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Electrostatics and the Chemical Bond.[1] I. Saturated Hydrocarbons

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Abstract: A model of the C–H bond is proposed in which each H atom in an alkane bears a formal charge of $+0.278 \times 10^{-10}$ esu (0.0581 electronic charge) and each C atom a neutralizing negative formal charge. Summing up all of the electrostatic interactions in an alkane due to these formal charges gives rise to a net stabilizing electrostatic energy for each alkane $E_{el}(C_nH_{2n+2})$ which depends only on the geometrical structure. This is then shown to lead to a surprisingly simple formula for the standard enthalpies of formation for alkanes given by: $\Delta H_f{}^\circ{}_{298}(C_nH_{2n+2}\text{ gas}) = -2.0(n + 1) - 0.5 + E_{el}(C_nH_{2n+2})$. This fits the observed values of $\Delta H_f{}^\circ{}_{298}$ for all the *n*-alkanes to *n*-C_7H_{16} and for the branched alkanes up to C_5H_{12} to ±0.2 kcal/mol. It is also shown that the observed dipole moments of propane and *i*-C_4H_{10} agree well with the formal charge distribution if proper account is taken of mutual group polarization. It is further shown that the barrier to rotation about single bonds and the unfavorable gauche conformations in hydrocarbons cannot be quantitatively accounted for by electrostatic interactions. The rotation barrier, the gauche interaction, and the anomalously large C–C–C and C=C—C angles in alkanes and olefins are discussed instead in terms of a purely van der Waals H···H interaction, predominantly repulsive.

The standard heats of formation of compounds from their elements ($\Delta H_f{}^\circ$) have been shown to follow more or less accurately simple additivity laws.[3] The law of group additivity is capable of reproducing known values of $\Delta H_f{}^\circ$ for most species to within the experimental uncertainty when small (*i.e.*, ≤1.0 kcal) corrections are made for recognizable steric effects. A few compounds of very high polarity, such as CH_3CF_3, CH_2CCl_2, and the cyanocarbons, deviate from group additivity by amounts which may be as large as 8–9 kcal/mol, but such examples are so far relatively rare. In all such cases, it has been proposed that the deviations arise from polar interactions[4-6] and relatively simple electrostatic models have been used to rationalize these deviations.[7]

The law of group additivity is based on the decomposition of molecular properties into contributions from groups, a group being defined as a polyvalent atom together with all of its atomically bound neighbors (*e.g.*, C_2H_6 is composed of two identical groups, C–(C)(H)$_3$, carbon bound to three H atoms, and one C atom). The fact that group additivity works so well, particularly for the not-too-polar compounds and radicals,[3c] can be rationalized by the deduction that interactions between next-next-nearest neighbors is very small. The group, by definition, includes all interactions between nearest neighbors (bonded atoms) and next-nearest neighbors (1,3-nonbonded interactions).

The law of bond additivity, which is the next simpler stage in the hierarchy of additivity laws, uses a decomposition of molecular properties into sums of contributions from bonds. Average deviations of observed and calculated $\Delta H_f{}^\circ$ with this law are about ±3 kcal for nonpolar compounds, ±6 kcal for polar compounds, and up to ±12 kcal in extreme cases. It is the purpose of the present paper to examine the theoretical basis for these differences in accuracy between the laws of bond and group additivity and to present a very simple electrostatic model which can account quantitatively for the interactions responsible for the deviations observed.

I. The Methane Problem

The alkanes are considered the least polar of all organic compounds and, consequently, they should be expected to show the smallest deviations from simple bond additivity laws. In actual fact, they do follow reasonably well simple bond additivity schemes, but the observed deviations are not small. This is illustrated by the data in Table I showing values of $\Delta H_f{}^\circ$ for compounds in the series $CH_n(CH_3)_{4-n}$.

If these methyl-substituted methanes followed the law of bond additivity, then the change in $\Delta H_f{}^\circ$ on successive CH_2 insertion (*i.e.*, CH_3 for H substitution), given by the column labeled Δ_1, should be a constant. This constant would be equal to the contribution of one C–C bond plus two C–H bonds gained by the CH_2 insertion. In fact, we observe that Δ_1 becomes progressively more negative indicating progressively greater stability with increasing branching. This has been a somewhat unexpected finding, since one might have intuitively expected that the steric crowding of the methyls would lead to decreased stability. A comparison of the $\Delta H_f{}^\circ$ values for *i*-C_4H_{10} with *n*-C_4H_{10} and of neopentane with *n*-C_5H_{12} shows similarly that the branched compounds are 2.0 and 5.0 kcal/mol more stable respectively than their straight-chain isomers. This paradoxical result can be called "the methane problem."

The stability of the branched compounds might be ascribed to a general van der Waals' attraction of the CH_3 groups. However, the fact that the more stable form of *n*-butane occurs with the terminal-CH_3 groups trans to each other, rather than gauche, would conflict with such a hypothesis.

The methane problem is by no means unique to hydrocarbons, since we find similar behavior in the fluorinated methanes (Table II). We note in this case a much more pronounced increase in stability on F/H substitution than for CH_3/H substitution as seen by comparing the columns labeled Δ_1.

Table I. Heats of Formation of Methyl-Substituted Methanes, $CH_n(CH_n)_{4-n}$[a]

Compd	$-\Delta H_f°_{298}$, kcal/mol	$-\Delta_1$	$-\Delta_2$
CH_4	17.9		
		2.3	
$CH_3(CH_3)$	20.2		2.3
		4.6	
$CH_2(CH_3)_2$	24.8		2.7
		7.3	
$CH(CH_3)_3$	32.1		0.9
		8.2	
$C(CH_3)_4$	40.3		

[a] Values from J. D. Cox and G. Pilcher, "Thermochemistry of Organic and Organometallic Compounds," Academic Press, New York, N. Y., 1970. Uncertainties are about ±0.07 kcal/mol per C atom.

Table II. Heats of Formation of Fluorinated Methanes, CH_nF_{n-4}[a]

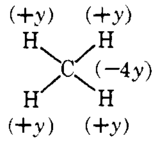
Compd	$-\Delta H_f°_{298}$, kcal/mol	$-\Delta_1$	$-\Delta_2$
CH_4	17.9		
		39	
CH_3F	56.8 ± 2		12
		51	
CH_2F_2	108 ± 1		7
		58	
CHF_3	166 ± 1		−1
		57	
CF_4	233 ± 1		

[a] Data from A. S. Rodgers, R. L. Wilhoit, and B. J. Zwolinski, in press.

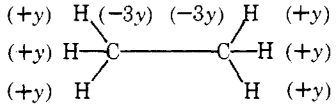
A number of purely empirical schemes[8-10] have been proposed to account for deviations from simple bond additivity. The simplest correction is to assume a contribution to $\Delta H_f°$ from interactions between each pair of 1,3-nonbonded atoms. (In such a scheme, $\Delta H_f°(CH_4)$ would be composed of contributions from 4(C–H) bonds + 6(H–H) interactions: $\Delta H_f°(CH_3F)$ has 3(C–H) bonds, 1(C–F) bond, 3(H–H) interactions, and 3(H–F) interactions.) Such a scheme would lead to a constant value of Δ_2, the difference in successive values of Δ_1. We see that such behavior is not obeyed in either series. A further contribution from nonbonded atoms, taken three at a time (we would add to the above, contributions from 4(HHH) interactions to $\Delta H_f°(CH_4)$ and for $\Delta H_f°(CH_3F)$ we would include contributions from 1(HHH) and 3(HHF) interactions), would lead to a variable value of the second difference, Δ_2, but a constant value of Δ_3 (not shown in Tables I and II), the difference between two successive values of Δ_2. Although such a relation is not obeyed in either series (Tables I and II), it requires only very minor adjustments in the $\Delta H_f°$, all within the limits of experimental error, to obtain a constant Δ_3. The final step in such an hierarchy, to include an interaction between atoms taken four at a time, would have no predictive value, since it would have as many parameters as data. However, the fact that even group additivity requires steric corrections and possibly polar corrections indicates that simple additive corrections to bond additivity can never be adequate.

II. An Electrostatic Model of Alkanes

Considerations stemming from the virial theorem, which we shall not discuss here, suggest that a profitable way of considering deviations from simple bond additivity schemes might be in terms of formal charge schemes similar to those used by Pauling in describing bond energies in heteronuclear diatomic molecules.[11] Such a model suggests that in a typical alkane molecule, the C–H bond has a polarity which can be represented by assigning a formal charge, $-y$, to C, and the opposite charge, $+y$, to H. We ignore for the moment the question of the absolute sign of y. This would lead to a CH_4 molecule in which each H atom had a charge of $+y$ and the central C atom, $-4y$.



The ethane molecule would have the charge distribution



In the straight chain paraffin molecules, the CH_2 groups would carry a $-2y$ charge on each C atom and again a $+y$ charge on each H atom. In branched paraffins the C–H tertiary group would have $-y$ on C and $+y$ on H, while the quaternary C atom would have no charge at all.

We can define E_{el}, an electrostatic energy, for any molecule which arises from the interaction of all the formal charges present in it. In most general terms

$$E_{el} = \sum_{i<j} q_i q_j / r_{i,j} \tag{1}$$

where $r_{i,j}$ is the distance between charges q_i and q_j. Since we are assuming a constant charge, $+y$, on H atoms and a counter charge, $-ny$, on carbon atoms (n = number of bonded H atoms on C), we see that E_{el} can be written as

$$E_{el} = y^2\left(\sum_{i<j} n_i n_j / r_{i,j}\right) \tag{2}$$

where the term in brackets is independent of y and depends only on the geometry of the molecule. ($n_i = +1$ for H atoms, 0 for quaternary C, −1 for tertiary C, −2 for secondary C, and −3 for primary C; we assume implicitly that the formal charge is spherically symmetrical and centered on the nucleus of each atom.) Using a standard tetrahedral geometry for all the alkanes with coplanar C atoms in staggered configuration, C–C distances of 1.538 Å with C–H distances of 1.093 Å, we have computed the values of E_{el} shown in Table III. (As we shall show later, E_{el} is relatively insensitive to small variations in geometry and bond lengths.)

We have stopped the table at n-C_7H_{16} since detailed analysis of the individual interactions shows that after n-C_5H_{12} there will be a constant increment of 2.62 y^2 units per CH_2 group. A comparison of the consecutive differences in E_{el} (Table III, column Δ_1) with the corresponding differences in $\Delta H_f°_{298}$ of the paraffin hydrocarbons, Δ_1 ($\Delta H_f°_{298}$, Table III), shows that E_{el} and $\Delta H_f°_{298}$ parallel each other strikingly. A direct identification or even direct proportion between $\Delta_1(E_{el})$ and $\Delta_1(\Delta H_f°_{298})$ is not appropriate since the insertion of a CH_2 group formed from the elements may be expected to be accompanied by some intrinsic change in $\Delta H_f°_{298}$. (A contribution of 0.6 kcal/mol comes just from the use of $\Delta H_f°_{298}$, rather than $\Delta E_f°_{298}$.)

A more interesting comparison is provided by the branched versus normal paraffins. Table IV shows some values of the $\Delta H_f°_{298}$ and E_{el} of the C_4 and C_5 alkanes. In these isomerization reactions, the number of C–C bonds and C–H bonds is constant so that by equating the heats of isomerization, $\Delta H_{isom}(298)$, with ΔE_{el} we calculate a unique value for y. Taking an average of the values from Table IV, we find $y^2 = 1.12 \pm 0.2$ [Å (kcal/mol)]. This

Table III. Electrostatic Energies of the n-Alkanes

n-Alkane	$-E_{el}{}^a/y^2$	Δ_1	$\Delta_1(\Delta H_f{}^\circ{}_{298})$, kcal/mol
CH_4	11.28		
		0.91	2.3
C_2H_6	12.19		
		2.58	4.6
C_3H_8	14.77		
		2.63	5.3
C_4H_{10}	17.40		
		2.62	4.9
C_5H_{12}	20.02		
		2.62	4.9
C_6H_{14}	22.64		
		2.62	4.9
C_7H_{16}	25.26		

[a] Units of E_{el} are y^2 Å^{-1}. To convert to kcal/mol, multiply by 14.4. y will be in units of esu × 10^{-10}.

Table IV. ΔE_{el} and ΔH_{isom} for C_4 and C_5 Paraffins

Paraffin	$-E_{el}{}^a/y^2$	$-\Delta E_{el}{}^a$-(isom)/y^2	$-H_{isom}$ (298), kcal/mol	$-\Delta H_{isom}$ (calcd),[b] kcal/mol
n-C_4H_{10}	17.40	1.62	2.0	1.8
i-C_4H_{10}	19.02			
n-C_5H_{12}	20.02	1.53	1.8	1.7
i-C_5H_{12}	21.55			
n-C_5H_{12}	20.02	4.90	5.2	5.5
Neopentane	24.92			

[a] Units are y^2 Å^{-1}. To convert to kcal/mol, multiply by 14.4 (y is in units of esu × 10^{-10}). [b] Last column is calculated with y^2 = 1.12 (kcal/mol) Å.

gives $|y|$ = 0.278 × 10^{-10} esu = 0.0581 electronic charge.

Comparing the observed and calculated values of $\Delta H_{isom}(298)$, using this value of y, gives agreement to within the experimental uncertainty. If now we use this same value, we can calculate the bond part of the CH_2 increment in the normal paraffins. At 298°K the total increment is 4.95 kcal/mol.[2] From Table III we see that $-\Delta_1(E_{el}) = 2.62y^2$ = 2.94 kcal/mol. The difference, $-4.95 + 2.94 = -2.0$ kcal/mol, we can take as the contribution of the C–C and C–H bonds to $\Delta H_f{}^\circ$ of insertion of a CH_2 group.

$$\Delta H_f{}^\circ{}_{298}(CH_2) = 1(C-C) + 2(C-H) \text{ bonds} + \Delta E_{el} \quad (3)$$

With this value and the calculated values of E_{el}, we can now calculate the $\Delta H_f{}^\circ(298)$ values of all the paraffin hydrocarbons, starting with one of them, let us say, C_2H_6. A typical example might be n-C_5H_{12} for which we could calculate

$$\Delta H_f{}^\circ{}_{298}(n\text{-}C_5H_{12}) = \Delta H_f{}^\circ{}_{298}(C_2H_6) + \Delta E_{el} + 3(-2.0)$$
$$= -35.0 \text{ kcal/mol} \quad (4)$$

in excellent agreement with the observed value, −35.1 kcal/mol.

If we examine the significance of what is meant by "heat of formation from the elements," we can attempt to make an absolute identification. Let us choose diamond, rather than graphite, as the standard state for carbon. Then the equation for $\Delta H_f{}^\circ$ of a typical alkane, C_nH_{2n+2}, can be written as

$$n\text{C(diamond)} + (n + 1)\text{H}_2\text{(gas)} \longrightarrow \text{C}_n\text{H}_{2n+2}\text{(gas)} \quad (5)$$

The heat of this reaction would be given by

$$\Delta H_f{}^\circ{}_{298}(C_nH_{2n+2})_{\text{diamond}} = \Delta H_f{}^\circ{}_{298}(C_nH_{2n+2})_{\text{graphite}} - 0.5n$$

where 0.5 kcal/mol is the heat of formation of diamond from graphite. This makes our CH_2 bond contribution to $\Delta H_f{}^\circ{}_{298}$ (diamond) equal to −2.5 kcal/mol.

Now the diamond lattice is made up of "pure" nonpolar, symmetrical bonds, such as we have postulated for paraffin hydrocarbons. Similarly, the homonuclear bond in H_2 is symmetrical and nonpolar. If we write the above equation in terms of bonds formed and broken, we have (1 mol of diamond has 2 mol of C–C bonds since each C atom has four nearest neighbors)

$$2n(C-C) \text{ bonds} + (n + 1)(H-H) \text{ bonds} \longrightarrow$$
$$(n - 1)(C-C) \text{ bonds} + (2n + 2)(C-H) \text{ bonds} \quad (6)$$

We see that the net change in bonds is

$$(n + 1)(C-C) \text{ bonds} + (n + 1)(H-H) \text{ bonds} \longrightarrow$$
$$2(n + 1)(C-H) \text{ bonds} \quad (7)$$

$\Delta H_{298}{}^\circ$ for this reaction which is what is meant by $\Delta H_f{}^\circ{}_{298}$ (diamond) can then be set equal to $(n + 1)CH_2$ bond increments plus the change in electrostatic energy. Since this latter is zero in the symmetrically bonded elements, ΔE_{el}, the difference is just the value we have calculated for the alkanes. Hence, we have

$$\Delta H_f{}^\circ{}_{298}(C_nH_{2n+2})_{\text{diamond}} =$$
$$-(n + 1)2.5 + E_{el}(C_nH_{2n+2}) \quad (8)$$

or reducing back to graphite as standard state by subtracting $-0.5n$

$$\Delta H_f{}^\circ{}_{298}(C_nH_{2n+2})_{\text{graphite}} =$$
$$-2.0n - 2.5 + E_{el}(C_nH_{2n+2}) \quad (9)$$

Values so calculated for the paraffins up to n-C_7H_{16} are shown in Table V. With the exceptions of CH_4, for which the deviation though small is outside experimental error, all the other calculated values agree to within experimental uncertainty with the reported value. (Another exception may be isopentane whose calculated value of $\Delta H_f{}^\circ$ should be diminished by a steric repulsion due to a gauche conformation of CH_3 groups. This might make this discrepancy as large as 0.8 kcal/mol. We say "might" because only a complete treatment using all nonbonded interactions could decide (see next section).) It is also worth noting that the agreement is about the same if we choose 0°K as our reference temperature. Here the CH_2 bond contribution becomes 0.7 kcal rather than 2.0 kcal.

The present model which does surprisingly well for the hydrocarbons is not, however, complete in that it does not include the interactions of nonbonded H atoms (*i.e.*, ortho, cis, and gauche interactions). Although these are each small, i.e., of the order of 0.8 to 1.0 kcal each, they can become quite significant in large, highly branched molecules. We make no effort to be more complete in the present paper since electrostatics contributes something to such interactions, and a more extensive analysis would be required than we can now make.

III. Rotational Conformations

The origin of the barrier to rotation about single bonds has been a subject of controversy for some time. Explanations have varied from those of a pure electrostatic nature to those involving very complex properties of the molecular orbitals involved.[12] Some time ago, Clinton[13] pointed out an interesting empirical relation between the changes in ΔV_{nn}, the difference in nuclear potential energy in eclipsed and staggered conformations, and the magnitude of the rotational barrier V_0 in systems with threefold barriers. Empirically it was observed that $V_0 \sim 0.6\Delta V_{nn}$ and an electrostatic model was suggested to account for this relation. With the

Table V. Comparison of Calculated and Observed Values of $\Delta H_f{}^\circ{}_{298}$ (kcal/mol) for Alkanes

Compd	$-H_f{}^\circ{}_{298}$ (obsd)	$-\Delta H_f{}^\circ{}_{298}$ (calcd)	Δ(obsd − calcd)
CH_4	17.9	17.2	−0.7
C_2H_6	20.2	20.2	0.0
C_3H_8	24.8	25.0	0.2
n-C_4H_{10}	30.1	30.0	0.1
i-C_4H_{10}	32.1	31.8	−0.3
n-C_5H_{12}	35.1	35.0	−0.1
i-C_5H_{12}	36.9	36.7	−0.2
Neopentane	40.3	40.5	0.2
n-C_6H_{14}	40.0	39.9	−0.1
n-C_7H_{16}	44.9	44.9	0.0

present disposition of formal charges based on heats of formation, we can test such a model. Using the observed (for C_2H_6) values[14] of $r_{C-C} = 1.534$ Å/$r_{C-H} = 1.093$ Å, and all tetrahedral angles, and assuming no significant geometry changes on rotation, we can calculate a contribution to the rotation barrier of 0.030 kcal/mol, the staggered model having the lower energy. This is negligible compared to the experimental barrier of 2.9 kcal/mol.[14,15]

If we use the disposition of charges suggested by Clinton's model which would correspond to an almost ionic bond, we would find enormous electrostatic energies for the paraffins. This would seem to rule out rather definitively the purely electrostatic rotation barrier. The other simple model is one involving a steric repulsion between H atoms. On the basis of closest, nonbonded H···H distances in the crystalline hydrocarbons and their measured sublimation energies, Huggins[16] has proposed a set of empirical potential functions for nonbonded C–H, H–H, and C–C interactions. ($V_{H\cdots H}$ (kcal/mol) $= 4 \times 10^5 \exp(-5.4r) - 47r^{-6} - 98r^{-8} - 205r^{-10}$. The simpler function of McCullough and McMahon,[26] $V_{H\cdots H}$(kcal/mol) $= 43473r^{-12} - 105.9r^{-6}$, fits the data nearly as well.) These were fitted to the experimental rotation barrier in C_2M_6 as well (see Figure 1).

It has a potential minimum at $r_{H\cdots H} = 3.0$ Å ($V_{\min} \simeq -0.050$ kcal/mol) and a zero of interaction at $r_{H\cdots H} = 2.7$ Å. All the other potential functions which have been proposed are more repulsive at the closest $r_{H\cdots H}$ distances of 2.27 Å, which occur in the eclipsed form of ethane. Any proposal which ignores this strong repulsion will give unreasonable values for the H···H nonbonded distances in hydrocarbon crystals or incorrect sublimation energies. This H···H repulsion seems to us the most reasonable solution to the barrier problem and related structural anomalies of hydrocarbons.

The most recent theoretical analyses of the rotational barrier have come to the same conclusion; namely, that closed shell repulsion is the best description. Over the past decade there have been a number of efforts[18] to account for the anomalies in bond lengths and angles occurring in hydrocarbons including very branched molecules and strained rings. These treatments have required the use of a potential function for all bonded and nonbonded interactions. It is only in the most recent[18d] that electrostatic interactions have been introduced. The torsion potential has varied from a completely repulsive H···H interaction to one in which repulsion plays no role. The most recent efforts[18d] have employed H···H potentials very similar to Huggins! It is clear from this work that there is probably no unique choice of all of the potential parameters. For these reasons it is of considerable interest to try to introduce additional considerations, such as dipole moments and heats of formation, in an effort to further delineate the possible choices.

Another test of the model is to calculate the difference in energies between the trans and gauche conformations in n-C_4H_{10}. The presently computed model with $|y| = 0.0581$ electronic charge gives an energy of 0.15 kcal/mol, favoring the trans form compared to an experimental value of 0.8 ± 0.1 kcal/mol.[3b] If we construct a tetrahedral model of gauche butane, we find that in a perfectly staggered conformation, the nearest H atoms on the C-1 and C-4 atoms are only 1.8 Å apart, an impossibly close position. If we spread the C–C–C angles to the observed values of about 112.4°,[17] this distance increases to about 2.1 Å, still too close. Slight twists of about 13° in each of the terminal CH_3 groups could increase this separation to a very small interaction at $r_{H\cdots H} \sim 2.6$ Å at an energy cost of about 1.5 kcal/mol. While this is far too great compared to the empirical 0.8 kcal/mol, it suggests that even smaller twists and bends uniformly distributed over the molecule could reduce the H···H repulsion at a smaller energy cost. The calculation of these small energy changes would require the use of the complete potential function of the molecules which we are not yet in a position to make, but which has been done in many similar cases[18] in good quantitative agreement with our conclusions.

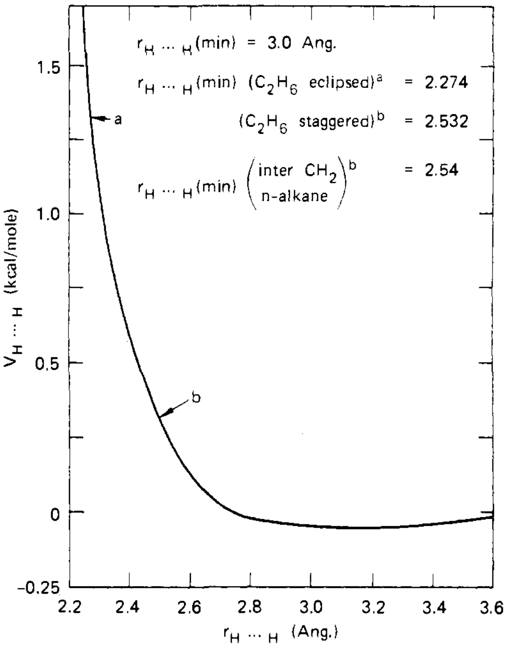
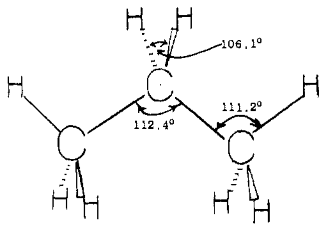


Figure 1. Graphic presentation of Huggins' nonbonded H···H interaction potential function.

Another piece of evidence which supports this steric H···H repulsion is the anomalous spreading of the C–C–C angle in n-paraffins from the expected tetrahedral angle at 109.5° to about 112.4°.[17] We have made calculations of E_{el} of the paraffins using this angle and find that it changes by a negligible amount, of the order of −0.02 kcal/mol per interaction. However, it does change the H···H distance of proximate H atoms on alternate CH_2 groups from 2.49 to 2.54 Å. (This changes further to 2.59 Å if we make allowance for the H–C–H angle in the CH_3 groups being reduced from tetrahedral (109.5°) to the observed 107.7°.) This would reduce the total H···H repulsion by about 0.22 kcal, using Huggins' potential function.[16] Allowance for the CH_3 conical angle contraction increases the savings to 0.40. If we calculate the energy necessary to bend the C–C–C angle from 109.5 to 112.4° using the known frequency of about 350 cm^{-1}, we find a value of 0.2 kcal/mol, in excellent agreement. This is also in accord with earlier, more extensive analyses.[18]

We find a similar phenomenon in the C=C–C bond



$$\mu_{CH_2} = 2\mu_{CH}\cos 53.1^\circ = 1.20\,\mu_{CH}$$

$$\mu_{CH_3} = 3\mu_{CH}\cos 68.8^\circ = 1.90\,\mu_{CH}$$

$$\mu_{C_3H_8} = \mu_{CH_2} - 2\mu_{CH_3}\cos 56.2^\circ = 0$$

$$\mu_{ind}(CH_2)_\perp = 0.151\ D$$

$$\mu_{ind}(CH_3)_\parallel = 0.062\ D$$

$$\mu_{net}(C_3H_8) = 0.089\ D\ (calc.)$$

$$= 0.083\ D\ (obs.)$$

Figure 2. Intrinsic and induced dipole moments for CH_3 and CH_2 groups in propane calculated from the observed geometrical structure of the molecule.

angle in olefins. Instead of the expected bond angle of 120°, we find a bond angle in the range 124 ± 1°.[19,20] In propylene this would make for a H···H distance of 2.40 Å between the H on the terminal CH_2 and the coplanar H of the *cis*-CH_3 group. This would correspond to a repulsion of about 0.5 kcal/mol using the Huggins' potential.[16] A slight twist of about 15° in the CH_3 group would increase H···H to about 2.6 Å and reduce their repulsion to about 0.1 kcal. We shall discuss this in more detail in a later paper.

IV. Dipole Moments

The formal charge model we have described so far is one which has been based exclusively on energy considerations. It leads to a C–H bond dipole moment of

$$\mu_{CH} = y r_{CH} = 0.278 \times 1.093\ D$$
$$= 0.304\ D$$

This value is in unexpectedly good agreement with values which had been suggested on the basis of stick-dipole models of substituted hydrocarbons[21] and also spectroscopic data on infrared intensities.[22] We can further compare it with the dipole moments of hydrocarbons which have been available from microwave measurements of Stark effects.[23]

The first hydrocarbon to show a dipole moment is propane, C_3H_8. The center of symmetry of CH_4 and C_2H_6 precludes such a property. If propane were composed of completely tetrahedral angles and constant C–H distances, it would not have a dipole moment. In actual fact, its observed dipole is very small, namely 0.083 D. Using the known geometry and the value of y obtained here, we calculate a dipole moment of 0.000 D (Figure 2)!

The zero value arises from a curious cancellation of compensating effects, namely, a closing of the H–C–H angle in CH_2 to 106.1° and a spreading of the C–C–C angle to 112.4°. Both of these effects would give a net moment of about 0.027 D were they not precisely canceled by a contraction of the CH_3 cone angle from tetrahedral (70.5°) to 68.6°.

If the observed dipole does not arise from the given disposition of charge, we can conclude that this disposition is not correct or the assumption of spherically symmetric formal charge distributions is incorrect. No reassignment of formal charges can satisfy both the energy considerations and the observed dipole moment. Thus we could fit the dipole moment by assigning a greater charge to each H in CH_3 of 25%, but this would completely vitiate the simple energy relations found.

The most satisfactory solution lies in the distortion of the electronic clouds in the CH_2 and CH_3 groups caused by the unsymmetrical electrostatic fields acting on them. Let us, for simplicity, consider the CH_2 and the CH_3 groups respectively as polarizable spheres carrying point dipoles, centers on the symmetry axis of each group, and located 0.36 Å from the C atom in CH_3 and 0.33 Å from the C atom in CH_2; both correspond to the projected positions of the H atoms along the symmetry axes.

We calculate an induced moment of 0.151 D in the CH_2 group (using $\alpha_{CH_2} = 1.8$ Å^3) by the two CH_3 groups. This is the induced component along the molecular symmetry axis. For the two CH_3 groups we calculate a net induced moment along the symmetry axis of 0.062 D), leading finally to a net molecular dipole of 0.089 D, in surprisingly good agreement with the observed 0.083 D. (The finite dipole model for CH_3 and CH_2 (using the assigned point charges located at the nuclei) and calculating the polarizations at each atom gives essentially the same result, $\mu = 0.079$ D.) The negative end of the dipole is located at the CH_2 group and the positive end at the methyls.

If we calculate the energy associated with these induced dipole moments, it is of the order of 0.1 kcal/mol and hence negligibly small. Laurie and Muenter[24] have discussed the polarity of the dipole moment in alkanes based upon some observations associated with D/H substitution $\mu(CH_3CD_2CH_3) = 0.094$ D, an increase of about 0.01 D. The accompanying change in the C–D bond length is a decrease of about 0.0035 Å. *i*-C_4H_{10} and *i*-$CD(CH_3)_4$ show the same quantitative change as does the pair CH_3F/CD_3F. Since in CH_3F the F end is certainly negative, the author's conclusion was that D/H substitution increases μ when it occurs at the positive end of the dipole. This is consistent with the substitution effects in propanes and isobutanes but not in methyl acetylenes.

However, the magnitudes of the changes are very different and suggest other effects are at work in D/H substitution. The direction of the $C^-{-}H^+$ bond dipole is more directly determined from the dipole moments of the halo *o*-, *m*-, and *p*-toluenes.[23] The observation $\mu_{ortho} < \mu_{para}$ indicates that the C–X bond dipole must have the same polarity as the H–C dipole. This is also in accord with the dipole moments of *cis*- and *trans*-1-halopropenes where it is found that $\mu_{trans} > \mu_{cis}$.

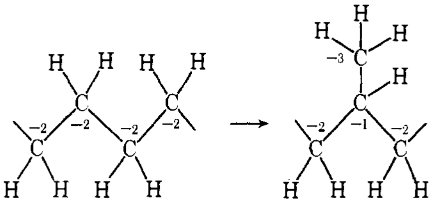
A similar analysis for isobutane which has a dipole moment of 0.132 D, about 50% greater than that of propane, gives again a net dipole dominated by the induced moment of the three methyl groups. The calculated value is about 0.125 D for a point dipole model and about 0.120 D for a point charge model. Again, the energies associated with these induced dipoles are negligible. (The energy of a dipole-induced dipole interaction is given classically by $E = 2\mu^2\alpha/r^6$ where μ is the point dipole, α the polarizability of the spherical matter, and r their distance apart.)

Discussion

The model presented for bonding in the hydrocarbons gives a very simple picture for the relative stability of the alkanes. If we explore the detailed contributions which make up E_{el}, for example, we find we can give a very simple explanation of the stability of the highly branched alkanes relative to the normal alkanes. In an *n*-paraffin chain the main stabilizing contribution to E_{el} is the attraction of bonded C and H atoms. Considering each neutral group CH_n in the chain separately, all other interactions are repulsive. The largest repulsive contributions come from adjacent CH_2 groups. When we isomerize an *n*-alkane to a branched alkane, we convert two CH_2 groups into a CH plus a CH_3 group. This gives a small increase in C–H attraction since the increase in charge on carbon going from methylene carbon ($-2y$) to methyl carbon ($-3y$) more than compensates the loss in C–H attraction going from CH_2 to CH. However, there is a bigger decrease in C–C repulsion since the methyl group we have created at the expense of a CH_2 now finds itself attached to a CH group as shown in the following diagram.

Table VI. Net Electrostatic Interactions of CH_3 and CH_2 Groups with Other Groups in the Normal Paraffin Chain of C_7H_{16}

	Net interaction energy (kcal/mol) with *n*th neighboring CH_2				
Group	1st	2nd	3rd	4th	5th
CH_3	0.609	0.139	0.0186	0.0131	0.0012
CH_2	0.356	0.116	0.0027	0.0131	



Considering only C–C repulsions we note a net change of $3(4)/r_{cc} = 12/r_{cc}$ in the *n*-paraffin going to $(2 + 2 + 3)/r_{cc} = 7/r_{cc}$ in the isomer.

It is also instructive to look at the detailed interaction in a long chain. Electrostatic interactions fall off inversely with distance and hence it might be expected that all groups in a paraffin chain would interact strongly with each other. In actual fact, each unit in a chain is electrically neutral and thus can be looked upon as a dipole whose interaction with other dipoles falls off as r^{-3} and thus very rapidly. This is seen in Table VI where we have itemized the detailed energies of interaction of a terminal CH_3 with successive CH_2 units in *n*-C_7H_{16} and also the interaction of a CH_2 group with successively more distant CH_2 groups. We see that all of the interactions are repulsive and small (*i.e.*, less than 1 kcal). They also fall off so rapidly that after the one to next-next-nearest neighbor, they can be neglected. Even the next-nearest neighbor is very small. This explains why group additivity rules can work so well since it includes all of the near-neighbor interactions implicitly.

We see that even with a more polar family of compounds, since E_{el} varies as y^2, that for bonds which might be even fourfold more polar than C–H (*i.e.*, $\mu \sim 1.0$ D) the electrostatic interactions would fall off very rapidly.

It has already been commented on that E_{el} is relatively insensitive to small changes in angle. This is again a consequence of the smallness of the nonbonded interactions. It is also not too sensitive to internuclear distances, a given per cent error in r_{bond} giving rise to about the same per cent error in E_{el}. Thus individual variations in C–H bonds in hydrocarbons which are of the order of 1% or less contribute negligibly to errors in E_{el}. The repulsive contribution, being very small, even 3% variations in C–C distances (*i.e.*, ±0.05 Å) would contribute negligibly to errors in E_{el}.

In subsequent papers we will deal with the unsaturated hydrocarbon molecules and free radicals which fit the data as well as the saturated species. We will also deal with polar compounds, halogens, oxygen, and nitrogen compounds in which polarization effects are much more important and which also show good agreement with the data. Here the quantitative agreement is not quite so good as with the hydrocarbons and the large polarization effects introduce another significant parameter.

In concluding, we should like to acknowledge the work of Professor V. A. Palm[25] which was brought to our attention during the preparation of this manuscript and which represents a very similar approach with parallel conclusions.

References and Notes

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