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Intramolecular Nonbonded Attractive Interactions: 1-Substituted Propenes

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Abstract: Whereas *cis*-substituted alkenes are normally significantly less stable than the *trans*-isomers, there is a group of 1-substituted propenes (X = F, OMe, Cl, Br, SMe) where the *cis*-isomers are the more stable. The calculated structures show that there is steric repulsion with the *cis*-isomers. However, this is overcome by attractive Coulombic interactions when X = F or OMe and by attractive dispersive interactions when X = Cl or Br. It was possible to calculate the magnitude of the latter term via the summation of the appropriate MP2 pair energies. The calculated and observed energy differences could be reproduced by a summation of steric, electrostatic, and dispersive interactions.

The *cis*-isomers of disubstituted ethenes are normally less stable than the corresponding *trans*-isomers as a result of a steric interaction between the substituents. As an example, *cis*-2-butene has a higher energy (1.1 kcal/mol) than *trans*-2-butene.[1] Nonbonded intramolecular interactions that stabilize molecules have been of considerable interest. Some 1-substituted propenes are examples of compounds that apparently exhibit attractive intramolecular interactions as evidenced by the fact that the *cis*-isomers are more stable than the *trans*-isomers. These compounds have received considerable study, both experimental[2,3] and computational.[4,5] The experimental observations are recorded in Table 1 along with the derived $\Delta G°$ values and their estimated uncertainties.

The *cis*-isomers of these 1-substituted propenes must be stabilized enough to overcome the normal steric interactions that beset such molecules. These stabilizing interactions may include (1) attractive Coulombic interactions between the substituents, which could result from interaction of bond dipoles that are oriented appropriately;[3b] (2) delocalization of valence electrons associated with one group into a vacant orbital on the other group;[5] and/or (3) stabilizing van der Waals interactions between the groups.

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Table 1. Observed Equilibrium Compositions and Free Energy Differences of 1-Substituted Propenes at 30−40° C

compound	% cis	$\Delta G°$ (kcal/mol)	ref
$CH_3CH=CHOMe$	71	0.53 ± 0.06	3a
$CH_3CH=CHOEt$	81	0.86 ± 0.08	3a
$CH_3CH=CHCl$	76	0.68 ± 0.06	3b
$CH_3CH=CHBr$	68	0.45 ± 0.06	3c
$CH_3CH=CHCN$	61	0.26 ± 0.04	3b

In order to gain further information about the intramolecular interactions within these molecules, we have carried out geometry optimizations at the HF, DFT, and MP2 levels using the aug-cc-pVTZ basis set. CCSD(T)/aug-cc-pVTZ calculations were carried out using the MP2 geometries. The HF calculations do not include electron correlation, so the effect of nonbonded van der Walls attractive terms will not be seen. The use of the density functionals will allow some correction for electron correlation but may not correctly reproduce van der Waals (dispersive) interactions,[6] MP2 provides modest correction for electron correlation, and CCSD(T) gives superior correction for this effect. The latter methods would be expected to reproduce the van der Waals terms.[7] Thus, it was anticipated that a comparison of the relative energies at these different levels would give information on the nature of the intramolecular interactions present in 1-substituted propenes.

Table 2. Relative Energies (Trans ⇌ Cis) of 1-Substitued Propenes[a]

X	HF	B3LYP	MP2	CCSD[b]	CCSD(T)[b]
F	−0.53	−0.56	−0.70	−0.63	−0.65
OMe	−0.56	−0.63	−0.95	−0.76	−0.80
CN	0.09	−0.11	−0.72	−0.37	−0.50
CH$_3$	1.56	1.25	1.04	1.13	1.06
Cl	0.01	−0.33	−0.77	−0.49	−0.60
Br	0.18	−0.27	−0.99	−0.63	−0.79
SMe	0.65	−0.26	−0.57	−0.14	−0.35

[a] No zero-point or thermal corrections, in kcal/mol, using aug-cc-pVTZ. [b] aug-cc-pVTZ using MP2/aug-cc-pVTZ geometries.

The substituents F, Cl, Br, CN, and CH$_3$ lead to conformers that have C_s symmetry with a methyl hydrogen eclipsing the C−C double bond.[8] With X = OMe or SMe, the substituent rotates so that a lone pair may interact with the carbon−carbon double bond. The situation with respect to the enamine, X = NMe$_2$, was somewhat more complex. The *trans*-isomer of the enamine with C_s symmetry was a stationary point on the potential energy surface with no imaginary frequencies. However, the *cis*-isomer was a transition state, and rotation of the substituent to allow the lone pair to interact with C=C led to a lower energy structure. An MP2 optimization of the *trans*-structure with reduced symmetry also led to a lower energy structure. The rotated structures were minima at B3LYP and CCSD as well as MP2. However, whereas the *trans*-isomer of the enamine presented no steric problems, a methyl of the NMe$_2$ group in the *cis*-isomer interfered with the terminal methyl at C(2). As a result, the relative energies of the enamine (X = NMe$_2$) are not comparable to those of the other 1-substituted propenes and will not be further considered.

Since we are primarily interested in the purely electronic interactions that lead to the energy differences, Table 2 gives the results of the calculations, without correction for zero-point energies or the change in energy with temperature. It was not practical for us to carry out geometry optimizations at the CCSD/aug-cc-pVTZ level, and therefore these energies were calculated using the MP2/aug-cc-pVTZ optimized geometries.

Inspection of the results summarized in Table 2 reveals that for the first-row substituents, X = F or OMe, the calculated relative energies are essentially independent of the method used. However, with X = Cl, the HF relative energy is essentially zero, and it became positive, favoring the *trans*-isomer, with X = Br or SMe. In contrast to the HF results, the *cis*-preference is maintained when X = Cl, Br, or SMe using all of the methods that include electron correlation. Taking the CCSD(T) relative energies as the more reliable, MP2 overcorrects somewhat, as is often observed.[9] The negative triple excitations, e(T)$_{ijk}$, partly cancel the positive semijoint third-order pair coupling terms, e$^{(3)}_{ij,jk}$, so the CCSD(T) relative energies are about halfway between the MP2 and the CCSD results. The DFT models also reproduce the *cis* preference and therefore *appear* to include short-range dispersion effects even though they have no terms that include true R^{-6} dispersive effects.[10]

The change in relative energies at the HF level is probably largely the result of steric interactions, as is suggested by

Table 3. Calculated C=C-Me Angles for 1-Substituted Propenes, MP2/aug-cc-pVTZ

X	cis	trans
F	125.24	122.38
Cl	126.78	122.64
Br	127.00	122.63
CN	125.21	123.78
CH$_3$	127.22	124.59
OMe	124.54	122.70
SMe	125.14	123.66

Table 4. Calculated CH$_3$ Rotational Barriers and CH$_3$ Torsion Frequencies (in cm^{-1}), B3LYP/aug-cc-pVTZ

X	cis	ν	trans	ν
F	1.07 (1.06)[a]	151i	2.14 (2.20)[a]	223i
OMe	0.71	108i	2.12	219i
CN	1.44 (1.39)[a]	168i	1.91	212i
Me	0.98	128i	1.96	207i
Cl	0.75 (0.62)[a]	109i	2.02 (2.17)[a]	215i
Br	0.73	116i	2.00	214i
SMe	0.56	92i	1.91	203i

[a] Observed values (ref 11).

the data presented in Tables 3 and 4. The results summarized in Table 3 indicate that the C=C-Me bond angle is larger with the *cis*-isomers than with *trans*-isomers, and this difference increases on going from X = F to Cl and Br. The effect may also be seen in comparing *cis*- and *trans*-2-butene where the *trans*-form is favored.

The data summarized in Table 4 show that the *cis*-isomers have a smaller methyl rotational barrier than *trans*-isomers as observed experimentally[11] and that the methyl torsion frequency is smaller for *cis*-isomers than *trans*-isomers. Both of these observations are consistent with a repulsive interaction between the methyl group and the *cis*-substituent.

The observation that the experimentally observed preference for the *cis*-isomer of 1-fluoropropene is reproduced at all theoretical levels, whereas this is not true for the other halogens, implies that the origin of the *cis*-preference in 1-fluoropropene is different than that responsible for the *cis*-preference of the other 1-halopropenes. In view of the large electronegativity of fluorine in comparison with the other halides, a reasonable hypothesis is there is a significant attractive Columbic interaction between the negatively charged fluorine at C(1) in the *cis*-isomer and the presumably positively charged methyl (a result of being attached to a double bond as well as the inductive effect of the 1-fluoro substituent) as suggested some time ago by Crump.[3b] The effect would be larger for the *cis*-isomer than for the *trans*-isomer because the former has the shorter nonbonded F···Me distance.
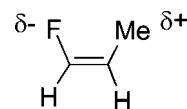
One might examine the validity of this hypothesis by evaluating the magnitude of the electrostatic interaction. This requires some method of obtaining the relevant atomic charges. This has been a continuing problem since atomic

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Table 5. Calculated Dipole Moments of Haloethenes (CH$_2$=CHX) Using aug-cc-pVTZ

compound	calculation	μ_x	μ_y	μ_{total}
CH$_2$=CHF	CCSD	1.267	0.748	1.471
	Hirshfeld atomic	0.944	0.526	1.081
	Hirshfeld dipole	0.319	0.219	0.387
	Hirshfeld total	1.263	0.745	1.467
CH$_2$=CHCl	CCSD	1.197	0.907	1.501
	Hirshfeld atomic	0.963	0.712	1.198
	Hirshfeld dipole	0.261	0.173	0.280
	Hirshfeld total	1.185	0.884	1.478
CH$_2$=CHBr	CCSD	1.156	0.924	1.480
	Hirshfeld atomic	0.953	0.740	1.206
	Hirshfeld dipole	0.201	0.161	0.258
	Hirshfeld total	1.154	0.901	1.464

Table 6. Effective Atomic Charges Based on the Hirshfeld Charges and the Dipole Moments[a]

compound	X	C$_1$H	C$_2$H	CH$_3$	μ(D)
cis-CH$_3$CH=CHF	−0.218	0.190	−0.010	0.038	1.464 (1.555)
trans-CH$_3$CH=CHF	−0.226	0.189	−0.009	0.039	1.873 (1.889)
cis-CH$_3$CH=CHCl	−0.156	0.101	0.023	0.035	1.533 (1.553)
trans-CH$_3$CH=CHCl	−0.172	0.102	0.027	0.044	2.032 (1.837)
cis-CH$_3$CH=CHBr	−0.031	0.126	0.075	0.029	1.613 (1.608)
trans-CH$_3$CH=CHBr	−0.071	0.145	0.076	0.031	1.865 (1.891)

[a] Values in parentheses are the ab initio MP2/aug-cc-pVTZ calculated values.

charges in molecules are not well defined, and different methods for calculating them give different results.[12]

In order to try to obtain some additional information, we have studied the haloethenes (CH$_2$=CHX). The structures of the haloethenes were calculated at the CCSD/aug-cc-pVTZ level of theory, and the dipole moment components were reoriented to place the C=C bond along the *x* axis. The calculated dipole moments are given in Table 5.

There is remarkably little difference in the dipole moments of the haloethenes and their components (z is out-of-plane so μ_z is zero), despite the large difference in electronegativity among the halogens. This is the result of a compensating increase in C-X bond length as the smaller electronegativity decreases the halogen charge. One of the more successful definitions of atomic charges is that of Hirshfeld[13] that also gives the atomic dipoles, originating from nonspherical charge distribution about the atoms. The results of these calculations are included in Table 5. It can be seen that the Hirshfeld charges reproduce the ab initio calculated dipole moments quite well when the atomic dipoles are included.

The MP2/aug-cc-pVTZ calculated dipole moments of the 1-halopropenes are summarized in Table 6. Again, there is little change in going from one halogen to another. In this case, we examined several models for calculating atomic charges. One computational method, ChelpG,[14] uses a least-squares fit to the electrostatic potential, with the dipole moments used as a constraint. However, an examination of the halopropenes found large differences in these charges on going from *cis*- to *trans*-isomers (Supporting Information), whereas all other methods for obtaining charges find little difference in charge between *cis*- and *trans*-forms. Therefore, they are clearly not satisfactory for the present purpose.

The atomic charges for the 1-halopropenes were obtained using the NPA,[15] AIM,[16] and Hirshfeld[13] definitions. The CH bond dipoles calculated using NPA are known to be

exaggerated,[17] and so the hydrogen charges were combined with the carbon charges. The dipole moments calculated using the NPA and AIM charges[18] varied considerably and did not agree with those from the ab initio calculations. However, the moments calculated using the Hirshfeld charges did not vary much on going from 1-fluoropropene to 1-chloropropene, although they were somewhat too small if the atomic dipoles are not included. Therefore, we further examined the Hirshfeld charges. In order to simplify the calculations, the atomic dipoles were neglected, and the atomic charges were scaled to account for this neglect.

With X = F and Cl, the average ratio of the ab initio dipole moments to those obtained using the Hirshfeld charges was 1.51 ± 0.06. The charges were scaled by this ratio giving the charges summarized in Table 6. The last column in Table 6 has the dipole moments calculated from these charges, and they can be seen to compare favorably with the ab initio values given in parentheses. As expected, the charge on X decreases on going from F to Cl and Br.

Clearly, these effective charges are just approximations, but they do fit the ab initio calculated dipole moments fairly well, and the halogen charges change in the expected fashion. They are, in any event, the best we have been able to obtain.

The differences in the intramolecular electrostatic interactions present in the *cis*- and *trans*-isomers were calculated using these charges, and the results are presented in Table 7. As noted some time ago by Westheimer and Kirkwood,[19] one must account for the fact that the polarizable C=C group lies between the substituents in the *trans*-isomer, and a hydrocarbon dielectric constant of 2 was used for this purpose.

Table 7 also includes *cis*- and *trans*-2-butene in order to have a case where the normal trans preference is found. In order to compare the results with the HF energy differences, it is necessary to include the steric repulsions between the methyl hydrogens and the substituents. They were estimated by calculation of the Pauli repulsion for H···X in the $^3\Sigma$ state and scaling the result by 0.4 in order to reproduce the rotational barrier in ethane (see the Supporting Information). The sum of the Coulombic and steric term fairly well reproduce the HF energy differences, although the steric term for X = F appears to be a little too large as compared to that for X = Cl.

Now, it remains to explain the difference between the HF and MP2 relative energies for the isomers. The MP2 correlation energy is a sum of *pair energies*, one for each pair of occupied SCF orbitals:

$$E^{(2)} = \sum_{i<j}^{occ} e_{ij}^{(2)} = \sum_{i<j}^{occ} \left\{ \sum_{a<b}^{virt} \frac{|\langle \boldsymbol{ij}||\boldsymbol{ab}\rangle|^2}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b} \right\}$$

The sum of these pair energies is invariant to unitary transformations among the occupied orbitals.[20] We are therefore free to localize the occupied orbitals.[21] The resulting second-order pair correlation energies between halogen lone pair electrons and methyl C−H bond electrons (Figure 1) can be interpreted as *intra*molecular dispersion energies. The details are included as Supporting Information. The method we use is essentially the same as the method employed by Grimme, Műck-Lichtenfeld,

Table 7. Interpretation of the HF Results for 1-Halopropene Isomers

X	qX	qMe	r(X···Me)	qq/r^a	Δqq/r	Pauli H···X	scaled	total	$\Delta E_{HF}{}^b$
cis-F	−0.218	0.038	2.908	−0.946	−0.553	0.775	0.310	−0.243	−0.521
trans-F	−0.226	0.039	3.725	−0.393					
cis-Cl	−0.156	0.035	3.199	−0.567	−0.261	0.997	0.391	0.130	0.101
trans-Cl	−0.172	0.044	4.103	−0.306					
cis-Br	−0.031	0.039	3.299	−0.122	−0.036	1.282	0.513	0.477	0.373
trans-Br	0.071	0.031	4.246	−0.086					
cis-Me	0.007	0.007	3.151	0.005	0.003	3.752	1.501	1.504	1.640
trans-Me	0.006	0.006	3.909	0.005					

^{a} The Coulombic effect for the trans isomers were reduced by a factor of 2 (see text). ^{b} $E_{cis} - E_{trans}$.
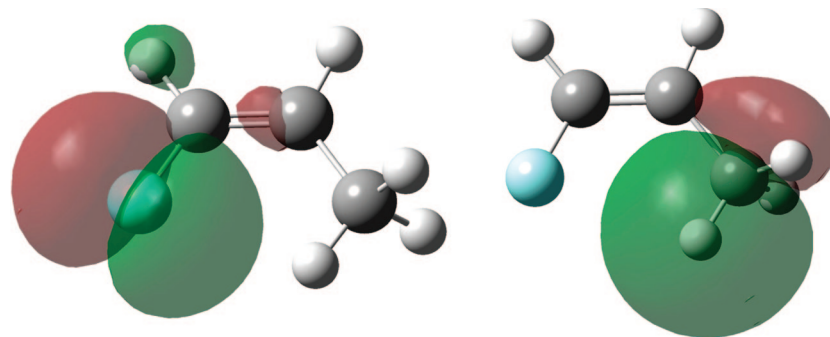
Figure 1. Examples of MP2 localized orbitals for 1-fluoropropene. The full set may be found in the Supporting Information.

Table 8. Interpretation of the HF-MP2 Relative Energy Differences^a

X	E_{HF}	E_{MP2}	ΔE_{HF}	ΔE_{MP2}	$\Delta E_{MP2} - \Delta E_{HF}$	ΔE_{Disp}	Disp^b
cis-F	−216.00815	−216.77183	−0.521	−0.707	−0.186	−0.221	−10.634
trans-F	−216.00732	−216.77071					−10.413
cis-Cl	−576.05438	−576.75803	0.101	−0.763	−0.864	−0.926	−12.559
trans-Cl	−576.05454	−576.75681					−11.673
cis-Br	−2688.99619	−2698.74332	0.373	−0.989	−1.362	−1.208	−12.909
trans-Br	−2688.99676	−2698.74174					−11.701
cis-Me	−156.16616	−156.86107	1.640	1.039	−0.601	−0.792	−11.612
trans-Me	−156.16877	−156.86273					−10.820

^{a} The total energies are given in atomic units (H), and the energy differences are given in kcal/mol. ^{b} Total interatomic pair energies not including geminal interactions.

Table 9. Components Contributing to the Relative Energies of the *cis*- and *trans*-Isomers of 1-Substitued Propenes^a

X	qq/r	steric	Disp	total	MP2	CCSD^b	CCSD(T)
F	−0.553	0.320	−0.221	−0.464	−0.70	−0.63	−0.65
Cl	−0.261	0.391	−0.926	−0.796	−0.77	−0.49	−0.60
Br	−0.036	0.513	−1.028	−0.731	−0.99	−0.63	−0.79
CH$_3$	0.003	1.501	−0.792	0.712	1.04	1.13	1.06

^{a} No zero-point or thermal corrections, in kcal/mol, using aug-cc-pVTZ. ^{b} At MP2/aug-cc-pVTZ geometries.

and Antony.[22] These intramolecular dispersion energies are compared with the total MP2 energy differences in Table 8. Given that we are looking at small differences between large numbers, the agreement is rather good. The contribution of the correlation energy to the *cis−trans* energy differences is in all cases almost entirely due to intramolecular dispersion.

Combining the results from Tables 7 and 8, we obtain a detailed explanation for the calculated *cis−trans* energy differences in Table 2. The summary in Table 9 demonstrates that electrostatic, steric, and dispersion interactions all play significant roles in determining the relative stability of the *cis*- and *trans*-isomers of 1-substituted propenes. In short, the relatively constant energetic preference found favoring the *cis*-isomers of 1-halopropenes

masks the varying roles of electrostatic and dispersion interactions within these molecules.

Summary

Although the *cis*-1-substituted propene with X = F, OMe, CN, Cl, Br, and SMe are more stable than their *trans*-isomers, the structural parameters indicate that they are subject to steric repulsion as is found with most compounds of this type. The observed *cis*-preference is due to a combination of Coulombic attraction between X and the terminal methyl (particularly important with X = F or OMe) and a dispersion interaction between X and the terminal methyl group (particularly important with X = Cl, Br, or SMe). The contribution of each of these terms to the relative energies has been estimated making use of model steric calculations,

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Hirshfeld atomic charges, and MP2 pair energies. The results are in satisfactory agreement with the differences in calculated total energies.

Calculations

All of the ab initio calculations were carried out using a development version of Gaussian.[23] The Hirshfeld charges were obtained using a local program.[24] The MO plots were made using Gaussview.

Supporting Information Available: Calculated energies and structures, comparison of calculated atomic charges, detailed information concerning the MP2 pair energies and the complete ref 23. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Pedley, J. R. *Thermochemical Data and Structures of Organic Compounds*; Thermodynamics Research Center: College Station, TX, 1994.

(2) For a review, see: Lowe, J. P. *Prog. Phys. Org. Chem.* **1968**, *6*, 1.

(3) (a) Salomma, P.; Nissi, P. *Acta Chem. Scand.* **1967**, *21*, 1386. (b) Crump, J. W. *J. Org. Chem.* **1963**, *28*, 953. (c) Harwell, K. E.; Hatch, L. F. *J. Am. Chem. Soc.* **1955**, *77*, 1682.

(4) Hagen, K.; Stolevik, R. *J. Mol. Struct.* **1996**, *376*, 83.

(5) (a) Epiotis, N. D.; Bjorkquist, D.; Bjorkquist, L.; Sarkanen, S. *J. Am. Chem. Soc.* **1973**, *95*, 7558. (b) Epiotis, N. D. *J. Am. Chem. Soc.* **1973**, *95*, 3087. (c) Allen, L. C.; Scartzafava, E. *J. Am. Chem. Soc.* **1971**, *93*, 311. (d) Hu, Z.-Q.; Zhu, X.-D. *Youji Huaxue* **2002**, *22*, 200. (e) Rois, B.; Taddei, F. *THEOCHEM* **1998**, *430*, 113.

(6) Tsuzuki, S.; Uchimara, T.; Tanabe, K. *Chem. Phys. Lett.* **1998**, *287*, 202.

(7) Jeziorski, B.; Szalewicz, K. In *Encyclopedia of Computational Chemistry*; Schleyer, P. v. R., Ed.; Wiley: Chichester, U.K., 1998; pp 1379−1388.

(8) This is the usual observation for alkenes: Wlodarczak, G.; Demaison, J.; Heineking, N.; Csaszar, A. G. *J. Mol. Spectrosc.* **1994**, *167*, 239.

(9) Cremer, D. In *Encyclopedia of Computational Chemistry*; Schleyer, P. v. R., Ed.; Wiley: Chichester, U.K., 1998; pp 1706ff.

(10) Hu, C.-H.; Chong, D. P. In *Encyclopedia of Computational Chemistry*; Schleyer, P. v. R., Ed.; Wiley: Chichester, U.K., 1998; p 675.

(11) (a) Siegel, S. *J. Chem. Phys.* **1957**, *27*, 989. (b) Beaudet, R. A.; Wilson, E. B., Jr. *J. Chem. Phys.* **1962**, *37*, 1133. (c) Beaudet, R. A. *J. Chem. Phys.* **1962**, *37*, 2398. (d) Beaudet, R. A. *J. Chem. Phys.* **1964**, *40*, 2705. (e) Lesarri, A. G.; Cosleoo, J.; Li, X.; Wlodarczak, G.; Demaison, J. *J. Mol. Spectrosc.* **1995**, *172*, 520. (f) Durig, J. R.; Guirgis, G. A. *J. Raman Spectrosc.* **1982**, *13*, 160.

(12) Wiberg, K. B.; Rablen, P. *J. Comput. Chem.* **1993**, *14*, 1504.

(13) Hirshfeld, F. L. *Theor. Chim. Acta* **1977**, *44*, 129. Nalewajski, R. F.; Parr, R. G. *Proc. Natl. Acad. Sci.* **2000**, *97*, 8879. Parr, R. G.; Ayers, P. N.; Nalewajski, R. F. *J. Phys. Chem. A* **2005**, *109*, 3957.

(14) Breneman, C. M.; Wiberg, K. B. *J. Comput. Chem.* **1990**, *11*, 361.

(15) (a) Reed, A. E.; Weinstock, R. B.; Weinhold, F. A. *J. Chem. Phys.* **1985**, *83*, 735. (b) Reed, A. E.; Weinhold, F. A.; Curtiss, L. A. *Chem. Rev.* **1988**, *88*, 899.

(16) Bader, R. F. W. *Atoms in Molecules. A Quantum. Theory*; Clarendon Press: Oxford, U.K., 1990..

(17) Reed, A. E.; Weinhold, F. *J. Chem. Phys.* **1986**, *84*, 2428.

(18) When the atomic dipoles are included, the AIM charges do reproduce the calculated dipole moments. Although these charges are well defined and useful, they are not as convenient as the Hirshfeld charges in comparing charges between related molecules because of the sensitivity of the atomic volumes to changes in electronegativity.

(19) Westheimer, F. H.; Kirkwood, J. G. *J. Chem. Phys.* **1938**, *6*, 513. (a) Kirkwood, J. G.; Westheimer, F. H. *J. Chem. Phys.* **1938**, *4*, 506. (b) Cf. Eucken, A. *Angew. Chem.* **1932**, *45*, 203.

(20) Ochterski, J. W.; Petersson, G. A.; Montgomery, J. A., Jr. *J. Chem. Phys.* **1996**, *104*, 2598.

(21) Montgomery, J. A., Jr.; Frisch, M. J.; Ochterski, J. W.; Petersson, G. A. *J. Chem. Phys.* **2000**, *112*, 6532.

(22) Grimme, S.; Műck-Lichtenfeld, C.; Antony, J. *Phys. Chem. Chem. Phys.* **2008**, *10*, 3327.

(23) Frisch, M. J. et. al. Gaussian development version, 2006. The full reference is given in the Supporting Information.

(24) Rablen, P. R. Ph.D. thesis, Yale, 1994.

CT900059E