structure II or IV is more stable. Starting with structure II one might expect that the next two CH_4 molecules would go not to the H atoms at the back of the CH_5^+ molecule but to the acidic protons of the two CH_4 molecules engaged in the three-center bonds. The resulting structure V is shown in Figure 5. The next, i.e., fifth, molecule must go then to an "outer" position compared with the positions available for the third and fourth molecule, and have a weaker binding energy. The van't Hoff plots (Figure 1) are compatible with such a situation. If the third, fourth, and fifth molecules went to similar positions one would have observed small and gradually decreasing gaps between the van't Hoff plots for the (2,3), (3,4), and (4,5) equilibria. Examining Figure 1 one finds that the gap between (3,4) and (4,5) is actually bigger than the gap between (2,3) and (3,4). This could mean that the fifth molecule goes to a different and less favorable position and is in agreement with the buildup of structure II to structure V (Figures 4 and 5) and beyond.

Assuming that the more favorable structure for $CH_5^+\cdot CH_4$ is given by IV one would expect that the second molecule will go opposite the second acidic hydrogen of the three-center bond in CH_5^+, but that the third, fourth, and fifth molecule would go opposite the three remaining H atoms of the CH_5^+. This would mean three similar and gradually decreasing interactions and be actually incompatible with the somewhat larger (3,4) to (4,5) gaps in the van't Hoff plots discussed above, unless one invoked special steric hindrance for the incoming fifth molecule.

Structures as complicated as V or the alternative considered above cannot be established on the basis of energetics data alone. Therefore, it would not be profitable to speculate further. However, we think that the structures of the protonated methane clusters are interesting and that they might also be useful in considerations of the state of the proton in liquid hydrocarbon solutions.

References and Notes

(1) V. L. Talroze and A. L. Lyubimova, *Dokl. Akad. Nauk SSSR*, **86**, 509 (1952).
(2) M. S. B. Munson and F. H. Field, *J. Am. Chem. Soc.*, **87**, 3294 (1965).
(3) V. M. Volkov and A. A. Levin, *Zh. Strukt. Khim.*, **4**, 100 (1963).
(4) G. Farini, G. Majorino, and M. Simonetta, *Accad. Naz. Lincei, Ser. 8*, **38**, 775 (1965).
(5) T. Yonezawa, H. Nakatsuji, and H. Kato, *J. Am. Chem. Soc.*, **90**, 1235 (1968).
(6) L. C. Allen, "Quantum Theory of Atoms, Molecules and Solid State", P. Lowdin, Ed., Academic Press, New York, N.Y., 1966, p 62.
(7) G. A. Olah, G. Klopman, and R. H. Schlossberg, *J. Am. Chem. Soc.*, **91**, 3261 (1969); G. A. Olah, *Chem. Br.*, **8**, 281 (1972).
(8) A. Gamba, G. Morosi, and M. Simonetta, *Chem. Phys. Lett.*, **3**, 20 (1969).
(9) W. A. Lathan, W. J. Hehre, and J. A. Pople, *J. Am. Chem. Soc.*, **93**, 808 (1971); *Tetrahedron Lett.*, **31**, 2699 (1970).
(10) P. C. Hariharan, W. A. Lathan, and J. A. Pople, *Chem. Phys. Lett.*, **14**, 385 (1972).
(11) V. Dycymons, V. Staemmer, and W. Kutzelnigg, *Chem. Phys. Lett.*, **5**, 361 (1970).
(12) P. Kebarle, "Ions and Ion Pairs in Organic Reactions", Vol. 1, M. Szwarc, Ed. Wiley-Interscience, New York, N.Y., 1972, Chapter I; P. Kebarle, *Mod. Aspects Electrochem.*, **9**, 1 (1974).
(13) J. D. Payzant, A. J. Cunningham, and P. Kebarle, *Can. J. Chem.*, **51**, 3242 (1973).
(14) E. P. Grimsrud and P. Kebarle, *J. Am. Chem. Soc.*, **95**, 7939 (1973); K. Hiraoka, E. P. Grimsrud, and P. Kebarle, *ibid.*, **96**, 3359 (1974).
(15) K. Hiraoka and P. Kebarle, *J. Chem. Phys.*, **62**, 2267 (1975).
(16) F. H. Field and D. P. Beggs, *J. Am. Chem. Soc.*, **93**, 1585 (1971).
(17) A. J. Cunningham, J. D. Payzant, and P. Kebarle, *J. Am. Chem. Soc.*, **94**, 7627 (1972).
(18) K. Hiraoka and P. Kebarle, to be submitted for publication.
(19) P. Kebarle, S. K. Searles, A. Zolla, J. Scarborough, and M. Arshadi, *J. Am. Chem. Soc.*, **89**, 6393 (1967), collisional dissociation is discussed on p 6394.
(20) K. Hiraoka and P. Kebarle, "Studies of Clustering of Alkyl Ammonium Ions with H_2O Molecule", to be submitted for publication.
(21) D. P. Beggs and F. H. Field, *J. Am. Chem. Soc.*, **93**, 1567, 1576 (1971).
(22) S. L. Bennett and F. H. Field, *J. Am. Chem. Soc.*, **94**, 8669 (1972).
(23) W. I. Salmon and R. D. Poshusta, *J. Chem. Phys.*, **59**, 4867 (1973).

A Quantum Mechanical Approach to Conformational Analysis

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Abstract: The classic bulk approach to conformational preference in organic chemistry is shown to be less satisfactory than an approach which considers the energy components T, V_{ne}, V_{ee}, and V_{nn}. The attractive steric effect is shown to have its origin in the dominance of ΔV_{ne} over $\Delta V_{ee} + \Delta V_{nn}$. This is demonstrated through consideration of several ab initio SCF calculations. These include the methyl and ethyl rotations of *n*-butane; the conversion of chair cyclohexane to the twist-boat and boat conformations; and the axial vs. equatorial preference of methyl and fluoro substituted chair cyclohexanes. Moreover, the attractive steric effect is found to be crucial for a proper understanding of the gauche-anti reaction coordinate, and it can be important in cis and trans alkenes. Axial preference in chair cyclohexanes is caused by dominance of the ΔV_{ne} term.

Historically, discussions of steric and conformational effects have emphasized the repulsive terms arising from interactions between nonbonded atoms or groups. Such approaches assume that bringing two large nonbonded groups into closer proximity leads to unfavorable interactions. Thus, groups of greater "bulk" or "size" tend to be equatorial in cyclohexanes, anti in 1,2-disubstituted ethanes, or trans in alkenes with respect to other bulky groups.[1] However, this bulk approach to steric or conformational effects is unsatisfactory on two counts. First, it is often wrong; numerous examples are known where the system is actually more stable with the large groups closer. Axial preference can be found,[2] some disubstituted alkenes are more stable in the cis form,[3-5] and 1-chloro- and 1-bromopropane prefer the gauche conformation.[6] Second, this bulk approach is not quantitative and gives no real measure of the strength of the interaction between the groups. Moreover, in some cases where the bulk approach gives qualitatively correct predictions, the dominant interactions are really attractive rather than repulsive.

Table I. Changes in Scaled Energy Components as Two Atoms or Groups are Brought Closer

$\Delta T = -\Delta E$

$\Delta V_{\text{ne}} < 0$

$\Delta V_{\text{ee}} > 0$

$\Delta V_{\text{nn}} > 0$

$|V_{\text{ne}}| > \Delta V_{\text{ee}} + \Delta V_{\text{nn}} \Rightarrow$ steric attraction

$\Delta V_{\text{ee}} + \Delta V_{\text{nn}} > |\Delta V_{\text{ne}}| \Rightarrow$ steric repulsion

There now exists a simple analysis that does quantitatively describe the energy changes resulting from the movement of atoms or groups. In this method which has been employed extensively by Allen,[7-9] the total energy E of a system is partitioned into four components: T, the kinetic energy of the electrons; V_{ne}, the attraction of the electrons for the nuclei; V_{ee}, the interelectronic term; and V_{nn}, the internuclear repulsion.

$$\Delta E = \Delta T + \Delta V_{\text{ne}} + \Delta V_{\text{ee}} + \Delta V_{\text{nn}}$$

During a conformational change or an isomerization, the energy change ΔE is given by

$$\Delta E = \Delta T + \Delta V_{\text{ne}} + \Delta V_{\text{ee}} + \Delta V_{\text{nn}}$$

This partition provides a convenient quantitative way of describing an energy change in terms of fundamental interactions. We did not obtain the equilibrium geometries for our basis set but used ideal geometries and scaled the components to force them to conform to the virial theorem in the form[10,11]

$$\Delta E = -\Delta T$$

$$\Delta E = (\Delta V_{\text{ne}} + \Delta V_{\text{ee}} + \Delta V_{\text{nn}})/2$$

Consequently, after scaling the change in the total energy can be expressed in terms of the three potential energy components.

There exists a delicate balance between the various energy components. Yet we can usually predict the changes in these components that will result when two groups are moved. Although V_{ee} contains exchange integrals as well as the classical electron–electron terms, it is dominated by the repulsions. Consideration of Coulomb's law then indicates that bringing two nuclei and their associated electrons closer together will increase the magnitude of all potential energy terms. Therefore, unless there is a major redistribution of electron density away from the centers of interest, both V_{ee} and V_{nn} will increase while V_{ne} will become more negative (Table I).

The change in the total energy ΔE is small, and its direction depends upon the relative magnitudes of the various terms. If the sum $\Delta V_{\text{ee}} + \Delta V_{\text{nn}}$ is larger than the magnitude of ΔV_{ne}, the classic bulk approach to steric interactions gives qualitatively correct predictions. But when ΔV_{ne} is larger, the bulk approach fails. In this case there exists an attractive steric effect, and the system is actually more stable with the bulky groups closer. This analysis helps us to understand in a more quantitative and physical sense the conformational behavior of organic molecules. We have chosen several fundamental conformational problems and calculated the associated change in total energy and in the components. We assume in our discussion that the system under consideration is either a hydrocarbon or contains at most one heteroatom and that the change in the components is large.

Calculations

All calculations were fully ab initio and used the ATMOL programs and the atomic optimized Gaussian bases of Whitman and Hornback.[13] A set of 5s, 3p Gaussian functions on each heavy atom was contracted to the best 1s, 2s, $2p_x$, $2p_y$, and $2p_z$ atomic orbitals. The hydrogenic functions consisted of two s-type Gaussians optimized in methane and contracted to a single 1s atomic orbital.

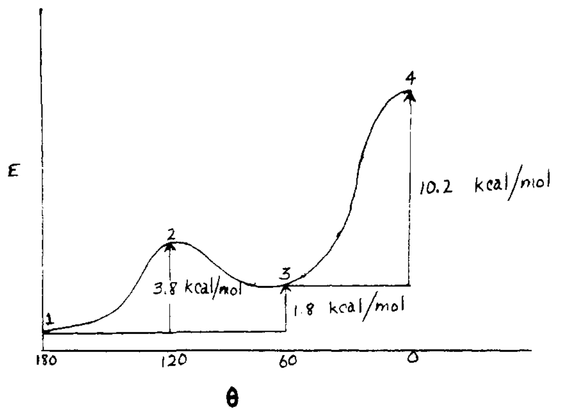


Figure 1. The reaction coordinate for ethyl rotation in *n*-butane.

Throughout these calculations a standard carbon–carbon distance of 1.54 Å, a standard carbon–hydrogen distance of 1.10 Å, and exact tetrahedral angles were assumed. Our choice of rigid ideal geometries may seem open to question. However, for hydrocarbons or systems containing no more than one heteroatom small changes in geometry should have no effect on the correctness of the analysis given in Table I since the total energy difference for a conformational change has been shown to be relatively insensitive to the choice of basis set and the precise geometry.[14-18]

To illustrate, consider the conversion of chair to boat cyclohexane. All reasonable calculations will yield an energy difference of approximately +8 ± 2 kcal/mol. For scaled components, it then follows that

$$\Delta T = -\Delta E \approx -8 \text{ kcal/mol}$$

$$\Delta V_{\text{ne}} + (\Delta V_{\text{ee}} + \Delta V_{\text{nn}}) \approx +16 \text{ kcal/mol}$$

Furthermore

$$\Delta V_{\text{ee}} > 0$$

$$\Delta V_{\text{nn}} > 0$$

$$\Delta V_{\text{ne}} < 0$$

It must follow for all reasonable calculations that

$$\Delta V_{\text{ee}} + \Delta V_{\text{nn}} > |\Delta V_{\text{ne}}|$$

Thus, although the components themselves are sensitive to choice of bases and geometry,[14,17] it seems that the inequalities of Table I are not. Therefore, the use of true geometries, many of which are not known exactly, would not lead to significantly different results than our use of the more convenient ideal geometries.

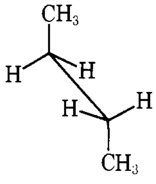
***n*-Butane.** In an alkane such as *n*-butane, both ethyl and methyl rotational possibilities exist. The anti conformation **1** is most stable, but rotation about the C_2–C_3 bond leads successively to the transition state **2**, the gauche formation **3**, and finally the transition state **4**, which separates gauche formations. Furthermore, both the anti form **1** and the gauche form **3** can undergo methyl rotation to **5** and **6**, respectively.

The results of our calculations are presented in Table II while the reaction coordinate for ethyl rotation is illustrated in Figure 1. The values in Table II are in hartrees and those in Figure 1 are in kilocalories per mole.

The transition state **2** is calculated to lie 3.8 kcal/mol above the anti conformation **1**, in good agreement with the

Table II. The Component Analyses for Methyl and Ethyl Rotation in *n*-Butane

	1	2	3	4	5	6
			Unscaled			
T	153.6393	153.6716	153.6667	153.7634	153.6655	153.6874
V_{ne}	−619.3807	−620.9202	−625.2101	−628.9820	−619.4792	−625.2816
V_{ee}	178.5975	179.3548	181.4893	183.3325	178.6428	181.5198
V_{nn}	130.6089	131.3649	133.5219	135.3703	130.6412	133.5471
E	−156.5350	−156.5289	−156.5321	−156.5159	−156.5296	−156.5272
			Scaled			
T	156.5487	156.5422	156.5455	156.5282	156.5429	156.5404
V_{ne}	−625.2177	−626.6928	−631.0392	−634.6116	−625.2521	−631.0585
V_{ee}	180.2806	181.0222	183.1815	184.9734	180.3076	183.1969
V_{nn}	131.8398	132.5862	134.7668	136.5819	131.8587	134.7809
E	−156.5487	−156.5422	−156.5455	−156.5282	−156.5429	−156.5404



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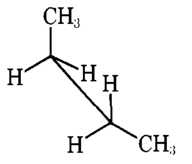
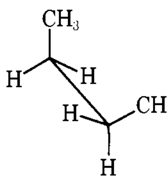


2

methyl rotation

5



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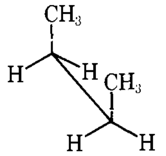


4

methyl rotation

6

value of 3.6 kcal/mol determined by Pitzer.[19] The gauche form **3**, which we assumed to have a dihedral angle of 60°, is found to be 1.8 kcal/mol less stable than **1**, while the commonly accepted value for the energy difference is 0.9 kcal/mol. However, our transition state **4** is calculated to lie over 10 kcal/mol above the gauche conformation **3**. This is somewhat higher than the value of 6.5 kcal/mol reported by Piercy and Rao.[21] Although our last value is probably high, there is no doubt about the directional changes in components. The data in Table I show quite clearly that as the two large methyl groups move nearer to each other V_{ee} and V_{nn} both increase, and V_{ne} becomes more negative.

Conventional arguments would imply that **3** is more stable than **2** because staggering the bonds decreases the repulsive interactions. However, the calculations show just the opposite. The repulsive energy, $V_{ee} + V_{nn}$, actually increases by 2722.4 kcal/mol. The attractive term V_{ne} becomes more negative by −2726.5 kcal/mol, and this makes **3** the more stable conformation. Thus the methyl-methyl interactions are more important than the torsional effect. These interactions cause the components to move in the opposite direction to the unsubstituted and monosubstituted eclipsed-staggered cases.[14] In a classical sense, **3** is the more stable geometry because of the attraction between the nuclei of one methyl group and the electrons of the other, and vice versa. There is, in essence, an attractive steric effect here.

Conversely, in passing from **3** to **2**, we proceed from a staggered geometry to an eclipsed one, and chemists generally assume that this torsional effect increases the energy through increased repulsions. However, there is, in fact, a decrease in both V_{ee} and V_{nn}. It is V_{ne} that increases and causes **2** to have the higher energy.

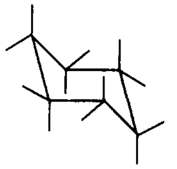
This is an extremely important result. The barrier between anti and gauche conformations exists in one direction (**1** ⟶ **2**) because, for the scaled components, the sum $\Delta V_{ee} + \Delta V_{nn}$ is larger than the magnitude of ΔV_{ne}, but it exists in the other direction (**3** ⟶ **2**) because the magnitude of ΔV_{ne} is greater.

The gauche conformation **3** is less stable than the anti conformation **1** because $\Delta V_{ee} + \Delta V_{nn}$ is greater than the absolute value of ΔV_{ne}. Here the classic bulk approach to conformational stability would be qualitatively correct. However, the bulk argument provides no information on the size of the changes in energy components and consequently ignores the delicate balance between repulsive and attractive effects. These must be considered in discussions of conformational preference.

We calculate that the barrier to methyl rotation is 3.4 kcal/mol for the anti conformation and 3.1 kcal/mol for the gauche conformer. The methyl rotational barriers in ethane,[22] propane,[23] and butane[24] are all in the neighborhood of 3 kcal/mol. In the series, the hydrogen in ethane is replaced first by methyl and then by ethyl. The bulk approach might lead one to expect larger barriers for the more bulky hydrocarbon groups. The component analysis, on the other hand, affords an explanation for the near constancy of these rotational barriers. When ΔV_{ee} and ΔV_{nn} increase, ΔV_{ne} decreases causing the total energy change ΔE to remain nearly constant.

Hoyland[25] has also reported on methyl and ethyl rotation in *n*-butane. Using basis sets that are comparable to ours, his calculated energy changes are in fine agreement with the experimental values, and his component analyses show the same trend as our own.

Cyclohexane. One of the most fundamental problems in conformational organic chemistry is the energy difference between chair **7** and boat **8** cyclohexanes. Reported values for ΔE range from 1.3[26] to over 10 kcal/mol[27] with most estimates in the range of 6.5–8 kcal/mol.[28] Hoyland, for example, calculates a value of 7.2 kcal/mol.[29]



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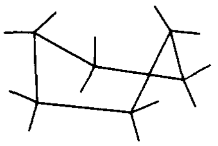

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The twist-boat conformation is also important. Hoyland reports a chair to twist-boat energy difference of 6.0 kcal/mol.[29] The results of our calculations are given in Table III.

Table III. The Component Analyses for Chair, Twist-Boat, and Boat Cyclohexanes

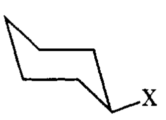
	Chair	Boat	Twist-boat
		Unscaled	
T	229.1496	229.2314	229.2026
V_{ne}	−1046.3988	−1049.2463	−1049.0547
V_{ee}	328.0926	329.4833	329.4057
V_{nn}	256.0073	257.3973	257.3070
E	−233.1493	−233.1343	−233.1394
		Scaled	
T	233.1667	233.1509	233.1563
V_{ne}	−1055.5311	−1058.1785	−1058.0641
V_{ee}	330.9560	332.2882	332.2347
V_{nn}	258.2416	259.5885	259.5168
E	−233.1667	−233.1509	−233.1563

We find the difference between **7** and **8** to be 9.4 kcal/mol while our chair to twist-boat energy difference is 6.2 kcal/mol.

Both conformational changes, chair to boat and chair to twist-boat, cause V_{ee} and V_{nn} to increase while V_{ne} becomes more negative. The sum $\Delta V_{ee} + \Delta V_{nn}$ is larger than the magnitude of ΔV_{ne} and a classic steric argument would be qualitatively correct. Yet if one looks at the change in the scaled components for chair and boat cyclohexanes, ΔV_{ne} has a value of −1661.8 kcal/mol, ΔV_{ee} equals 836.2 kcal/mol, and ΔV_{nn} is 845.4 kcal/mol. The energy decomposition gives a quantitative measure to the conformational change that is not possible from the classic steric description, and it is enlightening to see how large the change in components really is.

In passing from the chair to either the twist-boat or boat conformation, a number of unfavorable interactions are incurred. For example, in passing to the boat, the carbon atoms along each side go from a gauche butane conformation such as **3** to an eclipsed form of type **4**, and the 1,4-methylene groups move much closer. Furthermore, the change in the transannular interactions can be viewed as equivalent to methyl rotation in gauche butane **6**. Since all of these processes increase the energy, it is not surprising that **8** is the less stable system. However, one should not attribute the energy difference solely to repulsive interactions and assume the change in the repulsive energy to be in the neighborhood of 10 kcal/mol. The actual change is nearly 200 times this value. Only the large compensating change in the V_{ne} term keeps the total energy difference small.

Monosubstituted Cyclohexanes. In chair cyclohexane there are two positions that a substituent can occupy. The equatorial position **9** is generally preferred, but this conformation is in equilibrium with **10** in which the substituent occupies an axial position. Certain reactions such as the E2 elimination proceed readily only by way of **10**.[1]



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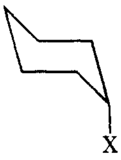


10

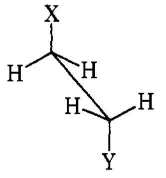
Regardless of the nature of **X**, we expect V_{ee} and V_{nn} to be less favorable in **10** while V_{ne} is more favorable. We chose both methyl and fluoro substituents, and even with these dissimilar substituents, we found the expected results (Table IV). Our calculated energy diffence for methylcyclohexane is 4.3 kcal/mol with equatorial preference. The experimental value is 1.8 kcal/mol.[30] For the fluoro derivative, our calculated energy difference is virtually zero while investigations indicate that the equatorial position is preferred by about 0.2 kcal/mol.[31,32]

Table IV. The Component Analyses for Axial and Equatorial Methyl- and Fluorocyclohexanes

	Equatorial methyl	Axial methyl	Equatorial fluoro	Axial fluoro
		Unscaled		
T	267.3636	267.4231	327.7493	327.7601
V_{ne}	−1281.5697	−1295.4339	−1428.0329	−1441.3271
V_{ee}	413.1722	420.0519	440.2086	446.9138
V_{nn}	329.0243	335.9560	328.4140	334.9922
E	−272.0097	−272.0029	−331.66104	−331.66107
		Scaled		
T	272.0298	272.0225	331.6727	331.6727
V_{ne}	−1292.7048	−136.5265	−1436.5549	−1449.9045
V_{ee}	416.7621	423.6478	442.8356	449.5734
V_{nn}	331.8831	338.8327	330.3739	336.9857
E	−272.0298	−272.0225	−331.6727	−331.6727

One generally assumes that a substituent preferentially occupies the equatorial position in six-membered rings, yet it is obvious that whenever ΔV_{ne} predominates, axial preference can occur. Cases of this sort have been found, and axial preference has always been difficult to explain. For example, with group HgBr, which is extremely large, the axial-equatorial ratio is at least unity and may be greater.[33]

1,2-Disubstituted Ethanes. 1,2-Disubstituted ethanes of the type CH_2XCH_2Y, where X and Y are substituents other than hydrogen, exist in both the anti conformation **11** and the gauche conformation **13**, while the eclipsed geometry **12** represents the transition state between them.



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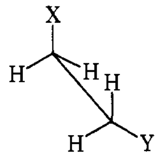

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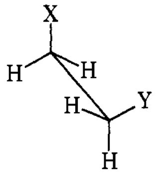

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In passing from **11** to **13**, V_{ee} and V_{nn} increase and V_{ne} becomes more negative. Whenever **13** is more stable than **11**, the net interaction between X and Y is attractive and ΔV_{ne} must predominate. Equally important in the behavior of gauche-anti systems is the attractive steric effect that exists in passing from the transition state **12** to the gauche geometry **13**. A proper understanding of the rotational reaction coordinate requires taking this into consideration. The fact that the system passes from an eclipsed geometry **12** to a staggered one **13** is less important than the fact that X and Y are moving closer together. These heavy nuclei and their associated electrons dominate the Hamiltonian, and the calculated energy change depends, to a large measure, on these interactions. Our calculations on *n*-butane show quite clearly that the stability of the gauche conformation relative to the eclipsed transition state is not due to the repulsive torsional effect but to ΔV_{ne}.

One may wonder whether it is ever possible for a system to exist in an eclipsed geometry rather than in a staggered one. The dithionite system $S_2O_4^{2-}$, while it does not conform to our assumption of being a hydrocarbon or containing only one heteroatom, has been shown to have the eclipsed structure **14**.[34]

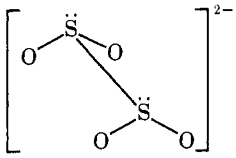

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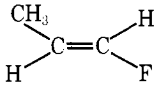
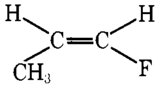
Table V. The Scaled Results of Scarzafava and Allen on *trans*- and *cis*-1-Fluoropropene

$\Delta E_{\text{cis-trans}} = -2.4$ kcal/mol
$\Delta T = +2.4$ kcal/mol
$\Delta V_{\text{ne}} = -3196.9$ kcal mol
$\Delta V_{\text{ee}} = +1613.3$ kcal/mol
$\Delta V_{\text{nn}} = +1578.8$ kcal/mol

Trans and Cis Alkenes. Ab initio SCF calculations on *trans*- and *cis*-1-fluoropropene (**15** and **16**) have been reported by Scarzafava and Allen and the cis isomer is calculated to be more stable by 2.4 kcal/mol.[35] An attractive steric effect is present. The scaled components have been reported (Table V). We see that ΔV_{ne} is larger in magnitude than the sum $\Delta V_{\text{ee}} + \Delta V_{\text{nn}}$. These results and those in the last section indicate that when the term $\Delta V_{\text{ee}} + \Delta V_{\text{nn}}$ is larger, the trans alkene or anti alkane is preferred. Conversely, the cis alkene or gauche alkane predominates when ΔV_{ne} is larger.[36]

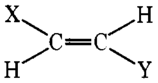


15

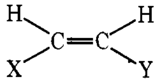


16

The 1,2-dihaloethylenes have been studied by Viehe and others,[3-5] and only 1,2-diiodoethylene is appreciably more stable in the trans geometry. Upon passing from the trans isomer **17** to the cis isomer **18** the effect is similar to that just discussed for 1-fluoropropene.



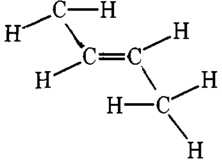
17



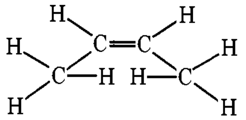
18

The cis-trans energy difference ΔE is small, and, furthermore, it remains small upon passing along the series F, Cl, Br, and I. The larger halogens have greater nuclear charge and more electrons, and the sum $\Delta V_{\text{ee}} + \Delta V_{\text{nn}}$ must increase considerably as one proceeds from fluorine to iodine. However, ΔV_{ne} moves in the opposite direction and compensates for this increase. Thus, ΔE changes only slightly because of these offsetting effects. For most of the 1,2-dihaloethylenes, ΔV_{ne} predominates, and the cis isomer is the more stable. With the diiodo compound, $\Delta V_{\text{ee}} + \Delta V_{\text{nn}}$ outweighs ΔV_{ne}, and the trans isomer is the more stable.

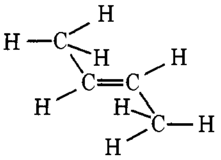
A final example of attractive steric effects involves *cis*- and *trans*-2-butene. Radom and Pople[37] have calculated the energies of *trans*- and *cis*-2-butene in different methyl rotated geometries. The ground states were reported to be **19** and **20**, respectively.[38] However, each methyl group can be rotated about its local C_3 axis by an angle θ. Rotation of both methyl groups in each isomer by 60° leads to **21** and **22**, and in these geometries *cis*-2-butene (**22**) is more stable than *trans*-2-butene (**21**). We indicate in Table VI the cis-trans energy difference as the two methyl groups in each isomer are rotated.



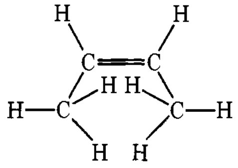
19



20



21



22

Table VI. The Cis-Trans Energy Difference in the 2-Butenes according to Radom and Pople

θ_1	θ_2	$\Delta E_{\text{cis-trans}}$, kcal/mol
0	0	+1.67
0	30	+1.13
0	60	+0.55
30	60	+0.02
60	60	−0.54

In **22**, we still have both methyl groups on the same side of the molecule, yet it is actually more stable than **21**. Clearly the bulk of the methyl groups is not a satisfactory explanation. Rotating the methyl groups leads to a favorable interaction in the cis isomer, an attractive steric effect, and this causes the methyl rotational barrier to be much smaller in this isomer.[39,40]

It is fairly obvious that the **20**-**19** energy difference occurs because $\Delta V_{\text{ee}} + \Delta V_{\text{nn}}$ outweighs ΔV_{ne} while for **22**-**21** ΔV_{ne} is larger in magnitude than $\Delta V_{\text{ee}} + \Delta V_{\text{nn}}$.

Discussion

Analyzing conformational problems in terms of attractive and repulsive energy components offers considerable advantage over a more traditional approach. Most importantly, it offers an explanation for the occurrence of an attractive steric effect which cannot be satisfactorily handled in other ways. Furthermore, it examines the conformational problem more thoroughly by taking into account the delicate balance between the different components. Through the energy partitioning one gains an appreciation for the considerable magnitude of the changes in repulsive and attractive energies that occur.

Even in the many cases where the bulk approach correctly predicts the existence and direction of a conformational energy difference, it may provide an incorrect explanation. This is dramatically illustrated by the passage of the gauche form of *n*-butane **3**, to the eclipsed transition state **2**. Conventional arguments attribute the barrier to a repulsive interaction associated with eclipsing the bonds. In reality, the repulsive term decreases significantly (in our calculation by −2722.4 kcal/mol). The change in V_{ne} more than compensates. Thus, the barrier must be attributed to the latter term, and, therefore, the conventional argument is misleading.

The energy decomposition we have used is not restricted to conformational problems. It is quite likely that many chemical reactions can be beneficially interpreted in the same way. For example, the attractive steric effect has ramifications in the field of stereoselectivity. Hoffmann has discussed steric attraction in the addition of unsymmetric carbenes to cis-disubstituted olefins in terms of orbital symmetry.[41] However, a component analysis can also provide an interpretation for such observations.

The component analysis approach to chemical behavior must, at this time, be considered an interpretive rather than a predictive tool. We cannot yet predict when the attractive steric effect will be present. But although the method provides no specific predictions, general implications are possible. For example, the analysis does not rule out the existence of stable eclipsed conformations.

The inequalities of Table I will be invariant in an overwhelming majority of cases for hydrocarbons or systems containing only a single heteroatom. However, there will exist a very few cases when the change in components is small where different calculations can lead to uncertainty in the direction of the changes in the scaled components. It should be emphasized that such failings will be rare, and in these cases the problem generally lies in not knowing the precise geometries rather than with the component analysis. For most cases, this method provides a convenient, reliable, and insightful way to describe conformational changes.

Conclusion

Conformational behavior can generally be interpreted in terms of a component analysis. For hydrocarbons or systems containing only a single heteroatom when atoms or groups are moved into closer proximity, V_{ee} and V_{nn} increase and V_{ne} decreases. The change in the total energy ΔE is small, and its direction depends upon the relative magnitudes of the various terms. If, for the scaled components, the sum $\Delta V_{ee} + \Delta V_{nn}$ is larger, a repulsive interaction exists between the groups. When ΔV_{ne} is larger, there exists an attractive steric effect, and the system is more stable with the bulky groups closer.

Even for those cases which are dominated by the repulsive terms, a component analysis provides greater insight into the magnitude of the energy changes and the causes of conformational preferences.

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References and Notes

(1) A. Liberles, "Introduction to Theoretical Organic Chemistry", Macmillan, New York, N.Y., 1968.
(2) E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis", Wiley-Interscience, New York, N.Y., 1965.
(3) H. G. Viehe, E. Franchimont, M. Reinstein, and P. Valange, *Chem. Ber.*, **93**, 1697 (1960).
(4) H. G. Viehe and E. Franchimont, *Chem. Ber.*, **96**, 3153 (1963).
(5) R. E. Wood and D. P. Stevenson, *J. Am. Chem. Soc.*, **63**, 1650 (1941).
(6) L. N. Ferguson, "The Modern Structural Theory of Organic Chemistry", Prentice-Hall, Englewood Cliffs, N.J., 1963, p 224.
(7) R. B. Davidson and L. C. Allen, *J. Chem. Phys.*, **54**, 2828 (1971).
(8) L. C. Allen, *Chem. Phys. Lett.*, **2**, 597 (1968).
(9) W. H. Fink and L. C. Allen, *J. Chem. Phys.*, **46**, 2261 (1967).
(10) P. O. Lowdin, *J. Mol. Spectrosc.*, **3**, 46 (1959).
(11) W. L. Clinton, *J. Chem. Phys.*, **33**, 632 (1960).
(12) V. R. Saunders, ATMOL Program, Atlas Computer Laboratory, Chilton, Berks., England.
(13) C. J. Hornbach, Thesis, Case Institute of Technology; see also, D. R. Whitman and C. J. Hornbach, *J. Chem. Phys.*, **51**, 398 (1969).
(14) A. Liberles, B. O'Leary, J. E. Eilers, and D. R. Whitman, *J. Am. Chem. Soc.*, **94**, 6894 (1972).
(15) E. Clementi and D. R. Davis. *J. Chem. Phys.*, **45**, 2593 (1966).
(16) R. M. Pitzer, *J. Chem. Phys.*, **47**, 965 (1967).
(17) L. Pedersen and K. Morokuma, *J. Chem. Phys.*, **46**, 3941 (1967).
(18) R. M. Stevens, *J. Chem. Phys.*, **52**, 1397 (1970).
(19) K. S. Pitzer, *J. Chem. Phys.*, **8**, 711 (1940).
(20) R. T. Morrison and R. N. Boyd, "Organic Chemistry", 2nd ed., Allyn and Bacon, Boston, 1966, p 97.
(21) J. E. Piercy and M. G. S. Rao, *J. Chem. Phys.*, **46**, 3951 (1967).
(22) D. R. Lide, Jr., *J. Chem. Phys.*, **29**, 1426 (1958).
(23) J. R. Hoyland, *J. Chem. Phys.*, **49**, 1908 (1968).
(24) K. S. Pitzer, *J. Chem. Phys.*, **5**, 473 (1937).
(25) J. R. Hoyland, *J. Chem. Phys.*, **49**, 2563 (1968).
(26) D. H. R. Barton, *J. Chem. Soc.*, 340 (1948).
(27) W. G. Dauben and K. S. Pitzer, "Steric Effects in Organic Chemistry", M. S. Newman, Ed., Wiley, New York, N.Y., 1956, p 15.
(28) W. S. Johnson, V. J. Bauer, J. L. Margrave, M. A. Frisch, L. H. Dreger, and W. N. Hubbard, *J. Am. Chem. Soc.*, **83**, 606 (1961).
(29) J. R. Hoyland, *J. Chem. Phys.*, **50**, 2775 (1969).
(30) C. W. Beckett, K. S. Pitzer, and R. Spitzer, *J. Am. Chem. Soc.*, **69**, 2488 (1947).
(31) P. Andersen, *Acta Chem. Scand.*, **16**, 2337 (1962).
(32) A. Berlin and F. R. Jensen, *Chem. Ind.* (*London*), 998 (1960).
(33) F. R. Jensen and L. H. Gale, *J. Am. Chem. Soc.*, **81**, 6337 (1959).
(34) J. D. Dunitz, *Acta Crystallogr.*, **9**, 579 (1956).
(35) E. Scarzafava and L. C. Allen, *J. Am. Chem. Soc.*, **93**, 311 (1971).
(36) A. Liberles, A. Greenberg, and J. E. Eilers, *J. Chem. Educ.*, **50**, 676 (1973).
(37) L. Radom and J. A. Pople, *J. Am. Chem. Soc.*, **92**, 4786 (1970).
(38) For a discussion of the geometry of *cis*-2-butene, see A. Almenningen, I. M. Anfinsen, and A. Haaland, *Acta Chem. Scand.*, **24**, 43 (1970); T. N. Sarachman, *J. Phys. Chem.*, **49**, 3146, (1968); L. O. Brockway and P. S. Cross, *J. Am. Chem. Soc.*, **58**, 2407 (1936).
(39) T. N. Sarachman, *J. Chem. Phys.*, **49**, 3146 (1968).
(40) J. E. Kilpatrick and K. S. Pitzer, *J. Res. Natl. Bur. Stand.*, **37**, 163 (1946).
(41) R. Hoffmann, C. C. Levin, and R. A. Moss, *J. Am. Chem. Soc.*, **95**, 629 (1973).

An Intramolecular Hydrogen Bond. Ab Initio MO Calculations on the Enol Tautomer of Malondialdehyde

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Abstract: Ab initio MO-LCAO-SCF calculations have been performed on the enol tautomer of malondialdehyde, the parent compound for β-dicarbonyls. The molecule contains an intramolecular hydrogen bond, the potential of which is found to be of the double-well type with a barrier height of 48 kJ/mol. The results of the calculations are presented with reference to experimental data on β-dicarbonyl compounds.

The chemical phenomenon of hydrogen bonding has been studied extensively by quantum-mechanical ab initio calculations.[2] These investigations have focussed primarily on *inter*molecular hydrogen bonding. Rather few calculations have dealt with *intra*molecular hydrogen bonds.[3,4] One reason for this seems to be the comparatively large molecular framework required to make an intramolecular hydrogen bond possible. This has tended to make such calculations rather time-consuming. However, the use of new efficient computer programs has reduced these calculation times considerably.

It is generally assumed[5] that the relative stability of enol tautomers of β-dicarbonyl compounds derives partially from the formation of an intramolecular hydrogen bond. Some controversy reigns as to whether such a bond is strong enough to have the proton effectively centered in a single-