Quantum Mechanical Size and Steric Hindrance

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Received: September 14, 2006; In Final Form: October 18, 2006

A quantum mechanical definition of molecular size and shape is formulated from the electronic second moment of the Hartree−Fock wave function. The shape tensor is defined to be invariant with respect to the origin. The geometric average of the eigenvalues of the tensor correlates very well with van der Waals and Bragg−Slater radii. There is also a close linear relationship between this definition of molecular size and molecular volumes determined computationally using isodensity contours. Furthermore, this definition of molecular size is effective in predicting the steric effects of substituents, as predicted by existing methods, such as the modified Taft E_S^e, *P*-values, and *n*-values.

1. Introduction

The shape and size of a molecule or substituent can be very influential on its physical and chemical properties. A predominant topic concerning substituent shape and size is steric hindrance. There are various methods that quantify steric effects; however, the result often varies with the method. While geometry provides important insight into how a substituent may interact sterically, it does not provide a quantitative measure of steric interaction. Therefore, most methods quantify the steric effects of substituents in terms of energy. The first steric constant, E_S, was defined by Taft[1] from a modified version of the Hammett equation.[2]

$$E_S = \log\left(\frac{k_X}{k_0}\right) \tag{1}$$

Taft's E_S values are determined from the reaction rates, k_X, of acid hydrolysis of substituted aliphatic esters, XCOOR, and the reaction rate, k_0, of acid hydrolysis of the ester CH_3COOR averaged over four different reaction conditions.[3] However, soon after the introduction of E_S, it was noticed that electronic effects, such as polar and resonance effects, were included in the steric constant. Various modifications have been made to Taft's E_S in an effort to eliminate electronic effects and determine steric constants, which are more generally applicable.[3] Dubois defined the Taft−Dubois steric parameter E'_S in the same manner as E_S; however, the rates were measured using only one standard reaction, the acid-catalyzed esterfication of carboxylic acids at 40 °C in methanol.[4] Hancock et al. modified the definition of E_S to account for the effect of hyperconjugation,[3]

$$E_s^c = E_s + 0.306(N - 3) \tag{2}$$

where N is the number of α-hydrogens. Another modification of E_S was presented by Unger and Hansch. They define $E_S^e(X) = E_S(CH_2X)$, which corrects for electronic contributions.[3] While these steric parameters are widely used, they are defined from a single type of reaction and hence are only moderately successful at predicting steric effects in general.

An alternative method to determining the steric effect of a substituent is through the energetics of conformational processes. The advantage of such an approach is that it avoids many other effects of a substituent that may be encountered in a chemical reaction, which are impossible to exclude. The simplest example is Anderson's *P*-values, which involve rotation around the C−C bond in ethanes.[5] However, bond length and geometry can have a large influence on the lateral interaction between the substituent of interest and the substituents on the neighboring carbon atom, which leads to unreliable steric information. Similar disadvantages are shared with *A*-values.[6] The *A*-value for a substituent X is defined as

$$A\text{-value} = -\Delta G^\circ = \frac{RT \ln K}{1000} \tag{3}$$

where K is the equilibrium constant for the equatorial and axial isomers of the monosubstituted cyclohexane. Like *P*-values, factors such as the bond length and the shape of the substituent lead to *A*-values that do not always correlate well with the spatial requirement of the substituent. A solution to such a problem may be the design of a conformational process, which involves a more multidimensional interaction with the substituent, such as the topomerization process shown in Figure 1.[7] The ring inversion of this system is used to determine the steric parameter, *n*-value[7] of X. The *n*-value is defined as the value of n such

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10.1021/jp066011h CCC: $33.50

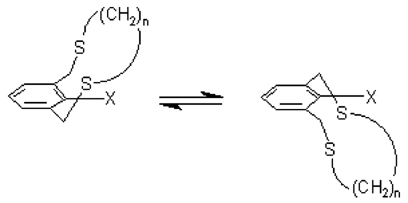

Figure 1. Topomerization of phane system with intra-annular substituent, *X*, used to determine *n*-values.[7]

that $\Delta G_c^{\ddagger} = 15$ kcal mol^{-1}. While the idea behind the *n*-value as a measure of the size of a substituent is promising, the application does have flaws. The determination of the *n*-values involves interpolation or extrapolation to $f(n) = \Delta G_c^{\ddagger} = 15$ kcalmol^{-1}, approximating $f(n)$ as linear. Yet, despite the flaws and small number of data points, relatively good results can be obtained.[7] While there are various methods to quantify the spatial requirement of a substituent, steric hindrance does not necessarily correlate perfectly with the shape and size or volume of a substituent.

Perhaps the oldest and most popular method to determine the volume of a molecule is through the atoms in molecules approach. By using the average radii of atoms in different environments,[8,9] determined by kinetic gas theory or X-ray crystallography, the shape and volume of molecules can be approximated.[8] Since the idea was introduced in the 1960s, there have been several algorithms developed for the calculation of the molecular volumes of many different types of compounds. One of the more recent algorithms, by Gavezzotti,[10] is capable of dealing with complicated structures such as cage compounds and inclusion compounds in crystalline matrices. These empirical calculations are widely used; however, the use of quantum mechanics to calculate molecular volumes is an alternative. In 1967, Bader et al. determined the size and shape of first row homonuclear diatomic molecules from outer contours of the Hartree−Fock electron density distribution.[11] Once the theory of atoms in molecules had advanced, such as the aforementioned volume algorithms, along with computational methods, determining molecular shapes and sizes was once again investigated by Bader et al.[12] The molecular shapes and volumes agreed well with the corresponding van der Waals volumes using density contours of 0.001 and 0.002 a.u. It was also found that the properties of various atoms and functional groups were transferrable from molecule to molecule, especially in the case of normal hydrocarbons.[12]

Another method of calculating size using quantum mechanics was introduced by Csizmadia et al.[13] when studying localized molecular orbitals (LMOs). A theoretical definition of the size of an electron pair, $\langle r_1^2\rangle_{R_a}$, is given as

$$\langle r_1^2\rangle_{R_a} = |\langle\psi_a|r_1^2|\psi_a\rangle_0 - R_a^2| \tag{4}$$

where R_a is the centroid of charge of the LMO,

$$|R_a| = \sqrt{\langle\psi_a|x_1|\psi_a\rangle_0^2 + \langle\psi_a|y_1|\psi_a\rangle_0^2 + \langle\psi_a|z_1|\psi_a\rangle_0^2} \tag{5}$$

calculated at some point R_0. While this definition cannot describe entire substituents, it can be successfully applied to bonds and lone pairs.[13] Later, Csizmadia focused on the components of $\langle r^2\rangle$, $\langle x^2\rangle$, $\langle y^2\rangle$, and $\langle z^2\rangle$, to define the shape of an electron pair.[14] The second moment tensor of an LMO, with respect to its own centroid of charge, was defined as

$$\Omega = \begin{pmatrix} [\langle x^2\rangle_0 - \langle x\rangle_0^2] & [\langle xy\rangle_0 - \langle x\rangle_0\langle y\rangle_0] & [\langle xz\rangle_0 - \langle x\rangle_0\langle z\rangle_0] \\ & [\langle y^2\rangle_0 - \langle y\rangle_0^2] & [\langle yz\rangle_0 - \langle y\rangle_0\langle z\rangle_0] \\ & & [\langle z^2\rangle_0 - \langle z\rangle_0^2] \end{pmatrix} \tag{6}$$

It is suggested that if the tensor is diagonalized,

$$U^{+}\Omega U = \begin{pmatrix} \langle x'^2\rangle & 0 & 0 \\ & \langle y'^2\rangle & 0 \\ & & \langle z'^2\rangle \end{pmatrix} \tag{7}$$

the diagonal values, $\langle x'^2\rangle$, $\langle y'^2\rangle$, and $\langle z'^2\rangle$ are aligned with the axes of an ellipsoid, which describes the shape of the LMO. A similar calculation could be applied to an entire molecule. Analagous to the definition of the second moment tensor of an electron pair, the second moment tensor of a molecule can be defined so that when diagonalized the diagonal values are the major and minor axes of an ellipsoid in which the molecule is inscribed. The process can then be taken a step further, by calculating the average radius of the ellipsoid and its volume. Such an approximation to molecular volume is calculated from expectation values of the Hartree−Fock wave function and is much less time-consuming than tracing a three-dimensional contour around a molecule. The radii and volumes determined for different substituents can then be used to predict steric effects.

2. Theory

2.1. Origin Invariant Electronic Second Moment Tensor of a Molecule. The second moment tensor of a molecule, calculated at some point $r_0 = (x_0, y_0, z_0)$, is given as

$$S = \begin{pmatrix} \langle x^2\rangle_{r_0} & \langle xy\rangle_{r_0} & \langle xz\rangle_{r_0} \\ & \langle y^2\rangle_{r_0} & \langle yz\rangle_{r_0} \\ & & \langle z^2\rangle_{r_0} \end{pmatrix} \tag{8}$$

Expectation values of the form $\langle ij\rangle$, $i = x$, y, or z and $j = x$, y, or z, are defined as follows

$$\langle ij\rangle = \int \Psi^*(r)\, ij\, \Psi(r)\, \mathrm{d}r \tag{9}$$

where Ψ is the Hartree−Fock wave function. It is seen that the second moment tensor depends on the origin; hence, a standard origin should be chosen, such as the center of nuclear charge. However, the second moment tensor can become origin invariant if it is defined in the following manner

$$\tilde{S} = \begin{pmatrix} \langle \tilde{x}^2\rangle & \langle \tilde{x}\tilde{y}\rangle & \langle \tilde{x}\tilde{z}\rangle \\ & \langle \tilde{y}^2\rangle & \langle \tilde{y}\tilde{z}\rangle \\ & & \langle \tilde{z}^2\rangle \end{pmatrix} \tag{10}$$

where

$$\langle \tilde{i}\tilde{j}\rangle = \langle ij\rangle_{r_a} - \frac{\langle i\rangle_{r_a}\langle j\rangle_{r_a}}{N} \quad i = x, y, \text{ or } z \text{ and } j = x, y \text{ or } z \tag{11}$$

N is the number of electrons and r_a is an arbitrary origin. The tensor $\tilde{S}$ is a real symmetric matrix and therefore can be diagonalized yielding a principle coordinate system.

$$Q^{+}\tilde{S}Q = \tilde{S}' \tag{12}$$

$$\tilde{S}' = \begin{pmatrix} \langle \tilde{x}'^2 \rangle & 0 & 0 \\ & \langle \tilde{y}'^2 \rangle & 0 \\ & & \langle \tilde{z}'^2 \rangle \end{pmatrix} \tag{13}$$

The eigenvalues, $\langle \tilde{x}'^2 \rangle$, $\langle \tilde{y}'^2 \rangle$, and $\langle \tilde{z}'^2 \rangle$, correspond to the principal axes of the electronic second moment of the molecule, Q, and can be associated with the major and minor axes of an ellipsoid. The geometric average, $\tilde{R}$, of these axes is given by

$$\tilde{R} = (\langle \tilde{x}'^2 \rangle \langle \tilde{y}'^2 \rangle \langle \tilde{z}'^2 \rangle)^{1/6} \tag{14}$$

and the volume of the ellipsoid, $\tilde{V}$, is

$$\tilde{V} = \frac{4\pi}{3}\tilde{R}^3 = \frac{4\pi}{3}\sqrt{\langle \tilde{x}'^2 \rangle \langle \tilde{y}'^2 \rangle \langle \tilde{z}'^2 \rangle} \tag{15}$$

3. Method

Calculation of the origin invariant second moment tensor and diagonalization were performed using the MUNgauss program.[15] All calculations, with the exception of HI, were performed at HF/6-31G(d)//HF/6-31G(d). The double-ζ Huzinaga basis set for iodine[16] was used for calculations on HI. Geometries were optimized using Gaussian03.[17]

4. Results and Discussion

4.1. Molecular Shape and Volume. The eigenvalues of the second moment tensor, $\tilde{S}$, the average radius, $\tilde{R}$, and the molecular volume, $\tilde{V}$, for each molecule studied are given in Table 1.

In an effort to investigate the validity of this method, the radii of the hydrides were compared to the corresponding van der Waals[8] and Bragg−Slater[9] atomic radii (Figure 2). The average radii of the hydrides correlate very well with both the van der Waals ($R^2 = 0.916$) and the Bragg−Slater ($R^2 = 0.910$) atomic radii. Most of the observed scatter is due to the number of hydrogens bonded to each atom. Negative deviations are seen with HF, HCl, and HBr, whereas NH_3, CH_4, and PH_3 deviate positively. An exception to this trend is the van der Waals radius of Si, which is underestimated by $\tilde{R}$ of SiH_4. Although, when comparing $\tilde{R}$ to the Bragg−Slater radius, the expected positive deviation is seen. While the radii predicted from the electronic second moment have been compared to experimentally determined values, the molecular volumes will be compared to an alternative computational method.

The molecular volume approximated by the second moment ellipsoid, $\tilde{V}$, and the molecular volumes enclosed by isodensity

TABLE 1: Molecular Shape and Volume from Origin Invariant Electronic Second Moment [HF/6-31G(d)//HF/6-31G(d)]

molecule	$\langle \tilde{x}'^2 \rangle$ (a.u.)	$\langle \tilde{y}'^2 \rangle$ (a.u.)	$\langle \tilde{z}'^2 \rangle$ (a.u.)	$\tilde{R}^a$ (a.u.)	$\tilde{V}^b$ (cm^3 mol^{-1})	$V_{\rho=0.001}$a.u.^{c} (cm^3 mol^{-1})	$V_{\rho=0.002}$a.u.^{d} (cm^3 mol^{-1})
H_2	1.507	1.507	2.151	1.303	0.83	10.75	7.78
HF	4.011	4.011	5.101	2.085	3.39	10.90	8.91
HCl	10.434	10.434	13.417	3.357	14.14	24.16	18.97
HBr	15.008	15.008	18.504	4.012	24.13		
HI	22.933	22.933	28.108	4.954	45.45		
H_2O	6.265	5.357	7.113	2.491	5.78	15.63	12.54
NH_3	9.156	7.571	9.156	2.931	9.42	20.20	15.88
CH_4	11.817	11.817	11.817	3.438	15.19	25.53	19.58
BH_3	14.520	5.173	14.520	3.208	12.34		
N_2	7.570	7.570	23.211	3.316	13.63	20.61	16.68
F_2	6.862	6.862	35.461	3.444	15.28	17.18	14.04
CO	7.351	7.351	24.169	3.306	13.51	21.10	16.62
CO_2	10.748	10.748	89.487	4.667	38.01	25.88	21.20
SO_2	17.474	14.722	135.731	5.717	69.85	33.10	27.20
HCN	8.600	8.600	31.016	3.632	17.90	25.18	20.07
HCP	14.665	14.665	62.507	4.876	43.34	36.66	29.78
H_2S	15.447	12.470	15.883	3.810	20.68		
PH_3	18.651	17.782	18.651	4.285	29.40	33.95	26.43
SiH_4	22.779	22.779	22.779	4.773	40.64		
HNO_2	21.222	11.504	80.515	5.195	52.41		
CHF_3	89.557	24.394	89.557	7.619	165.34		
CHOOH	25.834	12.333	93.234	5.565	64.43		
CH_3OH	16.714	15.712	50.256	4.861	42.94		
CH_2O	14.636	8.512	35.846	4.058	24.98		
CH_3SH	25.738	22.546	96.426	6.185	88.43		
trans-$CHOOCH_3$	38.764	22.553	226.840	7.636	166.47		
cis-$CHOOCH_3$	65.532	22.442	162.418	7.877	182.69		
ethane	22.062	22.062	65.160	5.626	66.57	39.54	31.10
ethane	21.047	11.432	48.943	4.770	40.56	25.46	20.45
ethyne	9.901	9.901	39.408	3.961	23.23	36.37	28.70
propane	50.001	32.376	144.150	7.846	180.57	53.64	42.76
cyclopropane	61.816	31.134	61.816	7.013	128.94	45.85	36.69
butane	63.342	42.694	318.801	9.756	347.09	67.64	54.34^e
isobutene	152.575	48.722	152.579	10.212	398.11	67.21	54.53
pentane	85.211	53.002	579.953	11.741	604.98	81.56	65.96
neopentane	161.286	160.288	168.659	12.782	780.56	80.78	65.95
hexane	99.825	63.310	974.114	13.538	927.49	95.71	77.62^e
cyclohexane (chair)	258.689	74.030	258.691	13.057	832.02	84.70	69.35
cyclohexane (twisted-boat)	245.442	82.461	258.837	13.179	855.58	84.70	69.35

[a] Defined by eq 14. [b] Defined by eq 15. [c ,d]Ref 12 (Table I). [e] Values calculated using Table III in ref 12; values in Table I have an error.

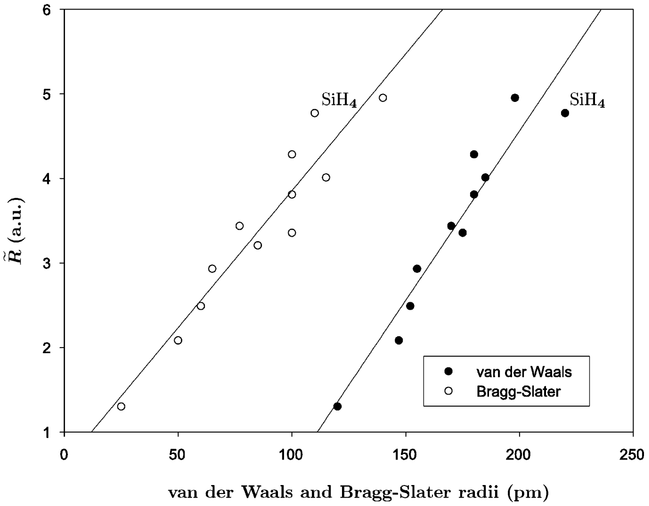

Figure 2. Comparison of average radii of hydrides to van der Waals and Bragg−Slater radii.

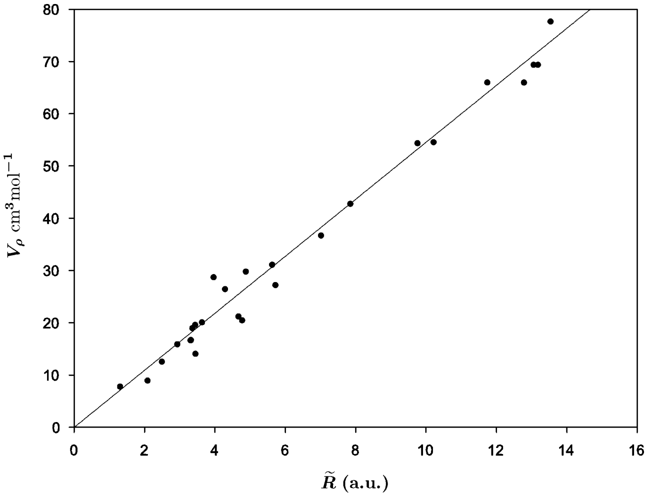

Figure 3. Comparison of electronic second moment average radius, $\tilde{R}$, to Bader isodensity contour molecular volume,[12] V_ρ ($\rho = 0.002$ a.u.).

contours ($\rho = 0.001$ and $\rho = 0.002$ a.u.)[12], V_ρ, were compared, and there is certainly a relationship between the two measures of molecular volume. However, for small molecules ($V_\rho < 35$ cm^3 mol^{-1}, $\rho = 0.002$ a.u.), $\tilde{V}$ underestimates V_ρ, and as molecules become larger, $\tilde{R}$ increasingly overestimates V_ρ. The growth of $\tilde{V}$ relative to V_ρ is mainly due to the nature of the second moment operator, $\hat{r}^2$. As the dimensions of a molecule increase, second moment expectation values increase in a quadratic fashion. Despite the differences in the behavior of the two measures of molecular volume, good agreement was found through the equation

$$V_\rho = a\left(\frac{\tilde{V}}{1\ \text{cm}^3\ \text{mol}^{-1}}\right)^b \qquad (16)$$

The values of a and b, when an isodensity contour of 0.001 a.u. is used to determine V_ρ, are $a = 9.4 \pm 0.7$ cm^3 mol^{-1} and $b = 0.331 \pm 0.012$ with $R^2 = 0.977$. For $\rho = 0.002$ a.u., the values are $a = 7.3 \pm 0.5$ cm^3 mol^{-1} and $b = 0.338 \pm 0.011$ with $R^2 = 0.982$. The values of b, $b \approx 1/3$ suggest that a simpler relationship exists between V_ρ and $\tilde{R}$, which is the case (Figure 3).

The Bader volume of a molecule, V_ρ, is proportional to the average radius of the origin invariant electronic second moment.

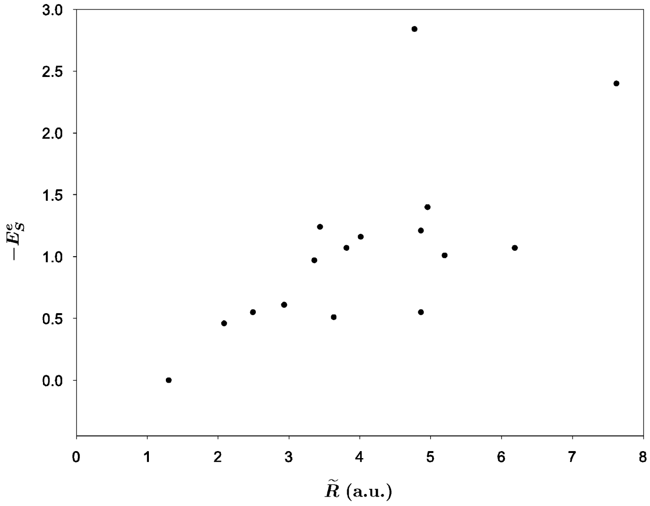

Figure 4. Relationship between the electronic second moment average radius, $\tilde{R}$, and the modified Taft steric constant, E_S^e.[3]

$$V_\rho = \alpha \tilde{R} \qquad (17)$$

Slightly better agreement is seen with $V_{\rho=0.002\text{a.u.}}$, where $\alpha = 5.45 \pm 0.15$ cm^3 mol^{-1} bohr^{-1} and $R^2 = 0.982$. When $\tilde{R}$ is related to $V_{\rho=0.001\text{a.u.}}$, $\alpha = 6.6 \pm 0.2$ cm^3 mol^{-1} bohr^{-1} and $R^2 = 0.977$. The largest deviation from this relationship (eq 17), for $\rho = 0.002$ a.u. and $\rho = 0.001$ a.u., is the Bader volume of ethyne. Using isodensity contours, the following relationship is observed, V_ρ (CH_2CH_2) < V_ρ (CHCH) < V_ρ (CH_3CH_3). However, the electronic second moment predicts $\tilde{V}$ (CHCH) < $\tilde{V}$ (CH_2CH_2) < $\tilde{V}$ (CH_3CH_3). Hence, it appears that the two methods apply different weights to diffuse π-bond density and the density surrounding terminal hydrogens. Yet, while the two methods differ greatly in complexity of calculation, they correlate quite well via eq 17.

4.2. Steric Effects. It is evident that the origin invariant electronic second moment tensor, $\tilde{S}$, is a valid property for determining the size of a molecule. The question is now asked, can $\tilde{S}$ be used to predict the steric effects of substituents? For a substituent X, the electronic second moment of the corresponding HX molecule is used. The relationship between $\tilde{R}$ and the Unger and Hansch-modified Taft steric constant,[3] E_S^e, is presented in Figure 4. There is a relationship between the modified Taft constant, E_S^e, and $\tilde{R}$, but there are some significant deviations. For halogens and first row hydrides, the linear relationship is followed quite closely. However, when a substituent is of the form $X = Y-Z$, such as $X = C{\equiv}N$, $O-CH_3$, $O-N-O$, and $S-CH_3$, $\tilde{R}$ overestimates E_S^e. The one significant positive deviation involves ethene, where $\tilde{R}$ predicts a much smaller steric effect. When steric factors are measured via a chemical reaction, there are several variables involved, including the conformation of the substituent during the rate-determining step. It is noticed that the E_S^e values for $X = OCH_3$ and OH are both -0.55, and the values for $X = SCH_3$ and SH are both -1.07. In those cases, it is evident that the reaction is affected by the O and the S and not the entire substituent as measured by $\tilde{R}$. In the case of ethene, the conformation of the vinyl substituent may directly interfere with the rate-determining step resulting in a very large E_S^e value. It appears that while $\tilde{R}$ correlates moderately well with E_S^e, it is necessary to consider the type of substituent and how it may effect the hydrolysis reaction.

In the case of halogens, there are P-values available for comparison.[7] A plot of $\tilde{R}$ against the P-values of the halogens

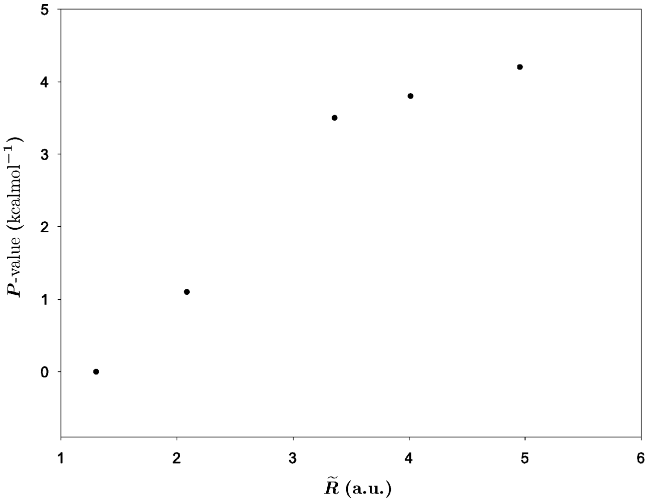

Figure 5. Relationship between the electronic second moment average radius, $\tilde{R}$, and the P-value.[5,7]

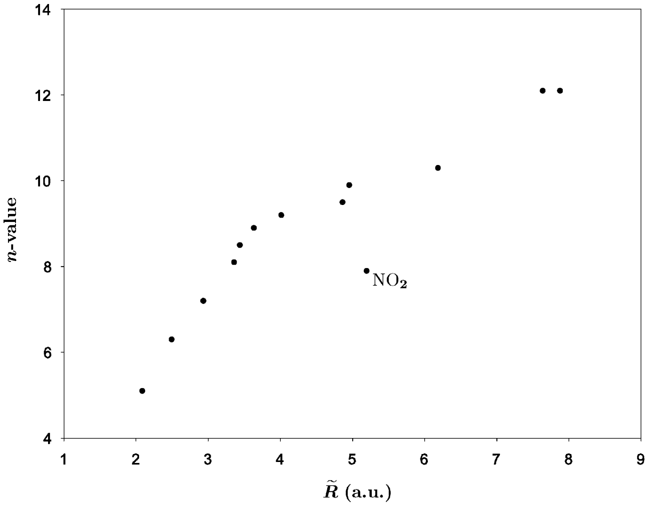

Figure 6. Relationship between the electronic second moment average radius, $\tilde{R}$, and the n-value.[7]

and hydrogen is given in Figure 5. As expected, $\tilde{R}$ predicts the same trend among these substituents. However, the relationship is not quite linear and is difficult to determine with few data points. There is more data available for the more extensive measure of the spatial requirement of substituents, n-values.

The n-values for various substituents, X, were also plotted against the average radius $\tilde{R}$ of molecules HX (Figure 6). The n-values for the substituents studied correlate quite well with $\tilde{R}$, $R^2 = 0.849$. The only significant deviation involves NO_2, where $\tilde{R}$ predicts a larger n-value than what is observed experimentally. For all other substituents, $\tilde{R}$ predicts the same order of spatial requirement. During a conformational process as the one described in Figure 1, other effects, such as electronic effects, are minimized but are still present and these effects vary among substituents. While the determination of n-values is quite successful with few data points and linear interpolation of $\Delta G_c^{\ddagger} = 15$ kcal mol^{-1}, it is possible that NO_2 interacts favorably with the aliphatic chain, resulting in a relatively lower n-value. The tensor $\tilde{S}$, and the value $\tilde{R}$ provide purely steric information; therefore, when compared with experimental measures, deviations will be observed when other effects become significant.

5. Conclusions

The origin invariant electronic second moment tensor, $\tilde{S}$, is a valid measure of molecular size and consequently the spatial requirement of a substituent. There are several pre-existing methods for determining such values, both experimentally and computationally. The shape and size of a molecule as defined here correlate well with many of these pre-existing methods and are relatively easy to compute. The tensor consists of one electron expectation values, which require far less complex and extensive calculation than existing quantum mechanical approaches. In most cases, the square root of the geometric average of the eigenvalues of $\tilde{S}$, $\tilde{R}$, can predict the steric effects of substituents as described by the modified Taft E_S^e, P-values, and n-values. While there are some deviations, consideration of the substituents being compared may lead to better estimates. Also, the shape as described by the principal axes of the second moment tensor, $\langle \tilde{x}'^2 \rangle$, $\langle \tilde{y}'^2 \rangle$, and $\langle \tilde{z}'^2 \rangle$, could be applied specifically when certain interactions are expected in a chemical reaction or conformational process.

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