# Substituent Effects. 3. A Comparison of Ethyl, Vinyl, Isopropyl, and Cyclopropyl Derivatives

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The structures and energies of a series of ethyl, vinyl, isopropyl, and cyclopropyl derivatives were calculated via ab initio MO theory using the 6-31G* basis set. The substituents were H, Li, BeH, $BH_2$, $CH_3$, $NH_2$, OH, F, $SiH_3$, $PH_2$, and Cl. The energies of isodesmic reactions were calculated, and in the exchange of H and X between isopropyl and cyclopropyl the electronegative groups were found to prefer the isopropyl group whereas the electropositive groups preferred the cyclopropyl group. This is in accord with the difference in electronegativity of isopropyl and cyclopropyl. A more complex relationship was found in comparing ethyl and vinyl groups. The bond path angles were calculated and were found to be correlated with the electronegativity of the substituent. The electron populations were calculated via numerical integration of the 6-31G** charge densities within properly defined atomic volumes. The unsubstituted carbons of the ethyl and isopropyl derivatives were only slightly affected by the substituents, a small effect was found with the cyclopropyl derivatives, and the largest effect was found with the vinyl derivatives. Much larger changes in population were found with the substituted carbons. The ethyl and isopropyl carbon charges were linearly related with a slope close to unity. The vinyl and cyclopropyl carbon charges also were linearly related to those for the ethyl derivatives, but here the slope was 0.87 for the vinyl derivatives.

## 1. Introduction

We have presented a detailed analysis of the charge distributions in a variety of substituted methanes.[1] A number of interesting observations were made, such as the relatively large positive charge induced at the methyl carbon of methoxide ion and the finding that the nitrogen bound to carbon in methyldiazonium ion had a negative charge rather than the positive charge suggested by its formal charge. A subsequent study of *n*-butyl and *tert*-butyl derivatives gave information on the transmission of substituent effects along an alkyl chain and the difference in response to substituents between primary and tertiary centers.[2]

We now present a corresponding study of ethyl, vinyl, isopropyl and cyclopropyl derivatives. A comparison of substituent effects in the first two series will give information on the transmission of charge through a C–C double bond vs a single bond. The latter two series will give information on the difference between a saturated chain and a cyclopropane ring in transmitting substituent effects.

There have, of course, been many theoretical studies of these compounds.[3] The 4-31G energies of many of the compounds of interest have been summarized by Greenberg and Stevenson, and their isodesmic group exchange energies have been studied.[4] Comparisons of cyclopropyl and isopropyl derivatives have been reported by Cremer and Kraka[5] and by Clark et al.[6] The structures and energies of vinyl derivatives also have been studied.[7] However, in no case have all of the substituents of interest to us been examined, and it is now recognized that polarization functions are required for the proper description of bonds between atoms having different electronegativities.[8] The analysis of the results of the calculations usually have been presented in the form of orbital interactions, but we have preferred to concentration on electronegativity and hybridization effects and on the resulting changes in charge distributions. Thus, the emphasis in this report will be somewhat different than that of previous work.

## 2. Structures and Energies

For each series, the first-row substituents Li, BeH, $BH_2$, $CH_3$, $NH_2$, OH, and F and the second-row substituents $SiH_3$, $PH_2$, SH, and Cl were studied. The conformations of the ethyl derivatives are well-established,[9] and in many cases the 6-31G* energies are known.[10] In the remaining cases, geometry optimizations were carried out using this basis set. For the later analysis of the wave functions, a better balanced basis set was desired,[11] and so 6-31G** calculations were carried out using the 6-31G* geometries. There is only a slight change in geometry on going from one of these basis sets to the other,[12] and therefore this procedure is satisfactory. The magnitudes of the rotational barriers also provide useful information, and therefore the structures and energies of the more significant rotamers of the compounds with X = $BH_2$, $CH_3$, $NH_2$, OH, $SiH_3$, $PH_2$, and SH were obtained (Table I).

The conformations of the vinyl derivatives were of more interest. The simple substituents, F, Cl, and BeH, can only take on conformation. Vinyl alcohol has been found to prefer the syn conformation,[13] but in order to examine the

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[1] Wiberg, K. B.; Breneman, C. M. *J. Am. Chem. Soc.* **1990**, *112*, 8765.

[2] Wiberg, K. B. *J. Org. Chem.* **1991**, *56*, 544.

[3] (a) Skanke, A.; Boggs, J. E. *J. Mol. Struct.* **1978**, *50*, 173. (b) Durmaz, S., Kollmar, H. *J. Am. Chem. Soc.* **1980**, *102*, 6942. (c) Lien, M. H.; Hopkinson, A. C. *J. Comput. Chem.* **1985**, *6*, 274. (d) Politzer, P.; Jayasuriya, K.; Zilles, B. A. *J. Am. Chem. Soc.* **1985**, *107*, 121.

[4] Greenberg, A.; Stevenson, T. A. *J. Am. Chem. Soc.* **1985**, *107*, 3488.

[5] Cremer, D.; Kraka, E. *J. Am. Chem. Soc.* **1985**, *107*, 3811.

[6] Clark, T.; Spitznagel, G. W.; Klose, R.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1984**, *106*, 4412.

[7] Heinrich, N.; Koch, W.; Frenking, G.; Schwartz, H. *J. Am. Chem. Soc.* **1986**, *108*, 593. Slee, T. S. *J. Am. Chem. Soc.* **1986**, *108*, 606. Dixon, D. A.; Fukunaga, T.; Smart, B. E. *J. Am. Chem. Soc.* **1986**, *108*, 1585. Dobbs, K. D.; Hehre, W. J. *J. Am. Chem. Soc.* **1986**, *108*, 4663.

[8] Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986; p 80ff.

[9] Callomon, J. H.; Hirota, E.; Kuchitsu, K.; Lafferty, W. J.; Maki, A. G.; Pote, C. S. *Landolt-Bornstein*; Springer Verlag: Berlin, 1976; New Series Vol. II/7. Callomon, J. H.; Hirota, E.; Iijima, T.; Kuchitsu, K.; Lafferty, W. *J. Landolt Bornstein*; Springer Verlag: Berlin, 1987; New Series Vol. II/15.

[10] Carnegie-Mellon University Quantum Chemistry Archive.

[11] Reference 8, p 82.

[12] In a series of compounds we have examined, the changes in calculated C–C and C–H bond lengths were generally less than 0.002 Å on going from 6-31G* to 6-31G**.

[13] Rodler, M.; Bauder, A. *J. Am. Chem. Soc.* **1984**, *106*, 4025. Wiberg, K. B.; Breneman, C. M.; LePage, T. J. *J. Am. Chem. Soc.* **1990**, *112*, 61.

0022-3263/92/1957-5092$03.00/0

**Table I. Calculated Energies of Ethyl, Vinyl, Isopropyl, and Cyclopropyl Derivatives**[a]

| | ethyl | | | vinyl | | | isopropyl | | | cyclopropyl | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| X | conf[b] | 6-31G* | 6-31G** | conf | 6-31G* | 6-31G** | conf[c] | 6-31G* | 6-31G** | conf[c] | 6-31G* | 6-31G** |
| H | | −79.228 76 | −79.238 24 | | −78.031 72 | −78.038 84 | | −118.263 65 | −118.276 16 | | −117.058 87 | −117.069 06 |
| Li | | −86.041 55 | −86.049 70 | | −84.861 39 | −84.866 80 | | −125.070 95 | −125.081 89 | | −123.877 94 | −123.886 46 |
| BeH | | −93.843 73 | −93.852 59 | | −92.658 74 | −92.664 72 | | −132.873 74 | −132.885 40 | | −131.680 63 | −131.689 76 |
| $BH_2$ | s | −104.473 45 | −104.483 58 | s | −103.289 66 | −103.296 84 | s | −143.505 49 | −143.518 55 | s | −142.314 53 | −142.324 89 |
| | e | −104.471 79 | −104.481 71 | e | −103.278 16 | −103.285 56 | e | −143.504 58 | −143.517 44 | e | −142.302 88 | −142.313 40 |
| $CH_3$ | st | −118.263 65 | −118.276 16 | syn | −117.071 47 | −117.081 62 | st | −157.298 98 | −157.314 56 | st | −156.095 93 | −156.109 16 |
| | e | −118.258 23 | −118.270 71 | anti | −117.068 18 | −117.078 31 | e | −157.293 00 | −157.308 58 | e | −156.091 35 | −156.104 53 |
| $NH_2$ | 56 | −134.247 73 | −134.262 83 | conj | −133.061 96 | 133.074 90 | 180 | −173.285 68 | −173.303 90 | 180 | −172.082 32 | −172.098 18 |
| | 180 | −134.247 61 | −134.262 79 | unc | −133.054 07 | −133.067 02 | 60 | −173.285 15 | −173.303 43 | 43 | −172.078 08 | −172.094 07 |
| | 0 | −134.244 22 | −134.259 45 | unc[d] | −133.052 03 | −133.064 96 | 119 | −173.281 00 | −173.299 37 | 0 | −172.077 41 | −172.093 37 |
| | 120 | −134.243 24 | −134.258 46 | | | | 0 | −173.280 68 | −173.299 01 | 106 | −172.074 31 | −172.090 36 |
| OH | 180 | −154.075 74 | −154.090 14 | syn | −152.888 89 | −152.901 00 | 60 | −193.115 42 | −193.132 96 | 72 | −191.907 42 | −191.922 57 |
| | 64 | −154.075 55 | −154.089 95 | anti | −152.885 39 | −152.897 66 | 180 | −193.115 06 | −193.132 61 | 180 | −191.903 31 | −191.918 59 |
| | 120 | −154.073 60 | −154.088 11 | ts | −152.881 58 | −252.893 73 | 0 | −193.113 21 | −193.130 90 | 163 | −191.903 29 | −191.918 57 |
| | 0 | −154.072 88 | −154.087 31 | | | | 122 | −193.112 82 | −193.130 41 | 0 | −191.902 88 | −191.918 25 |
| F | | −178.077 22 | −178.085 40 | | −176.881 95 | −176.887 57 | | −217.119 00 | −217.130 27 | | −215.905 70 | −215.914 49 |
| $SiH_3$ | st | −369.303 04 | −369.315 35 | syn | −368.112 51 | −368.122 11 | st | −408.334 94 | −408.350 18 | st | −407.137 55 | −407.150 28 |
| | e | −369.300 46 | −369.312 73 | anti | −368.109 88 | −368.119 49 | e | −408.331 94 | −408.347 16 | e | −407.134 90 | −407.147 62 |
| $PH_2$ | 180 | −420.519 75 | −420.531 88 | unc | −419.327 72 | −419.337 20 | 180 | −459.553 06 | −459.568 16 | 180 | −458.353 69 | −458.366 29 |
| | 58 | −420.519 21 | −420.531 31 | conj | −419.325 87 | −419.335 16 | 59 | −459.552 96 | −459.568 07 | 48 | −458.351 32 | −458.363 96 |
| | 0 | −420.515 93 | −420.528 07 | | | | 0 | −459.549 28 | −459.564 42 | 0 | −458.349 43 | −458.362 02 |
| | 117 | −420.515 79 | −420.527 90 | | | | 120 | −459.548 94 | −459.564 09 | 108 | −458.347 85 | −458.360 53 |
| SH | 63 | −476.736 21 | −476.747 94 | syn | −475.541 91 | −475.551 18 | 62 | −515.771 63 | −515.786 40 | 75 | −514.568 41 | −514.580 66 |
| | 180 | −476.735 72 | −476.747 40 | anti | −475.541 07 | −475.550 39 | 180 | −515.771 60 | −515.786 41 | 180 | −514.563 83 | −514.576 25 |
| | 123 | −476.733 72 | −476.745 48 | ts | −475.539 24 | −475.548 43 | 120 | −515.768 99 | −515.783 84 | 156 | −514.563 73 | −514.576 13 |
| | 0 | −476.733 37 | −476.745 14 | | | | 0 | −515.768 90 | −515.783 75 | 0 | −514.562 39 | −514.574 83 |
| Cl | | −538.131 52 | −538.139 34 | | −536.933 69 | −536.939 08 | | −577.169 36 | −577.180 31 | | −575.959 51 | −575.968 00 |

[a] The abbreviations are st = staggered, e = eclipsed. The conformers are listed in order of increasing energy. [b] Me–C–X–H torsional angles for X–OH or SH, Me–C–X–lp torsional angles for X = $NH_2$ or $PH_2$. [c] H–C–X–H torsional angles for X = OH or SH, H–C–X–lp torsional angles for X = $NH_2$ or $PH_2$. [d] Higher energy rotational transition state.

interaction between the hydroxyl hydrogen and the double bond, the anti conformer also was studied. The two conformers of vinyl thiol were studied for the same reason. The preferred conformer of propene is known to have a methyl hydrogen eclipsed with the double bond,[14] and the same was found with vinylsilane. The preferred conformer of vinylamine has the nitrogen lone-pair conjugated with the double bond. However, unlike amides which have a nearly planar amide group, in vinylamine the amino group was pyramidalized by 43.8°.[15] In order to see the effect of the conjugation, the two 90° rotated conformers also were examined. The one with the lone pair anti to the vinyl hydrogen had the lower energy and was pyramidalized by 54.0°. The conformer of vinyl phosphine that has the lone pair conjugated with the double bond was found to have the higher energy (77° pyramidalized vs 77.5° for the other form), and both conformers were studied. In order to complete the series, a less stable rotamer of vinylborane also was examined.

The conformations of the isopropyl derivatives are again fairyl well-established, and calculations for many of the compounds of interest have been reported at the 4-31G level.[6] The geometries for the series of compounds have now been obtained with the 6-31G* basis set. The rotational barriers were examined for the group of substituents indicated for the ethyl derivatives (Table I). With many of the cyclopropyl derivatives, there also have been 4-31G calculations.[6] The 6-31G* basis set was used in obtaining the structures and energies of the series of cyclopropyl derivatives. There was again the question of conjugative interactions between the cyclopropane ring and some substituents such as $BH_2$, $NH_2$ and $PH_2$.[16] The rotational barriers for these substituents, as well as the others noted above, were examined (Table I).

## 3. Substituent Interactions Examined via Isodesmic Reactions

The calculated energies of all of the compounds are given in Table I. The question of the interaction of a substituent with the double bond of ethylene or with the C–C bonds of cyclopropane has received considerable attention. One way in which to obtain information on this subject is to examine the energies of homoisodesmic reactions such as[4,6]

$$\mathrm{MeX + EtH \rightarrow MeH + EtX}$$

$$\mathrm{EtX + i\text{-}PrH \rightarrow EtH + i\text{-}PrX}$$

$$\mathrm{i\text{-}PrX + t\text{-}BuH - i\text{-}PrH + t\text{-}BuX}$$

$$\mathrm{EtX + VynH \rightarrow EtH + VynX}$$

$$\mathrm{EtX + CypH \rightarrow EtH + CypX}$$

$$\mathrm{i\text{-}PrX + CypH \rightarrow i\text{-}PrH + CypX}$$

$$\mathrm{VynX + CypH \rightarrow VynH + CypX}$$

The use of such reactions is known to lead to near-cancellation of electron correlation energies and to generally give energy changes close to those measured. In addition, the zero point energies and heat capacities should to a good approximation cancel between reactants and products. Energies of some of these reactions based on 4-31G energies have been reported,[4,6] but it is now recognized that polarization functions are needed in order to properly represent molecules having bonds between atoms with different electronegativities. The 6-31G* and 6-31G** basis sets give essentially the same energy changes, and the latter values in kcal/mol are given in Table II.

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[14] Lide, D. R.; Christensen, D. *J. Chem. Phys.* **1961**, *35*, 1374. Hirota, E.; Marino, Y. *Ibid* **1966**, *45*, 2326.

[15] The pyramidalization angle was taken as that between the C–N vector and a vector from the nitrogen to the midpoint of the two hydrogens.

[16] Rall, M.; Harmony, M. D.; Cassada, D. A.; Staley, S. W. *J. Am. Chem. Soc.* **1986**, *108*, 6184.

**Table II. Energies of Isodesmic Reactions, kcal/mol, 6-31G****

| X | methyl<br>ethyl | ethyl<br>isopropyl | isopropyl<br>*tert*-butyl | ethyl<br>vinyl | ethyl<br>cyclopropyl | isopropyl<br>cyclopropyl | vinyl<br>cyclopropyl |
|---|---|---|---|---|---|---|---|
| Li | 4.91 | 3.60 | 2.33 | -10.35 | -3.73 | -7.32 | 6.63 |
| BeH | 3.82 | 3.21 | | -7.24 | -3.98 | -7.19 | 3.25 |
| $BH_2$ | 1.07 | 1.85 | | -7.94 | -6.58 | -8.43 | 1.36 |
| $CH_3$ | -0.87 | -0.30 | 0.31 | -3.05 | -1.37 | -1.07 | 1.68 |
| $NH_2$ | -2.79 | -1.98 | | -7.20 | -2.84 | -0.87 | 4.35 |
| OH | -4.35 | -3.06 | -1.69 | -6.43 | -1.00 | 2.06 | 5.43 |
| F | -5.73 | -4.36 | -2.96 | -0.99 | 1.09 | 5.45 | 2.07 |
| $SiH_3$ | 1.92 | 1.94 | | -3.87 | -2.58 | -4.52 | 1.29 |
| $PH_2$ | 0.06 | 1.03 | | -2.96 | -2.25 | -3.28 | 0.71 |
| SH | -1.56 | -0.34 | | -1.66 | -1.19 | -0.85 | 0.46 |
| Cl | -3.07 | -1.91 | | 0.54 | 1.36 | 3.27 | 0.82 |

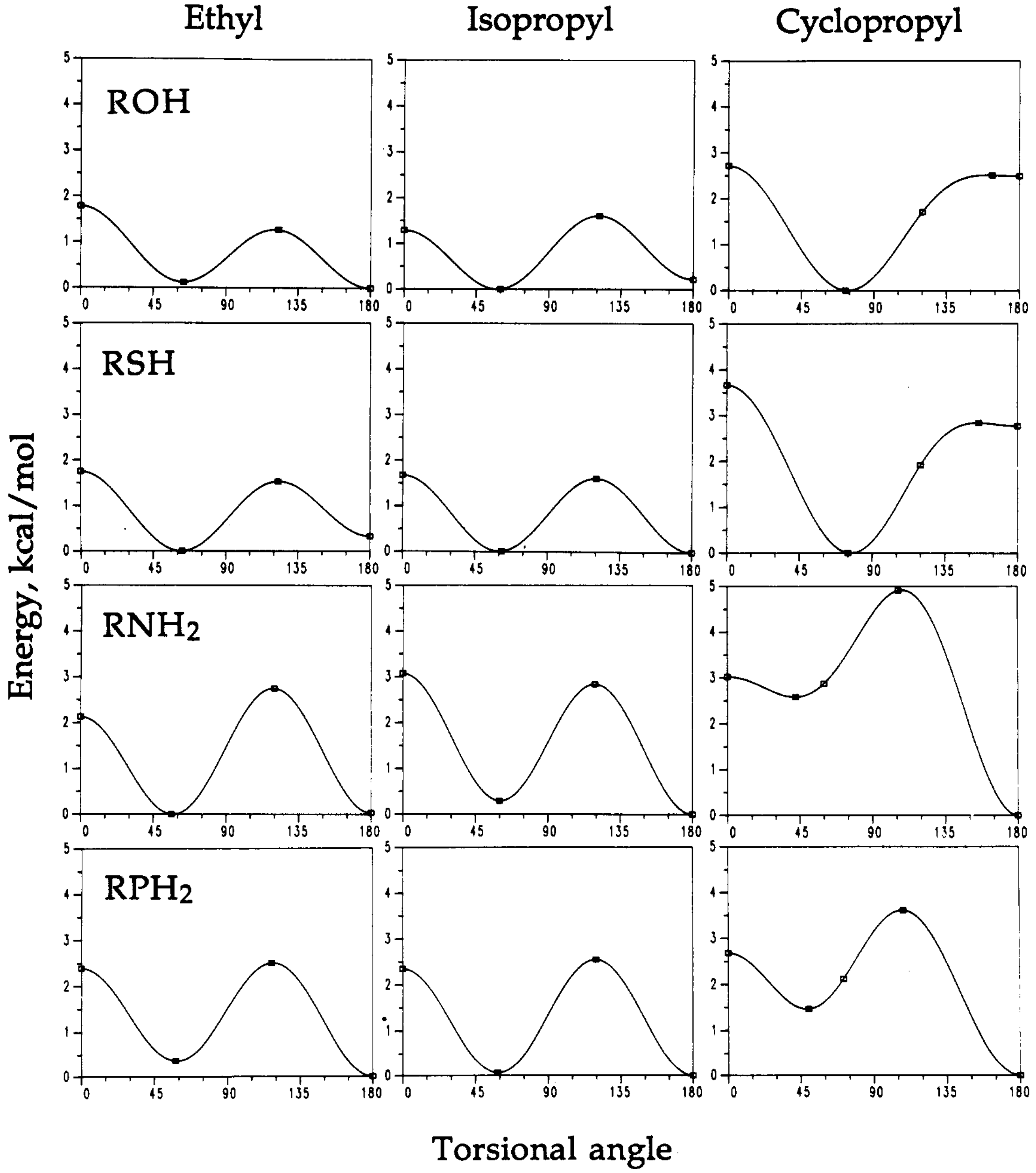

**Figure 1.** Rotational profiles for alcohols, thiols, amines, and phosphines. The torsional angles are defined as follows: for the ethyl compounds they are Me–C–X–H where X = O or S, and Me–C–X–lp where X = N or P and lp is the lone pair (assumed to be opposite to the average of the $NH_2$ or $PH_2$ hydrogens); and for isopropyl and cyclopropyl they are H–C–X–H where X = O or S and H–C–X–lp where X = N or P.

In the series methyl, ethyl, isopropyl, and *tert*-butyl, lithium prefers the less substituted carbon (e.g., methyl) and fluorine prefers the more substituted carbon (e.g., *tert*-butyl). A similar pattern is found for the second-row substituents. This has previously been observed in a comparison of methyl and isopropyl derivatives[6] and is related to the stabilization of carbocations by secondary centers as compared to primary and the corresponding destabilization of carbanions. As has been noted previously,[6] the isodesmic reaction energies are related to the

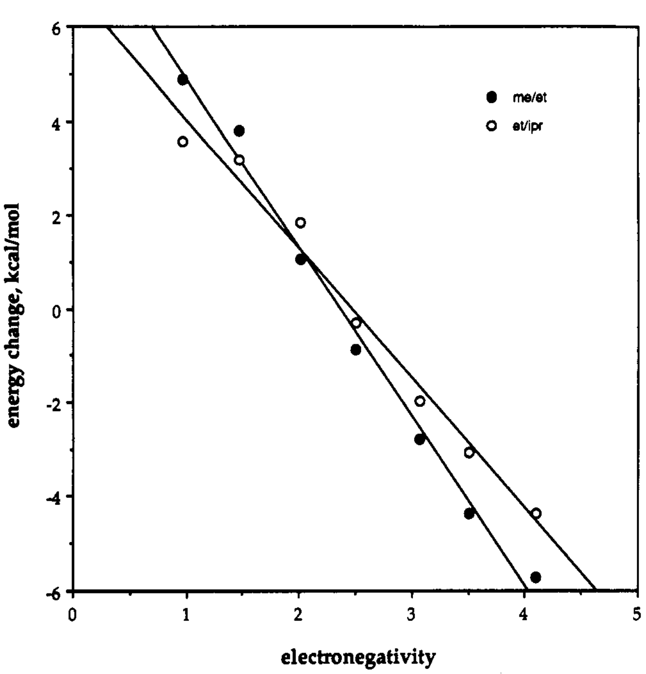

**Figure 2.** Relationship between isodesmic reaction energies and electronegativity. The solid circles give the energy changes for methyl derivatives reacting with ethane, and the open circles give the data for ethyl derivatives reacting with propane.

**Table III. Calculated Energy Changes between Rotamers, 6-31G****

| X | ethyl | vinyl | isopropyl | cyclopropyl |
|---|---|---|---|---|
| $BH_2$ | 1.2 | 7.1 | 0.7 | 7.2 |
| $CH_3$ | 3.4 | 2.1 | 3.8 | 2.9 |
| $NH_2$ | 2.7 | 4.9 | 3.1 | 4.9 |
| OH | 1.8 | 4.6 | 1.6 | 2.7 |
| $SiH_3$ | 1.6 | 1.6 | 1.9 | 1.7 |
| $PH_2$ | 2.5 | 1.3 | 2.6 | 3.6 |
| SH | 1.8 | 1.7 | 1.7 | 3.7 |

electronegativity[17] of the substituents (Figure 2). The methyl/ethyl comparison gives the better fit and a significantly larger slope than the ethyl/isopropyl comparison.

A comparison of isopropyl and cyclopropyl eliminates the difference in the number of carbons attached to the substituted center. Here, the groups that are electropositive with respect to carbon give an energetic preference for being attached to the cyclopropane ring, whereas the more electronegative groups prefer to be attached to the isopropyl group. This appears to be a simple hybridization effect.[6] The bond orbital used by the cyclopropane ring has about 33% s character whereas that used by the isopropyl group has about 25% s character. The electronegativity of a carbon increases with increasing s character, and thus the cyclopropane ring prefers the more electropositive substituents.[18] The one deviation from a simple correlation was found with X = $BH_2$, and here a much larger interaction with the substituent was found with the cyclopropyl case as compared to isopropyl (Table III). This is not surprising since cyclopropyl is known to be very effective in stabilizing carbocations, and the same type of stabilization should be found with the $BH_2$ group.

The ethyl–vinyl case does not show a simple pattern. Here, the reactions are generally exothermic in the direction written above indicating that the substituents prefer the vinyl group. The one exception is X = Cl where there is a weak preference for the ethyl group. Unfortunately, there are relatively few experimental data with which these calculated energy changes may be compared. With R = $CH_3$, the methyl group is known to prefer the double bond by 2.8 ± 0.3 kcal/mol,[19] in good agreement with the calculated value. When R = Cl, the experimental data indicate a preference for the ethyl group of 2.0 ± 0.8 kcal/mol.[19]. The direction of the preference is calculated correctly, although the magnitude of the value appears too small. However, in view of the difficulties in determining heats of combustion of halogen-containing compounds, the errors in the experimental values may well be somewhat greater than the reported standard errors. Since both the experimental data and the calculations indicate that chlorine prefers to be bonded to an ethyl group rather than vinyl, the C–Cl bond shortening in vinyl chloride as compared to ethyl chloride might better be attributed to the difference in hybridization rather than a stabilizing conjugative interaction in vinyl chloride. The substituents $BH_2$, $NH_2$, and OH clearly have significantly different interactions with vinyl than with ethyl as can be seen in the isodesmic reaction in Table II and the energy difference between rotamers in Table III.

The hybridization in the CH bonds of ethene and cyclopropane are very similar as judged by the $^{13}C$–H NMR coupling constants, the H–C–H bond angles, the CH bond lengths, and the CH stretching force constants.[20] It would then be possible to minimize the hybridization effect by comparing vinyl derivatives with cyclopropyl derivatives. The energy changes found in this comparison would in large measure reflect interactions other than that due to hybridization. Table II shows that all groups prefer vinyl to cyclopropyl. However, most of the energy differences are rather small. It would appear appropriate to concentrate on the three large differences which were found with X = Li, $NH_2$, and OH, and they will be further considered below. It is worth noting that the $NH_2$ and OH groups are ones for which a relatively large rotational barrier was calculated for the vinyl derivatives.

## 4. Rotational Barriers

The rotational barriers are given in Table III. With the number of compounds studied, it was not possible to examine the full rotational profiles, and in most cases only the minima and maxima were obtained. A cos $(n\theta)$ potential function was assumed and led to the rotational profiles shown in Figure 1 for the substituents $NH_2$, OH, $PH_2$, and SH.

The rotational barriers for the ethyl derivatives were similar to the well-studied methyl compounds. Even the potentially strongly interacting $BH_2$ group gave a small rotational barrier. The isopropyl derivatives are quite similar as might be expected. The remarkable similarity of the rotational profiles for the methyl, ethyl, and isopropyl derivatives again shows that the rotational barrier does not arise from a steric repulsion of the groups attached to the C–C bond, but rather is directly associated with the latter. This is seen most clearly with ethane where the only significant structural change that occurs on rotation about the C–C bond is the lengthening of this bond.[21]

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(17) Huheey, J. E. *Inorganic Chemistry*, 2nd ed.; Harper & Row: New York, 1978; p 148. The Allred–Rochow scale was used.

(18) A correlation between the position of the bond critical points and the difference in electronegativity of the atoms forming the bond has been demonstrated: Boyd, R. J.; Boyd, S. L. *J. Am. Chem. Soc.* **1992**, *114*, 1652. Making use of this correlation, they have shown that cyclopropyl is more electronegative than isopropyl.

(19) Pedley, J. B.; Naylor, R. D.; Kirby, S. P. *Thermochemical Data of Organic Compounds*, 2nd ed.; Chapman and Hall: London, 1986.

(20) Wiberg, K. B. In *The Chemistry of the Cyclopropyl Group*; Rappoport, Z., Ed.; Wiley: New York, 1987; p 17.

(21) Bader, R. F. W.; Cheeseman, J. R.; Laidig, K. E.; Wiberg, K. B.; Breneman, C. *J. Am. Chem. Soc.* **1990**, *112*, 6530.

The rotational barriers for the vinyl derivatives are quite different, with $BH_2$, $NH_2$, and OH all giving large barriers. The largest was found with $BH_2$ where one might expect the $\pi$-electrons of the double bond to be effectively delocalized into the empty p-orbital at boron. The barriers for the $NH_2$- and OH-substituted compounds presumably arise from a similar but weaker interaction between the lone pair electrons and the double bond. Here, of course, the substituent acts as a $\pi$-electron donor rather than acceptor.

In view of the very effective stabilization of a carbocation center by a cyclopropane ring, it is not surprising to find that the rotational barrier for cyclopropylborane is the same as for vinylborane. Other substituents that give relatively large calculated rotational barriers were $NH_2$, $PH_2$, and SH. The unique feature of the cyclopropyl derivative rotational barriers is the relatively constant high energy for OH and SH rotamers with H-O-C-H torsional angles from 120-180° with respect to the cyclopropane ring hydrogen and for $NH_2$ and $PH_2$ rotamers with lp-N-C-H torsional angles between 0 and 45°. These are the rotamers for which a hydrogen of the substituent lies over the cyclopropane ring. The origin of the unusual rotational profile for the cyclopropane derivatives will be considered in more detail at a later time.

## 5. Charge Density Analysis

In order to gain further information that might prove useful in analyzing the energy changes, and in studying the details of the interaction between the substituents and the four groups that were studied, we have analyzed the charge density distribution making use of Bader's theory of atoms in molecules.[22] This involves first locating the bond path which joins a pair of bonded atoms (the path of maximum charge density) and the bond critical point along the path. The latter is the point of minimum charge density along the path, but still a maximum in charge density in all other directions. A surface separating two bonded atoms is then formed by starting at the bond critical point and developing rays corresponding to a maximum rate of decrease in $\rho$ with distance. The surfaces serve to separate the molecule into atomic domains, within which numerical integration of the charge density leads to the electron population.

**a. Bond Properties.** The following properties were obtained for each of the bonds in each of the molecules: the location of the bond critical point, the value of $\rho$ at the critical point ($\rho_c$), the Laplacian of $\rho$ (the sum of the three curvatures in $\rho$ with respect to the coordinates) at the critical point, and the ellipticity of $\rho$ at the critical point ($\epsilon$). In addition, the bond paths (the paths of maximum charge density between a pair of bonded atoms) were traced, and the angles between the bond paths were compared with the conventional bond angles. The bond path angles are defined as the angle between the tangents of the bond paths at a given nucleus. If the bond paths are bent, there will be a difference between the bond path and conventional angles. The full data are available as supplementary material, and only some special features will be summarized below.

We have examined the relationship between bond angles and hybridization[1] and have noted that whereas the conventional angles often do not follow the expectations for bonds between atoms having different electronegativities, the angles between the bond paths do show the expected relationship. This also is found with the present group of compounds. The bond path angles at the substituted carbon are given in Table IV.

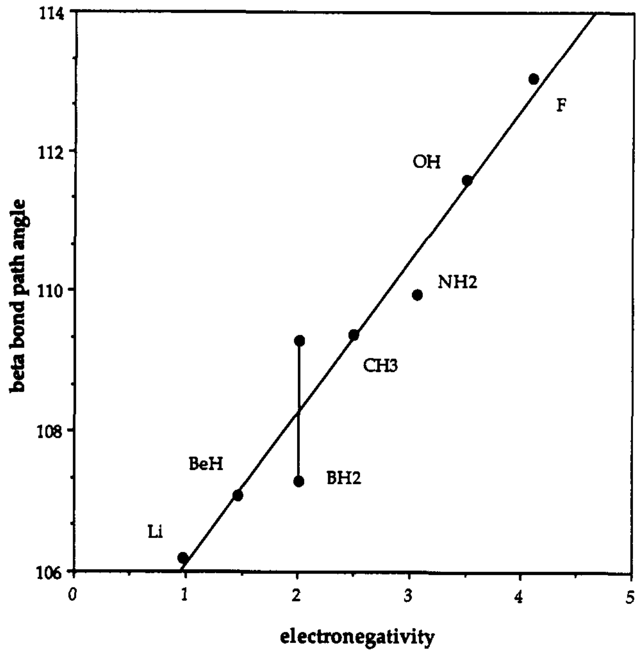

**Figure 3.** $\beta$ bond path angles for ethyl derivatives as a function of electronegativity. In the case of ethyl borane there was a large difference in bond path angle between rotamers, and both values are given.

An electronegative substituent will prefer to be bonded to an orbital having relative high p-character,[23] and as a result, the other bonds to that center will have relatively high s-character. Thus, the bond angle to the substituent should decrease, and the bond angles between the other groups attached to the center should increase. The reverse should be found with an electropositive substituent.

An examination of the bond path angles for ethyl derivatives (Table IV) shows that the expected trend is approximately followed. With the second-row elements which generally give more simple interactions, the $\beta$-angles (opposite to the substituent) increase steadily with increasing electronegativity. The same trend is found with the first row substituents. The general trends also are found with the $\alpha$-angles (adjacent to the substituent), but the changes are in the opposite direction from the $\beta$-angles. A plot of the $\beta$ bond path angles as a function of the atomic number of the substituent (Figure 3) gives a reasonable linear relationship for all the substituents except $BH_2$. This also is the case in which there is a large difference in angle between the two conformers that were studied. Thus, the small barriers found with the substituents should not be taken to indicate a lack of interaction. With $BH_2$, it appears that the energy associated with the interaction of its empty orbital with the ethyl group does not have a strong angular dependence, as is found with classical carbocations.

The isopropyl compounds follow essentially the same trends as the ethyl derivatives. It might be noted that the conventional bond angles are quite different than the bond path angles, and are less clearly related to the electronegativity of the substituents.

In the case of the vinyl derivatives where interactions between the vinyl group and the substituents often are large (Table III), data are given for different rotamers. Here, the range of $\beta$-bond path angles, 109° for Li vs 134°

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[22] Bader, R. F. W. *Acc. Chem. Res.* **1985**, *18*, 9. Bader, R. F. W. *Atoms in Molecules. A Quantum Theory*; Clarendon Press: Oxford, 1990.

[23] Bent, H. A. *Chem. Rev.* **1961**, *61*, 275.

for F, is remarkably large when compared with the corresponding angles for the ethyl, isopropyl, or cyclopropyl derivatives. In general, vinyl derivatives behave in a significantly different fashion than the other derivatives.

There has been much interest in the interaction between the cyclopropane ring and substituents both experimentally[16,24] and theoretically.[3,5,6] A simple examination of the geometry of these compounds is flawed because the effects of bond angle bending is not taken into account, and with cyclopropane the bond bending is quite severe. We have examined the ring bond angles for cyclopropane giving the results shown in Table V. Here, the conventional and bond path angles are compared, and the calculated C–C bond lengths are given. It would, of course, be desirable to obtain the bond path angles at a theoretical level that includes correction for electron correlation. This was not practical with the large number of compounds in this report, but it may be noted that with cyclopropane itself, the MP2/6-31G* bond path angles are only slightly smaller than the HF/6-31G* angles,[25] suggesting that the angles in Table V will be satisfactory for comparisons.

An initial examination of the second-row substituents might be helpful since conjugative interactions will be reduced with these compounds. Here, a simple pattern emerges. Increasing electronegativity leads to an increase in the C–C–C bond path angle at the substituted carbon. It might be noted that this trend is not as easily seen in the conventional angles. A corresponding increase in the C2–C3 bond length is seen. The change in the bond path angles at the other carbon is much smaller, but there is a steady decrease in the C1–C2 bond length with increasing electronegativity. All of these changes are in good accord with the simple idea that electronegative substituents prefer to be bonded to orbitals having relatively high p-character.[23] An increase in p-character for the external bond would lead to increased s-character in the attached C–C bond, an increase in the C–C–C bond angle, and a decrease in the C–C bond length.[16]

The same pattern is found with the substituents $CH_3$ through F, and the values for X = H are about the same as for X = $CH_3$ in accord with the observed similarity in electronegativity.[1] A somewhat mixed pattern is seen with the substituents Li through $BH_2$ indicating that factors other than electronegativity are important for determining the changes in geometry for this group of compounds.

**b. Atomic Properties.** The electron populations and kinetic energies were obtained for each of the atoms in the compounds in this study. The full data are available as supplementary material. Some of the special features of the calculated charge distributions will be summarized below.

The atomic charges derived by subtracting the electron populations from the atomic number for the carbons of the four groups of compounds are shown in Table VI. The first part of Table IV (a) gives the charges for the carbons not attached to the substituent, and the second part (b) gives the charges for the carbons directly attached to the substituents. With the vinyl group, the first number gives the charge for the lower energy rotamer, whereas the second (in parentheses) gives the population for the higher energy rotamer.

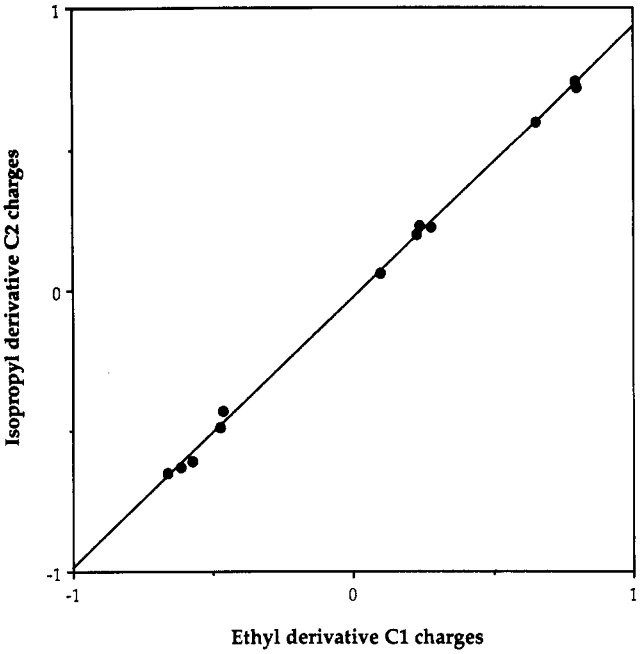

**Figure 4.** Correlation between isopropyl and ethyl charges at the substituted carbons.

The unsubstituted carbons of the ethyl and isopropyl compounds have a similar pattern: essentially no change with substituents. The $\beta$ carbons of the cyclopropyl derivatives show a slightly larger variation with substitution. The decrease in charge as compared to ethyl and isopropyl is a reflection of the difference in hybridization. However, by far the largest changes are found with the vinyl compounds, suggesting the importance of the $\pi$-electrons in transmitting electrical effects.

The difference in electron density at the terminal methylene carbon on rotation of vinylamine and vinyl alcohol are interesting. In both cases, electron density is removed from this carbon in the "conjugated" forms with respect to the rotated ("unconjugated") forms. This is the opposite of that expected from the traditional $\pi$-electron interaction model. It is not possible to separate $\sigma$ and $\pi$ components with the equilibrium geometry of the "conjugated" form of vinylamine because the nitrogen is nonplanar. In an earlier study in which the amino group was forced to be planar, some $\pi$–donation from the lone pair to the vinyl group was found, but the $\sigma$-inductive effect of the $sp^2$ hybridized nitrogen was the dominant factor in determining the total charge distribution.[26] On rotation, the amino nitrogen changes its hybridization in order to place the lone pair in an orbital with high s-character, resulting in a decrease in the $\sigma$-electron withdrawing character of the nitrogen.

The largest changes are, of course, found with the carbons directly attached to the substituents. But, even here, a relatively simple picture emerges. Figure 4 shows a correlation of the isopropyl and ethyl charges, and not surprisingly, there is a good correlation with an essentially unit slope (0.96, $r^2$ = 0.998). Similarly, there is a good correlation between the cyclopropyl and vinyl charges (slope = 1.15, $r^2$ = 0.989, Figure 5). Of more interest, the vinyl and ethyl charges also were well correlated (slope = 0.87, $r^2$ = 0.985, Figure 6), as were the cyclopropyl and ethyl charges (slope = 1.01, $r^2$ = 0.996, Figure 7). Thus, except for the differences in sensitivity toward substituents

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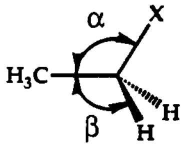
[24] (a) Harmony, M. D.; Nandi, R. N.; Tietz, J. V.; Choe, J.-I.; Getty, S. J.; Staley, S. W. *J. Am. Chem. Soc.* **1983**, *105*, 3947. (b) Taylor, W. H.; Harmony, M. D.; Cassada, D. A.; Staley, S. S. *J. Chem. Phys.* **1984**, *81*, 5379. (c) Durig, J. R.; Nease, A. B.; Berry, R. J.; Sullivan, J. F.; Li, Y. S.; Wurrey, C. J. *J. Chem. Phys.* **1986**, *84*, 3663. (d) Schwendeman, R. H.; Jacobs, G. D.; Krigas, T. M. *J. Chem. Phys.* **1964**, *40*, 1022.

[25] Wiberg, K. B.; Artis, D. R.; Bonneville, G. *J. Am. Chem. Soc.* **1991**, *113*, 7969.

[26] Wiberg, K. B.; Rosenberg, R. E.; Rablen, P. R. *J. Am. Chem. Soc.* **1991**, *113*, 2890.

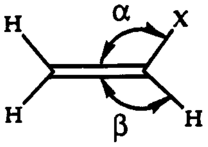
**Table IV. Bond Path Angles**

a. ethyl derivatives



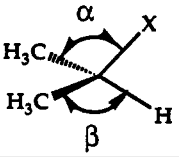
| | α | | | β | | |
|---|---|---|---|---|---|---|
| substitnt | conv | bond path | Δ | conv | bond path | Δ |
| H | 111.21 | 110.26 | −0.95 | 111.21 | 110.26 | −0.95 |
| Li | 118.00 | 115.18 | −2.82 | 108.28 | 106.18 | −2.10 |
| BeH | 116.16 | 114.49 | −1.67 | 108.91 | 107.08 | −1.83 |
| $BH_2$ | 117.07 | 114.90 | −2.17 | 110.24 | 109.30 | −0.94 |
| $BH_2$ (ts) | 108.64 | 109.14 | 0.50 | 108.57 | 107.28 | −1.29 |
| $CH_3$ | 112.78 | 111.07 | −1.71 | 109.39 | 109.38 | −0.01 |
| $CH_3$ (ts) | 113.25 | 111.26 | −1.99 | 109.82 | 109.59 | −0.23 |
| $NH_2$ | 115.51 | 111.11 | −4.40 | 109.59 | 109.94 | 0.35 |
| $NH_2$ (ts) | 117.06 | 114.90 | −2.16 | 110.24 | 109.30 | −0.94 |
| OH | 108.02 | 108.05 | 0.03 | 110.07 | 111.59 | 1.52 |
| OH (ts) | 112.92 | 107.95 | −4.97 | 109.89 | 111.23 | −1.34 |
| F | 109.48 | 106.79 | −2.69 | 111.57 | 113.06 | 1.49 |
| $SiH_3$ | 114.12 | 111.84 | −2.28 | 109.74 | 109.40 | −0.34 |
| $SiH_3$ (ts) | 114.60 | 112.04 | −2.56 | 109.45 | 109.24 | −0.20 |
| $PH_2$ | 116.64 | 112.09 | −4.55 | 110.19 | 110.97 | 0.78 |
| $PH_2$ (ts) | 112.42 | 110.12 | −2.30 | 109.87 | 110.59 | 0.72 |
| SH | 109.65 | 107.14 | −2.51 | 110.33 | 111.82 | 1.49 |
| SH (ts) | 113.77 | 108.84 | −4.93 | 110.21 | 111.86 | 1.65 |
| Cl | 111.49 | 107.12 | −4.37 | 111.80 | 113.82 | 2.02 |

b. vinyl derivatives



| | α | | | β | | |
|---|---|---|---|---|---|---|
| substitnt | conv | bond path | Δ | conv | bond path | Δ |
| H | 121.74 | 122.82 | −1.08 | 121.74 | 122.82 | −1.08 |
| Li | 110.01 | 126.38 | 7.37 | 112.39 | 108.80 | −3.59 |
| BeH | 121.92 | 125.92 | 4.00 | 115.45 | 112.83 | −2.62 |
| $BH_2$ (conj) | 121.14 | 124.03 | −2.89 | 117.86 | 116.39 | −1.47 |
| $BH_2$ (unconj) | 127.01 | 127.94 | 0.93 | 117.42 | 117.12 | −0.30 |
| $CH_3$ | 125.20 | 125.09 | −0.11 | 115.87 | 113.32 | −2.55 |
| $CH_3$ | 124.83 | 124.68 | −0.15 | 116.54 | 113.69 | −2.85 |
| $NH_2$ (conj) | 126.75 | 124.70 | −2.05 | 119.96 | 125.23 | 5.27 |
| $NH_2$ (unconj) | 121.95 | 123.12 | 1.17 | 119.85 | 124.54 | 4.69 |
| OH (syn) | 126.95 | 122.57 | −4.38 | 122.37 | 129.18 | 6.81 |
| OH (anti) | 122.70 | 122.69 | −0.01 | 121.72 | 128.88 | 7.16 |
| OH (unconj) | 123.64 | 121.68 | −1.95 | 122.11 | 128.57 | 6.47 |
| F | 122.33 | 120.06 | −2.27 | 125.77 | 133.93 | 8.16 |
| $SiH_3$ | 123.60 | 125.19 | 1.59 | 117.77 | 118.25 | 0.48 |
| $PH_2$ (unconj) | 121.40 | 122.55 | 1.15 | 119.37 | 122.30 | 2.93 |
| $PH_2$ (conj) | 126.41 | 125.46 | −0.95 | 118.96 | 122.21 | 3.25 |
| SH (syn) | 127.78 | 124.71 | −3.07 | 120.74 | 126.89 | 6.15 |
| SH (anti) | 123.58 | 122.58 | −1.00 | 121.02 | 127.27 | 6.25 |
| SH (unconj) | 124.66 | 122.60 | −2.06 | 120.88 | 126.82 | 5.91 |
| Cl | 123.31 | 120.95 | −2.36 | 123.89 | 132.06 | 8.17 |

c. isopropyl derivatives

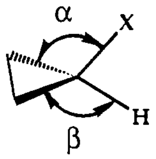


| | α | | | β | | |
|---|---|---|---|---|---|---|
| substitnt | conv | bond path | Δ | conv | bond path | Δ |
| H | 109.39 | 109.38 | −0.01 | 109.39 | 109.38 | −0.01 |
| Li | 114.15 | | | 106.46 | 104.56 | −1.90 |
| BeH | 112.94 | 113.16 | 0.22 | 106.98 | 105.63 | −1.35 |
| $BH_2$ | 114.38 | 113.69 | −0.69 | 107.19 | 106.41 | −0.78 |
| $BH_2$ (ts) | 110.08 | 110.71 | 0.63 | 107.92 | 107.93 | 0.01 |
| $CH_3$ | 111.04 | 110.20 | −0.84 | 107.85 | 108.73 | 0.88 |

**Table IV** (Continued)

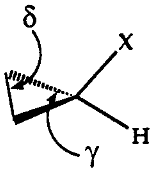
| | α | | | β | | |
|---|---|---|---|---|---|---|
| substitnt | conv | bond path | Δ | conv | bond path | Δ |
| $CH_3$ (ts) | 111.23 | 110.19 | −1.03 | 107.52 | 108.69 | 1.16 |
| $NH_2$ | 108.87 | 108.56 | −0.31 | 107.93 | 109.30 | 1.37 |
| $NH_2$ (ts) | 111.22 | 108.70 | −1.69 | 107.52 | 109.33 | 1.81 |
| OH | 110.92 | 108.16 | −2.76 | 108.80 | 111.29 | 2.49 |
| OH (ts) | 108.70 | 108.06 | −0.64 | 108.75 | 110.94 | −2.20 |
| F | 107.98 | 105.74 | −2.24 | 110.08 | 112.57 | 2.49 |
| $SiH_3$ | 111.73 | 110.80 | −0.93 | 107.86 | 108.13 | 0.27 |
| $SiH_3$ (ts) | 112.18 | 110.97 | −1.21 | 107.56 | 108.11 | 0.55 |
| $PH_2$ | 109.92 | 108.63 | −1.29 | 108.52 | 110.06 | 1.54 |
| $PH_2$ (ts) | 112.40 | 109.77 | −2.63 | 107.62 | 109.28 | −0.45 |
| SH | 112.03 | 108.61 | −3.42 | 108.74 | 110.97 | 2.23 |
| SH (ts) | 110.35 | 107.78 | −2.57 | 108.95 | 111.38 | 2.43 |
| Cl | 109.34 | 105.74 | −3.60 | 110.10 | 113.04 | 2.94 |

d. cyclopropyl derivatives



| | α | | | β | | |
|---|---|---|---|---|---|---|
| substitnt | conv | bond path | Δ | conv | bond path | Δ |
| H | 118.14 | 113.81 | −3.33 | 118.14 | 113.81 | −3.33 |
| Li | 124.69 | | | 110.01 | 103.93 | −6.08 |
| BeH | 121.63 | 118.48 | −3.15 | 112.44 | 106.95 | −5.49 |
| $BH_2$ | 118.62 | 115.97 | −2.65 | 114.28 | 110.05 | −4.23 |
| $BH_2$ (ts) | 123.66 | 118.04 | −5.61 | 114.51 | 109.69 | −4.83 |
| $CH_3$ | 114.18 | 116.64 | 2.46 | 115.54 | 112.59 | −2.95 |
| $CH_3$ (ts) | 121.02 | 114.94 | −6.09 | 114.94 | 112.38 | −2.57 |
| $NH_2$ | 117.05 | 112.71 | −4.34 | 116.15 | 113.89 | −2.26 |
| $NH_2$ (ts) | 120.66 | 115.25 | −5.41 | 116.11 | 114.44 | −1.67 |
| OH | 122.03 | 112.78 | −9.25 | 117.74 | 116.82 | −0.92 |
| OH (ts) | 117.52 | 112.29 | −5.23 | 117.90 | 116.75 | −1.15 |
| F | 117.28 | 109.79 | −7.49 | 120.69 | 119.54 | −1.15 |
| $SiH_3$ | 121.08 | 115.97 | −5.11 | 114.48 | 110.95 | −3.53 |
| $SiH_3$ (ts) | 114.18 | 118.22 | 4.04 | 114.33 | 111.05 | −3.28 |
| $PH_2$ | 118.91 | 113.48 | −5.43 | 115.55 | 113.57 | −4.50 |
| $PH_2$ (ts) | 121.72 | 115.00 | −6.72 | 115.44 | 113.45 | −1.99 |
| SH | 123.22 | 113.93 | −9.29 | 116.95 | 115.93 | −1.02 |
| SH (ts) | 120.11 | 112.64 | −7.47 | 117.17 | 116.32 | 0.85 |
| Cl | 119.52 | 110.77 | −8.75 | 119.22 | 118.99 | −0.23 |

**Table V. Ring Angles and Bond Lengths for Cyclopropyl Derivatives**



| | γ | | | δ | | | | |
|---|---|---|---|---|---|---|---|---|
| substitnt | conv | bond path | Δ | conv | bond path | Δ | $C_1C_2$ | $C_2C_3$ |
| H | 60.00 | 78.88 | 18.88 | 60.00 | 78.88 | 18.88 | 1.4974 | 1.4974 |
| Li | 58.70 | 72.30 | 13.60 | 60.65 | 79.15 | 18.50 | 1.5211 | 1.4912 |
| BeH | 58.36 | 72.98 | 14.62 | 60.82 | 77.74 | 16.92 | 1.5218 | 1.4841 |
| $BH_2$ | 57.70 | 71.14 | 13.44 | 61.15 | 76.34 | 15.19 | 1.5266 | 1.4733 |
| $BH_2$ (ts) | 59.85 | 78.90 | 19.05 | 60.08 | 78.75 | 18.67 | 1.5027 | 1.4993 |
| $CH_3$ | 60.15 | 80.07 | 19.92 | 59.93 | 79.26 | 19.33 | 1.4973 | 1.5006 |
| $CH_3$ (ts) | 59.90 | 79.95 | 20.05 | 60.05 | 79.53 | 19.48 | 1.4994 | 1.4971 |
| $NH_2$ | 60.25 | 82.13 | 21.88 | 59.87 | 78.82 | 18.95 | 1.4942 | 1.4999 |
| $NH_2$ (ts) | 60.61 | 81.54 | 20.93 | 59.69 | 80.12 | 20.43 | 1.4933 | 1.5071 |
| OH | 61.07 | 82.57 | 21.50 | 59.46 | 80.21 | 20.75 | 1.4891 | 1.5132 |
| OH (ts) | 61.05 | 83.16 | 22.11 | 59.47 | 80.12 | 20.55 | 1.4868 | 1.5104 |
| F | 61.41 | 84.78 | 23.37 | 59.30 | 79.32 | 20.02 | 1.4806 | 1.5119 |
| $SiH_3$ | 59.03 | 77.01 | 17.98 | 60.48 | 77.99 | 17.51 | 1.5108 | 1.4886 |
| $SiH_3$ (ts) | 58.95 | 76.99 | 18.04 | 60.52 | 78.14 | 17.62 | 1.5112 | 1.4872 |
| $PH_2$ | 59.31 | 78.80 | 19.49 | 60.34 | 78.25 | 17.91 | 1.5057 | 1.4901 |
| $PH_2$ (ts) | 59.66 | 80.16 | 20.50 | 60.17 | 78.87 | 18.70 | 1.5018 | 1.4942 |
| SH | 60.50 | 83.08 | 22.58 | 59.75 | 79.15 | 19.40 | 1.4926 | 1.5039 |
| SH (ts) | 60.29 | 82.67 | 22.38 | 59.86 | 79.34 | 19.48 | 1.4941 | 1.5006 |
| Cl | 60.65 | 84.37 | 23.72 | 59.68 | 78.76 | 19.08 | 1.4882 | 1.5026 |

**Table VI. Atomic Charges at Carbons**

a. unsubstituted carbons

| X | ethyl | vinyl[a] | isopropyl | cyclopropyl |
|---|---|---|---|---|
| H | 0.237 | 0.081 | 0.226 | 0.106 |
| Li | 0.241 | −0.065 | 0.222 | 0.077 |
| BeH | 0.241 | 0.004 | 0.221 | 0.103 |
| $BH_2$ | 0.222 | 0.005 (0.076) | 0.227 | 0.113 |
| $CH_3$ | 0.221 | 0.080 | 0.217 | 0.092 |
| $NH_2$ | 0.241 | 0.150 (0.104) | 0.224 | 0.099 |
| OH | 0.241 | 0.183 (0.139) | 0.213 | 0.076 |
| F | 0.235 | 0.288 | 0.230 | 0.101 |
| $SiH_3$ | 0.237 | 0.055 | 0.223 | 0.112 |
| $PH_2$ | 0.243 | 0.099 (0.075) | 0.224 | 0.113 |
| SH | 0.242 | 0.163 (0.127) | 0.239 | 0.116 |
| Cl | 0.254 | 0.205 | 0.249 | 0.130 |
| avg | 0.238 ± 0.006 | 0.104 ± 0.074 | 0.226 ± 0.007 | 0.103 ± 0.011 |

b. substituted carbons

| X | ethyl | vinyl | isopropyl | cyclopropyl |
|---|---|---|---|---|
| H | 0.237 | 0.081 | 0.226 | 0.106 |
| Li | −0.467 | −0.497 | −0.429 | −0.519 |
| BeH | −0.661 | −0.695 | −0.654 | −0.760 |
| BH2 | −0.573 | −0.627 (−0.699) | −0.611 | −0.745 |
| $CH_3$ | 0.226 | 0.023 | 0.195 | 0.082 |
| $NH_2$ | 0.654 | 0.513 (0.493) | 0.601 | 0.532 |
| OH | 0.791 | 0.575 (0.613) | 0.741 | 0.724 |
| F | 0.795 | 0.478 | 0.723 | 0.682 |
| $SiH_3$ | −0.613 | −0.701 | −0.629 | −0.738 |
| $PH_2$ | −0.474 | −0.643 (−0.624) | −0.490 | −0.638 |
| SH | 0.095 | −0.171 (−0.115) | 0.060 | −0.048 |
| Cl | 0.277 | 0.055 | 0.221 | 0.144 |

[a] The values in parentheses are for the rotational transition state.

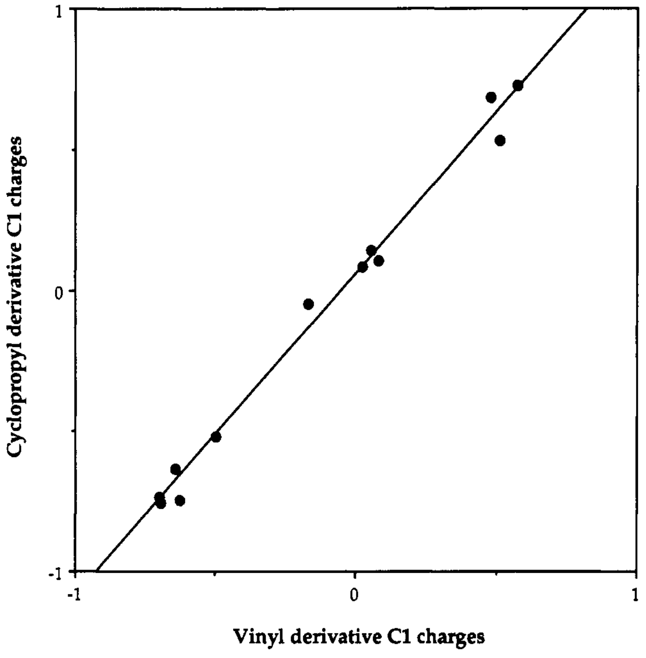


**Figure 5.** Correlation between cyclopropyl and vinyl charges at the substituted carbons.

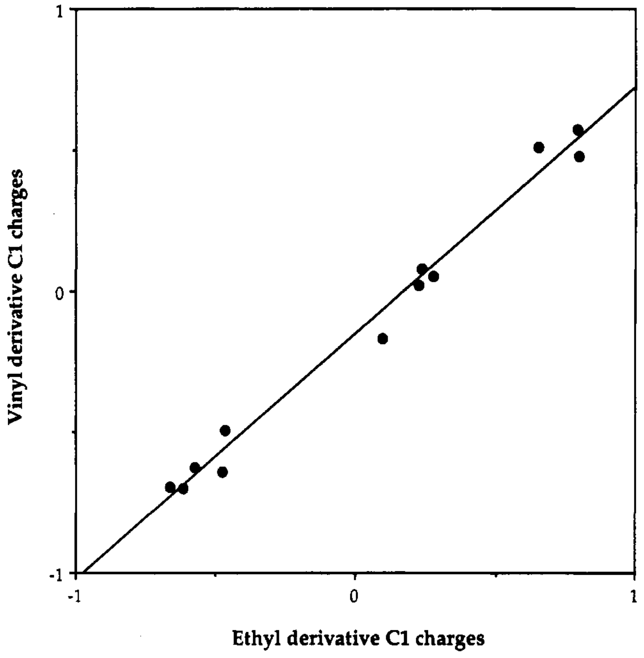


**Figure 6.** Correlation between vinyl and ethyl charges at the substituted carbons.

(given by the slopes), the effects on the substituted carbons are essentially the same in all cases.

## 6. A Further Consideration of the Isodesmic Reactions

The atoms in molecules treatment allows the kinetic energies of each of the atoms to be obtained, and the virial theorem states that the energy of an atom is the negative of its kinetic energy. The energies have been obtained for all of the compounds in this report and are available as supplementary material. It is not practical to analyze all of the data in any detail, and so we will focus on the effect of replacing hydrogen by lithium, methyl, and fluorine. This provides a wide range of electronegativities and should indicate the general nature of the substituent effects.

The energies of the groups Me, Et, i-Pr, t-Bu, vinyl, and cyclopropyl when attached to each of the above substituents is given in Table VII. It can be seen that, in all cases, the energy is lowest with lithium as the substituent and increases on going to methyl, hydrogen, and fluorine in that order. This is to be expected since the kinetic energy is related to the electron population and since the populations decrease in the above order. The range of change

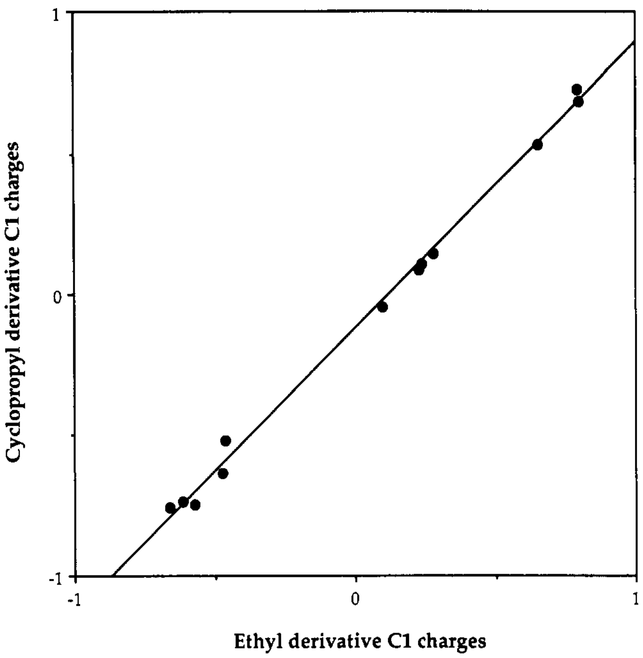


**Figure 7.** Correlation between cyclopropyl and ethyl charges at the substituted carbons.

**Table VII. Energy Changes on Changing Substituents, Hartrees**

a. energies of Groups Attached to Substituents

| group | Li | Me | H | F | range |
|---|---|---|---|---|---|
| | substitnt | | | | |
| $CH_3$ | −39.6210 | −39.6193 | −39.5538 | −39.2499 | 0.3711 |
| Et | −78.6464 | −78.6399 | −78.5765 | −78.3139 | 0.3325 |
| i-Pr | −117.6794 | −117.6634 | −117.6019 | −117.3696 | 0.3098 |
| t-Bu | −156.7160 | −156.6875 | −156.6303 | −156.4185 | 0.2975 |
| vinyl | −77.4820 | −77.4664 | −77.3919 | −77.0593 | 0.4227 |
| cyclopropyl | −116.4942 | −116.4860 | −116.4127 | −116.1352 | 0.3509 |

b. energies of substituents

| group | Li | Me | H | F |
|---|---|---|---|---|
| | substitnt | | | |
| Me | −7.4000 | −39.6193 | −0.6479 | −99.7899 |
| Et | −7.4030 | −39.6365 | −0.6621 | −99.7708 |
| i-Pr | −7.4030 | −39.6515 | −0.6775 | −99.7604 |
| t-Bu | −7.4015 | −39.6655 | −0.6847 | −99.7548 |
| vinyl | −7.3853 | −39.6151 | −0.6469 | −99.8281 |
| cyclopropyl | −7.3922 | −39.6231 | −0.6557 | −99.7782 |
| range | 0.0177 | 0.0504 | 0.0378 | 0.0733 |

is of some interest. It decreases in the order Me > Et > i-Pr > t-Bu. It is largest with vinyl, and cyclopropyl gives a range close to that of methyl. The order is in accord with the polarizability of the groups. A vinyl group has the highest polarizability because of its $\pi$-electrons, and the unusual bonding in cyclopropane leads to a high polarizability. With the alkyl groups, the C–H bond is easily polarized because of the small nuclear charge of hydrogen. As a result, the range of energies decreases as the number of hydrogens decrease.

With lithium as the substituent, its energy is almost unchanged on going from one alkyl group to another, and all of them give lower energies than vinyl or cyclopropyl (range = 0.0177). This is in accord with the high ionic character of the C–Li bond.[27] Here, it makes little difference which alkyl group is attached, but lithium is destabilized when associated with an $sp^2$-hybridized carbon. With hydrogen as the substituent, the order of increasing substituent energy is t-Bu < i-Pr < Et < cyclopropyl < Me ~ vinyl, with a range of 0.0378. Methyl gives the same order of increasing substituent energy, with a larger range of 0.0504. The small range for hydrogen is probably a reflection of its small atom energy. The order for fluorine as the substituent is reversed from that with methyl, i.e., vinyl < Me < cyclopropyl < Et < i-Pr < t-Bu, with a range of 0.0499. The observation that methyl and fluorine give opposite orders of energies, with a similar overall range of energies, is not unexpected. Methyl is known to stabilize alkyl groups, resulting in neopentane being the most stable of the pentanes.[2,28] When attached to $sp^2$-hybridized centers, a methyl group loses electron population and correspondingly has a decreased kinetic energy. This will correspond to an increased atom energy. Fluorine acts as an electron-attracting group and as a result gives the opposite trends from the other groups.

## 7. Conclusions

The results of this investigation present a consistent picture of the role of substituents in affecting the structures and energies of ethyl, isopropyl, and cyclopropyl groups. With these compounds, substituents have little effect on the $\beta$-carbons, and the effects at the $\alpha$-carbon are linearly related. An examination of the bond paths, especially for cyclopropyl derivatives, provides a clear indication of the importance of electronegativity in determining structures.

Two observations will require further study. The first is the unusual rotational profiles for some cyclopropyl derivatives. Why are they so different from the isopropyl derivatives? The second is concerned with the effect of substituents on the charge distribution for vinyl derivatives. Here, we are in the process of examining the changes at a higher level of theory including correction for electron correlation, and of examining the shifts in charge density via density difference plots which may better reveal the origins of the calculated changes.

## 8. Calculations

The ab initio calculations were carried out using GAUSSIAN-90[29] and the electron populations and kinetic energies were obtained from the wave functions using PROAIM.[30]

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**Supplementary Material Available:** Tables of bond and atom properties of all the compounds obtained at the HF/6-31 G** theoretical level (102 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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