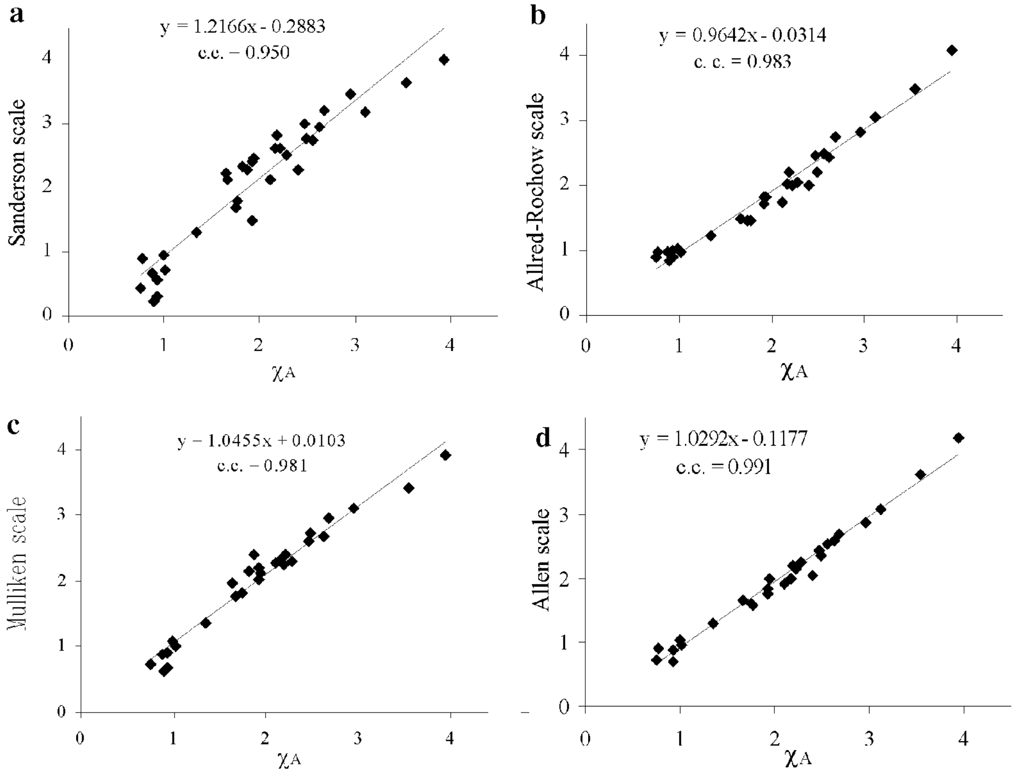

Figure 6. Correlation between the MESP bond critical point model based electronegativity (χ_A) and various other electronegativity scales (H is not included).

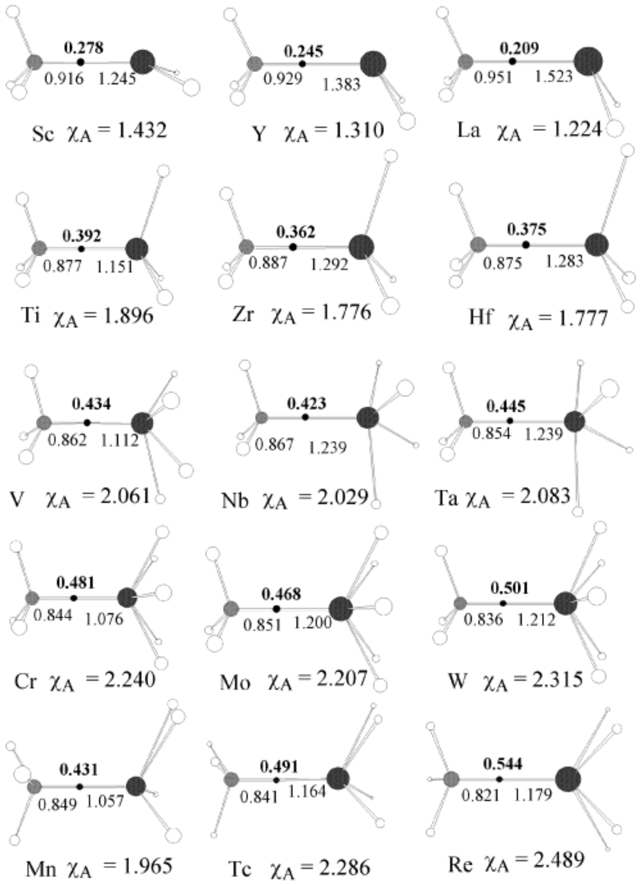

Figure 7. Geometries and the MESP bond CPs of earlier half of d-block transition elements. The dark point on the carbon−metal bond is the CP and near to it, its value is written in bold. The distance of the CP from carbon as well as from metal atom is also depicted. Further, the χ_A values obtained using eq 4 is given.

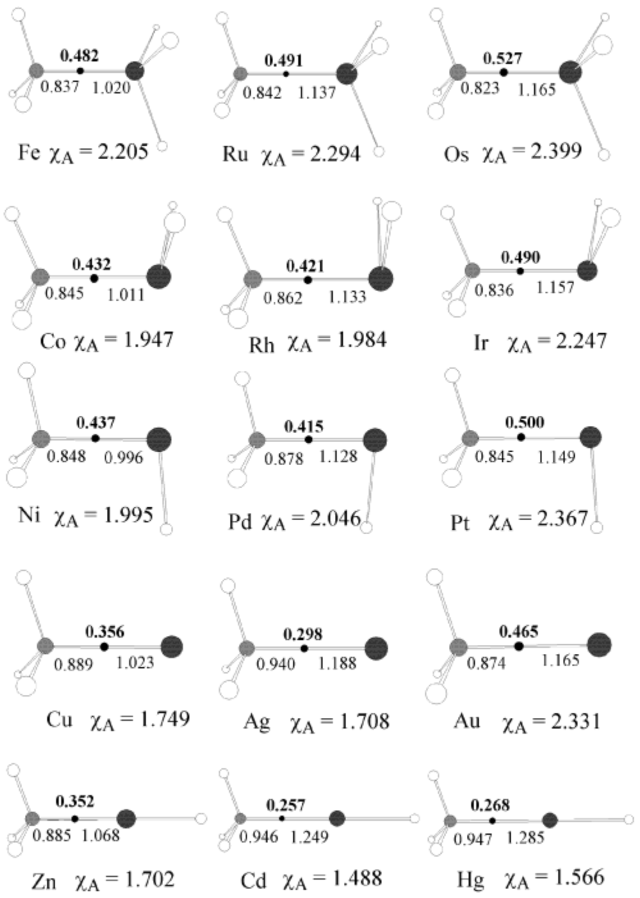

Figure 8. Geometries and the MESP bond CPs of later half of d-block transition elements. See also the caption of Figure 7.

compared to the distance of the CP from C in CH_3−CH_3, an additional increase in the electronegativity of E can be expected.

The correlation equation in Figure 5 suggests that a scale of atomic electronegativity, χ_A in Pauling unit can be written as

$$\chi_A = 6.1704(a^f) - 5.9331 \qquad (4)$$

In Figure 6, the correlation between χ_A and the popular electronegativity scales, viz., Sanderson, Allred−Rochow, Mulliken, and Allen are given. Among them, the best correlation is obtained with the Allen scale (correlation coefficient, c.c. = 0.991) and the worst correlation is found with the Sanderson scale (c.c. = 0.950). Moreover, except for the correlation equation obtained with Sanderson scale, all the other correlation equations have slope and y-intercept nearly equal to 1 and zero, respectively. The agreement between χ_A and these popular electronegativity scales including the Pauling scale strongly support the present approach of electronegativity based on the MESP bond critical point model of MEH systems. However, one may notice some minor discrepancies in the χ_A values of group 1 elements which in the order of Li, Na, K, Rb, and Cs is 0.771, 0.934, 0.760, 0.930, and 0.894, respectively. Li and K show slightly smaller values than their next nearest element down the group, which is opposite to the expected trend. Although the origin of this difference is not very clear at this point, it is felt that as compared to other groups of atoms the χ_A values of atoms of group I are very sensitive to the level of theory used because a very small change in the position and value of V_m can alter the ordering of their χ_A values.

(b) Transition Elements. It is seen that the position and value of the MESP bond CP corresponding to the C−E bond of a CH_3−EH_n could yield the electronegativity of E, a main block element. Such a method is expected to work for the entire periodic table except for the noble gases. In the case of TEs, the optimized geometries of CH_3−EH_n systems are shown in Figures 7 and 8.[53] These figures also depict the position and values of the MESP bond CP corresponding to the C−E bond. In Table 2, the MESP bond critical point model based electronegativity is given. To make a comparison of these values with other scales, the same table depicts the electronegativity scales of Pauling, Sanderson, and Allred−Rochow (the Allen values of electronegativity are not available and Mulliken values are available only for Cu, Zn, Ag, Cd, Au, and Hg). Unlike the Pauling, Sanderson, and Allred−Rochow values of electronegativity for the main block elements, their respective scales for the TEs do not show any good agreement between each other. For example, the c.c. for the (Pauling, Sanderson), (Pauling, Alred−Rochow), and (Sanderson, Allred−Rochow) plots of electronegativity are 0.317, 0.337, and 0.839, respec-

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(53) The DFT "wave functions" corresponding to the H_3C−EH_n systems (E = transition element) except the H_3C−MnH_4 system are stable "wave functions". Attempts to find a stable "wave function" for the H_3C−MnH_4 system failed. However, the geometry reported in this work for H_3C−MnH_4 is a minimum energy one and it is very similar to H_3C−TcH_4 and H_3C−ReH_4 systems. Therefore, we believe that the χ_A value obtained for Mn is reasonable.

Table 2. Different Scales of Electronegativity for Transition Elements

atom	χ_A	$\chi_{Pauling}$	$\chi_{Sanderson}$	$\chi_{Allred-Rochow}$
Sc	1.432	1.36	1.02	1.20
Ti	1.896	1.54	1.09	1.32
V	2.061	1.63	1.39	1.45
Cr	2.240	1.66	1.66	1.56
Mn	1.965	1.55	2.20	1.60
Fe	2.205	1.83	2.20	1.64
Co	1.947	1.88	2.56	1.70
Ni	1.995	1.91	1.94	1.75
Cu	1.749	1.90	1.98	1.75
Zn	1.702	1.65	2.23	1.66
Y	1.310	1.22	0.65	1.11
Zr	1.776	1.33	0.90	1.22
Nb	2.029	1.60	1.42	1.23
Mo	2.207	2.16	1.15	1.30
Tc	2.286	1.90		1.36
Ru	2.294	2.20		1.42
Rh	1.984	2.28		1.45
Pd	2.046	2.20		1.35
Ag	1.708	1.93	1.83	1.42
Cd	1.488	1.69	1.98	1.46
La	1.224	1.10		1.08
Hf	1.777	1.30		1.23
Ta	2.083	1.50		1.33
W	2.315	2.36	0.98	1.40
Re	2.489	1.90		1.46
Os	2.399	2.20		1.52
Ir	2.247	2.20		1.55
Pt	2.367	2.28		1.44
Au	2.331	2.54		1.42
Hg	1.566	2.00	2.20	1.44

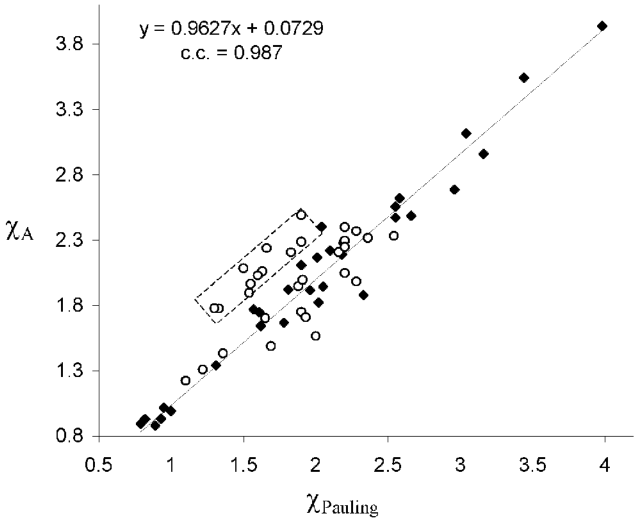

Figure 9. Comparison of the present scale (χ_A) and Pauling scale ($\chi_{Pauling}$) of electronegativity for the main block (filled square) and transition elements (circles).

Table 3. C−E Bond and d_1 Distances (in Å) and V_m (in kcal/mol) of $H_3C-EXYZ$ Systems and the Group Electronegativities of −EXYZ

group (−EXYZ)	C−E bond	V_m	d_1	χ_G	$\chi_{Inamoto}$	$\chi_{Mullaly}$	$\chi_{Marriot}$
$-CH_2CH_3$	1.5333	0.6044	0.7659	2.522	2.482	2.35	0.16
$-CH_2NH_2$	1.5352	0.6064	0.7657	2.534	2.538	2.42	0.15
$-CH_3$	1.5324	0.6094	0.7662	2.555	2.472	2.32	0.17
$-SCH_3$	1.826	0.5573	0.8218	2.577	2.592	2.46	0.1
$-SH$	1.837	0.558	0.8281	2.62	2.616	2.42	0.12
$-CH_2OH$	1.5255	0.632	0.7609	2.662	2.591	2.5	0.17
$-CH_2F$	1.5143	0.6644	0.7556	2.829	2.636	2.55	0.17
$-CHCH_2$	1.5024	0.6709	0.751	2.841	2.785	2.56	0.17
$-COCH_3$	1.5183	0.6724	0.7561	2.881	2.864	2.93	0.14
$-CONH_2$	1.5208	0.6729	0.7578	2.895	2.731	3.06	0.14
$-CHO$	1.5051	0.7008	0.7499	3.018	2.866	2.89	0.14
$-COOCH_3$	1.5082	0.7022	0.7520	3.040	2.832	3.16	0.19
$-COOH$	1.5056	0.7153	0.7508	3.113	2.824	3.15	0.18
$-NH_2$	1.4648	0.726	0.7407	3.117	2.992	3.15	0.33
$-NHMe$	1.4580	0.7348	0.7366	3.146	3.031	3.19	0.34
$-CF_3$	1.5050	0.7347	0.7497	3.226	2.985	3.10	0.17
$-NO_2$	1.5010	0.7750	0.7585	3.529	3.421	4.08	0.40
$-OH$	1.4245	0.8068	0.7288	3.542	3.494	3.97	0.43
$-OCH_3$	1.4147	0.8231	0.7229	3.606	3.545	4.03	0.44
$-F$	1.3992	0.8745	0.7253	3.938		4.73	0.52

tively. In fact, none of these scales have been considered as satisfactory for TEs. Therefore, a good correlation between any of these scales and the present scale may not be expected. In Figure 9, the present electronegativity values of TEs along with the electronegativity values of main block elements are plotted against the Pauling scale of electronegativity, and it shows that the majority of the electronegativity values of TEs fall on the same line of the main block elements. However, elements such as Ti, V, Cr, Mn, Fe, Zr, Hf, Nb, Ta, Tc, and Re are significantly deviated from the main block line (these elements are within the rectangle represented by the dotted lines). Considering the systematic nature of the present method, we expect that the new scale is more consistent and reliable than the Pauling scale of electronegativity.

Since we are using H_3C-EH_n systems with $n = 0, 1, 2, 3, 4,$ and 5 for the evaluation of electronegativity, we may consider that these electronegativities will correspond to the $(n + 1)$ valence state of E. In other words, by varying the number of H's attached to E, the same procedure can give us the electronegativity values for other valence states of a TE. This subject will be discussed elsewhere.

2. Group Electronegativity. For the atomic electronegativity calculation, we are always using methyl group substituted elemental hydrides (H_3C-EH_n). Therefore, in a true sense the χ values should represent the χ values of the group $-EH_n$. However, the hydrogen atoms are generally not considered as a substituent, or it is considered as a reference substituent to compare the electronic effects of other atoms or substituents. If one or more H's in H_3C-EH_n is replaced by another atom or group of atoms (say the resulting system is $H_3C-EXYZ$; XYZ stands for the various substituent groups), the position and values of the MESP bond CP at the C−E bond will give us a group electronegativity factor (g^f) given in eq 5.

$$g^f = V_m\,(CH_3-\,EXYZ) + d_1\,(CH_3-\,EXYZ) \qquad (5)$$

Similar to eq 4, it is therefore possible to define the group electronegativity (χ_G) as

$$\chi_G = 6.1704(g^f) - 5.9331 \qquad (6)$$

The constants used in eq 6 are the same as that used in eq 4. This procedure will give a straightforward way to express the group electronegativity. The important advantage of the method is that it will generate a group electronegativity scale completely compatible to the atomic electronegativity scale.

We have calculated the χ_G values of several substituent groups using eq 6 and they are depicted in Tables 3 and 4 along with Inamoto,[21] Mullay,[22] and Marriot[23] scales of group electronegativity. These tables also contain the values of C−E bond distance, V_m and d_1 distance. The χ_G values from the present

Table 4. C−E Bond and d_1 Distances (in Å) and V_m (in kcal/mol) of $H_3C-EXYZ$ Systems and the Present Scale and Inamoto Scale of Group Electronegativities of − EXYZ

group (–EXYZ)	C–E bond	V_m	d_1	χ_G	$\chi_{Inamoto}$
−MgBr	2.0792	0.2714	0.9396	1.539	1.295
−ZnMe	1.9549	0.3409	0.8862	1.639	1.336
$-AlMe_2$	1.9752	0.3461	0.8773	1.616	1.658
$-GaMe_2$	1.9808	0.3692	0.8758	1.749	1.658
$-GeMe_3$	1.9591	0.4234	0.8546	1.953	1.943
$-SiHMe_2$	1.8926	0.4426	0.8387	1.973	1.967
$-SiMe_3$	1.8946	0.4334	0.839	1.919	1.99
$-SiBr_3$	1.8625	0.5366	0.8279	2.487	2.028
$-SiCl_3$	1.8581	0.5435	0.8258	2.516	2.099
$-PH_2$	1.8763	0.4947	0.8362	2.279	2.19
$-PMe_2$	1.8672	0.4862	0.8305	2.191	2.249
$-SiF_3$	1.8431	0.5555	0.8191	2.549	2.299
$-PCl_2$	1.8505	0.5634	0.8228	2.620	2.343
−SeMe	1.9600	0.4942	0.8529	2.379	2.373
$-P(CN)_2$	1.8639	0.5791	0.8316	2.772	2.39
$-SeCF_3$	1.9639	0.529	0.8562	2.614	2.419
−SeCN	1.9792	0.5293	0.8636	2.662	2.475
$-CH_2Br$	1.5163	0.6712	0.758	2.886	2.502
$-PF_2$	1.8378	0.5602	0.8144	2.549	2.527
$-CH_2Cl$	1.5182	0.6666	0.7588	2.862	2.538
$-SO_2Cl$	1.8218	0.5999	0.818	2.816	2.734
$-CHF_2$	1.5061	0.7044	0.7505	3.044	2.807
−SOMe	1.8198	0.5745	0.8177	2.657	2.841
$-SO_2Me$	1.8213	0.5783	0.8181	2.683	2.998
$-NMe_2$	1.4574	0.7365	0.736	3.153	3.012
$-NHNH_2$	1.4590	0.742	0.7365	3.190	3.033
$-SO_2CF_3$	1.8183	0.6227	0.8163	2.946	3.043
$-SF_5$	1.8351	0.632	0.8249	3.057	3.076
−NCS	1.4261	0.8886	0.724	4.017	3.505
−NCO	1.4414	0.8455	0.732	3.801	3.552

study are plotted against Inamoto, Mullay, and Marriot scales in Figure 10a, b, and c, respectively. It shows that Inamoto and Mullay scales are in good agreement with the present χ_G values. In the Marriot scale, the χ_G values of strong electron-withdrawing groups such as $-CF_3$, −COOH, −CHO, and $-COOCH_3$ are showing larger deviation from the correlation line as compared to others. In fact, for these groups, the Marriot scale χ_G values are quite unrealistic ($-CF_3 = 0.17$, $-COOH = 0.18$, $-CHO = 0.14$, $-COOCH_3 = 0.19$) because according to that scale the χ_G value of $-CH_3$ is 0.17 and a further increase from this value is expected for more electron-withdrawing groups.

In general, if the E atom of $H_3C-EXYZ$ has a high electronegativity, the −EXYZ group will also show a high electronegativity. If the substituents X, Y, or Z atoms are more electronegative than E, the −EXYZ group will show higher electronegativity than E. For example, the (χ_A, χ_G) values of (C, COOH), (N, NO_2), (Mg, MgBr), (Si, SiF_3), (P, PCl_2), and (S, SO_2Cl) are (2.555, 3.113), (3.117, 3.529), (1.342, 1.539), (2.109, 2.549), (2.279, 2.620), and (2.620, 2.816), respectively.

Conclusions

A new reliable scale of atomic electronegativity (χ_A) is obtained for all the main group elements and d-block transition elements on the basis of theoretically calculated geometries of H_3C-EH_n (depending on the position of E in the periodic table, $n = 0, 1, 2, 3, 4$, and 5) and the MESP minimum on the C−E bond. The quantity χ_A can also be regarded as the electronegativity factor of the group $-EH_n$. Therefore, the present methyl group based approach can be easily extended to other systems where $-EH_n$ is any functional group so that a group electronegativity scale compatible to the atomic electronegativity scale can be obtained. On the basis of this procedure, group electronegativities of several substituent groups have been obtained.

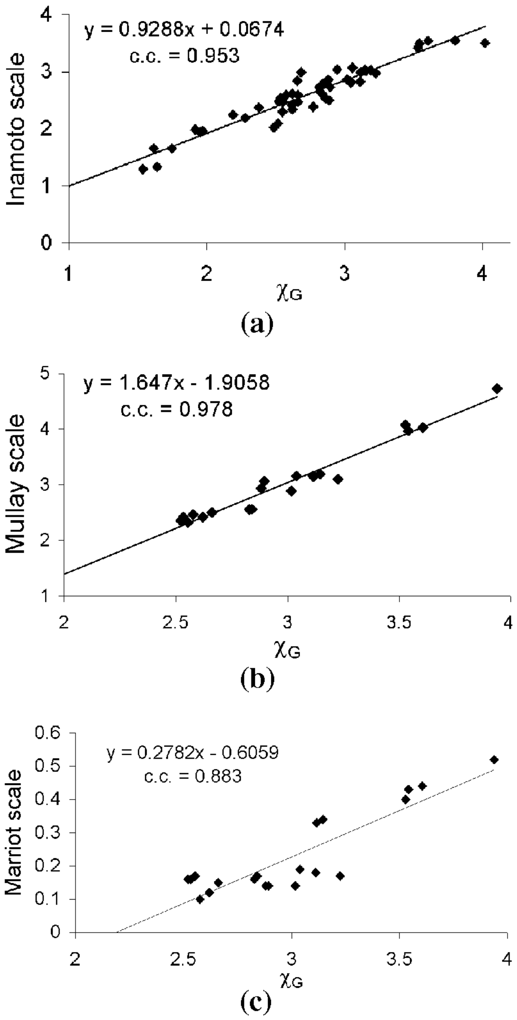

Figure 10. Correlations between the present scale of group electronegativity (χ_G) and (a) Inamoto, (b) Mullay, and (c) Marriot scales of group electronegativities.

Acknowledgment. The research was supported by the Grant-In Aid for Scientific Research on Priority Areas “Molecular Physical Chemistry” from the Ministry of Education, Culture, Sports, Science, and Technology. Part of the calculations was carried out at the Research Center for Computational Science of Okazaki National Research Institutes, Japan. C.H.S. gratefully acknowledges the Japan Society for the Promotion of Science (JSPS) for the award of a fellowship and Professor Shridhar R. Gadre at University of Pune for the encouragement.

JA017122R