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Properties of Atoms and Bonds in Hydrocarbon Molecules

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Abstract: The properties of atoms and bonds in hydrocarbon molecules are determined and discussed. The properties of a bond are characterized in terms of the properties of the bond path which links the same nuclei for the particular situation in which the forces on all the nuclei vanish. The value of the *total* charge density at a bond critical point is found to be characteristic for a bond of given formal order. The cyclopropenium and tropylium cations, which satisfy the Hückel $4m + 2$ rule, exhibit the same carbon–carbon bond order as benzene. A linear bond-order–bond-length relationship is obtained for carbon–carbon bonds in terms of this property of the total charge density. An in situ bond energy is defined in terms of an integral of the charge density over the associated interatomic surface. This relationship is based on a result obtained from the atomic statement of the hypervirial theorem. The strain energy of a bond, as measured relative to the carbon–carbon bond energy in ethane, is found to parallel the geometrical strain as determined by the curvature of the bond path. The average electron populations of the atoms are determined and their variation with changes in structure are discussed.

Introduction

The preceding paper[2] illustrated how the definitions of structure and structural stability evolved as consequences of the identification of an atom with a region of real space as determined by the topological properties of a molecular charge distribution. In the present paper we investigate the quantum mechanical consequences of this definition of atoms through a study of their properties and of the properties of the bonds which link them.[3]

II. Bond Properties

Bond Path and the Chemical Bond. The molecular graphs previously illustrated[2] are for molecules in their equilibrium geometries wherein the forces on all the nuclei vanish. In general, equivalent molecular graphs are obtained for all nuclear configurations in the neighborhood of an equilibrium or minimum energy geometry. As discussed in the preceding paper, this generic property of a molecular graph is essential for the definition of molecular structure. It is the property which enables one to associate a stable molecular structure with a minimum energy geometry of the nuclei, a geometry characterized by the vanishing of the forces exerted on the nuclei. Thus equivalent molecular graphs are necessarily obtained for molecular geometries removed from equilibrium, geometries in which the dominant interatomic interactions, as determined by the forces exerted on the nuclei, are either attractive or repulsive.

The term "bond" in the language of chemistry is used in a wide variety of physical contexts. Its single most important use, however, is to categorize the interactions between what are assumed to be bonded pairs of atoms in the situation where the forces on all the nuclei vanish, an equilibrium configuration. Thus physical properties ascribed to a bond such as bond length, bond force constant, bond order, and bond energy, along with the empirical laws which interrelate such properties, all implicitly refer to the properties of a molecule in a minimum-energy geometry. Measured physical properties are, of course, obtained as averages over the zero-point vibrational motions of this nuclear configuration. Clearly, if one wishes to retain this quantitative use of the term bond within the context of the present theory, then its use should be reserved to describe the situation wherein two atoms are linked by a bond path in an equilibrium geometry. Hence, the molecular graphs for equilibrium geometries[2] are to be interpreted as representations of the corresponding networks of bonds. The nature and properties of the bonds are to be characterized in terms of the properties of the bond paths which are themselves determined by the properties of the charge distribution for the particular situation in which the forces on all the nuclei vanish. As demonstrated below, the bond paths in such situations do indeed exhibit characteristic sets of properties for bonds of a given chemical type.

The Lewis model which equates one bond to one pair of valence electrons, when applied to hydrocarbons in singlet ground states, predicts the existence of four kinds of CC bonds. They may be described as possessing formal bond orders of 1, 1.5 (to replace the resonance model), 2, and 3. The chemistry of the hydrocarbons reflects the existence of four types of CC bonds, and their observed bond lengths fall neatly into four corresponding relatively narrow ranges of values. In addition to duplicating the network of Lewis bonds in the eqiulibrium geometries of the hydrocarbon molecules,[2] the properties of the individual bond paths reproduce in a quantitative manner, the characteristic properties which have been ascribed to the bonds of the Lewis model.

Bonded Radii of an Atom. The geometrical distance from the nucleus of an atom A to the bond critical point which links A to a neighboring atom B is called the bonded radius of A with respect to B[4] and is denoted by $R_B(A)$ in Tables I and II. Since atoms must be space-filling, must respond to a wide range of external forces, and may possess a continuously variable average electron population, one cannot expect constant values for bonded radii. The interesting observation that does emerge is that, while characteristic bond lengths are observed, this constancy is obtained at the expense of variable bonded radii. As an example, consider the molecule $C_3H_7^+$ previously illustrated[2] (Figure 1b[2]). In the Lewis model the CC bonds in this molecule are of order 1 and the bond length falls within the corresponding range, 2.8–2.9 au. To attain the zero force requirement of the equilibrium geometry, electronic charge is transferred from the terminal carbons to the central carbon atom. Thus $R_C(C')$ for the central carbon C′ increases to 1.82 au while that for the terminal carbons decreases to 1.02 au from the value 1.45 au found in ethane. What is remarkable is that in spite of this change of $\sim\pm30\%$ in the bonded radii determining the bond length, the overall CC bond length changes by only 3% from its value in ethane. Changes in carbon bonded radii are generally small for bonds in neutral saturated hydrocarbon molecules. However, they may be as large or larger than those noted above, for carbon atoms forming bonds of order 2 or 3 (see Table I).

The bonded radii of H bonded to C exhibit smaller variations (Table II). In the neutral hydrocarbons the values of $R_C(H)$ fall in the range 0.82–0.88 au. The associated $R_H(C)$ values range between 1.18 and 1.22 au. In the positively charge molecular ions the value of $R_C(H)$ decreases to 0.75–0.79 au. The exceptional value of $R_C(H)$ for $C_3H_3^+$ is discussed later.

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[2] R. F. W. Bader, T. H. Tang, Y. Tal, and F. W. Biegler-König, *J. Am. Chem. Soc.*, preceding paper in this issue.

[3] R. F. W. Bader, *J. Chem. Phys.*, **73**, 2871 (1980); R. F. W. Bader and T. T. Nguyen-Dang, *Adv. Quantum Chem.*, **14**, 63 (1981).

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Table I. Properties of CC Bonds (in atomic units)

molecule and bond[a]	R_e	$R_C(C')$[b]	$R_{C'}(C)$	$\rho(\mathbf{r}_c)$	$\nabla^2\rho(\mathbf{r}_c)$
Bonds of Order 1					
C_2H_6 B	2.906	1.453	1.453	0.241	−0.652
C_3H_8 C	2.912	1.477	1.435	0.241	−0.646
i-C_4H_{10} D	2.910	1.488	1.422	0.242	−0.650
$C_3H_7^+$ E	2.835	1.017	1.818	0.237	−0.419
C_3H_6 F	2.838	1.431	1.431	0.242	−0.613
C_4H_8 G	2.937	1.469	1.469	0.239	−0.636
C_4H_4 H	2.782	1.410	1.410	0.246	−0.588
C_4H_6 I1	2.776	1.406	1.406	0.243	−0.550
C_4H_6 I2	2.837	1.400	1.458	0.240	−0.579
C_3H_6 O	2.872	1.434	1.439	0.245	−0.665
C_4H_6 P	2.812	1.406	1.406	0.255	−0.697
C_3H_4 Q	2.821	1.339	1.511	0.237	−0.537
C_4H_6 R1	2.884	1.450	1.439	0.245	−0.652
C_4H_6 R2	2.957	1.481	1.481	0.233	−0.607
C_6H_6 T1	2.740	1.386	1.386	0.256	−0.628
C_6H_6 T2	2.872	1.489[c]	1.404	0.232	−0.524
C_6H_6 T3	2.872	1.394	1.479	0.245	−0.630
C_3H_4 U	2.804	1.209	1.596	0.248	−0.643
C_5H_8 V	2.920	1.468	1.460	0.240	−0.614
Bonds of Order 1.5					
C_6H_6 J	2.646	1.323	1.323	0.291	−0.800
$C_3H_3^+$ K	2.602	1.314	1.314	0.290	−0.770
$C_7H_7^+$ L	2.642	1.321	1.321	0.290	−0.822
$C_3H_5^+$ M	2.617	1.665	0.953	0.289	−0.580
$C_2H_5^+$ X	2.651	1.333	1.333	0.285	−0.827
Bonds of Order 2					
C_2H_4 N	2.468	1.234	1.234	0.329	−0.900
C_3H_6 O	2.472	1.006	1.466	0.328	−0.839
C_4H_6 P	2.481	1.106	1.375	0.326	−0.890
C_3H_4 Q	2.413	1.220	1.220	0.335	−0.890
C_4H_6 R	2.483	1.242	1.242	0.331	−0.917
C_6H_6 T4	2.513	1.257	1.257	0.321	−0.858
Bonds of Order 3					
C_2H_2 S	2.207	1.104	1.104	0.368	
C_3H_4 U	2.211	1.127	1.084	0.364	

[a] The identifying letters refer to the molecular graphs shown in Figure 2 of the preceding paper.[2] [b] $R_C(C')$ is the bonded radius of the least substituted atom in the bond. [c] C' is common to bonds 1 and 2 (Figure 2[2]).

Table II. Properties of CH Bonds (in atomic units)

molecule and bond[a]	R_e	$R_C(H)$	$R_H(C)$	$\rho(\mathbf{r}_c)$	$\triangle^2\rho(\mathbf{r}_c)$
CH_4 A	2.047	0.860	1.187	0.267	−0.678
C_2H_6 B	2.052	0.866	1.186	0.266	−0.673
C_3H_8 C1	2.052	0.867	1.186	0.266	−0.671
C_3H_8 C2	2.058	0.871	1.187	0.265	−0.668
C_4H_{10} D1	2.052	0.867	1.185	0.266	−0.670
C_4H_{10} D2	2.059	0.877	1.182	0.265	−0.666
$C_3H_7^+$ E1	2.058	0.786	1.272	0.261	−0.707
$C_3H_7^+$ E2	2.103	0.745	1.359	0.257	−0.770
C_3H_6 F	2.043	0.856	1.187	0.266	−0.671
C_4H_8 G	2.054	0.870	1.185	0.265	−0.666
C_4H_4 H	2.020	0.824	1.196	0.263	−0.665
C_4H_6 I1	2.049	0.856	1.192	0.266	−0.674
C_4H_6 I2	2.035	0.842	1.194	0.263	−0.656
C_6H_6 J	2.041	0.861	1.180	0.265	−0.670
$C_3H_3^+$ K	2.069	0.696	1.373	0.254	−0.809
$C_7H_7^+$ L	2.079	0.795	1.284	0.262	−0.713
$C_3H_5^+$ M1	2.079	0.760	1.319	0.261	−0.764
$C_3H_5^+$ M2	2.048	0.777	1.271	0.267	−0.740
C_2H_4 N	2.045	0.860	1.184	0.264	−0.663
C_3H_6 O1	2.050	0.859	1.191	0.267	−0.680
C_3H_6 O2	2.043	0.865	1.178	0.264	−0.656
C_3H_6 O3	2.050	0.867	1.184	0.263	−0.658
C_4H_6 P1	2.043	0.860	1.182	0.264	−0.755
C_4H_6 P2	2.050	0.862	1.189	0.263	−0.714
C_3H_4 Q1	2.054	0.868	1.186	0.263	−0.643
C_3H_4 Q2	2.032	0.828	1.204	0.262	−0.665
C_4H_6 R1	2.058	0.867	1.191	0.263	−0.658
C_4H_6 R2	2.045	0.861	1.183	0.261	−0.654
C_2H_2 S	2.013	0.809	1.204	0.265	−0.707
C_3H_4 U1	2.056	0.845	1.211	0.265	−0.680
C_3H_4 U2	2.011	0.817	1.194	0.264	−0.693

[a] Identifying letters refer to molecular graphs in Figure 2 of preceding paper.[2] Nonequivalent CH bonds are listed in the order CH_3, CH_2, CH. Since these properties of conformationally related CH bonds are nearly identical in value, only one such set of properties is listed.

Table III. CC Bond Path Lengths (BPL)

molecule	BPL, au	BPL/R_e	d,[a] au
cyclobutane	2.938	1.0004	0.024
cyclobutene	2.891 (R1)	1.002	0.090
	2.963 (R2)	1.002	0.085
	2.495 (double)	1.005	0.075
cyclopropane	2.889	1.018	0.182
bicyclo[1.1.1]pentane	2.931	1.004	0.127
benzvalene	2.799 (T1)	1.021	0.220
	2.924 (T2)	1.018	0.155
	2.875 (T3)	1.001	0.050
	2.520 (T4)	1.003	0.040
bicyclo[1.1.0]butane	2.841 (bridge)	1.024	0.222
	2.884	1.017	0.174
tetrahedrane	2.847	1.023	0.230
cyclopropene	2.881 (single)	1.021	0.200
	2.457 (double)	1.018	0.180
cyclopropenium cation	2.641	1.015	0.185

[a] Perpendicular displacement of (3,−1) critical point from internuclear axis.

Bond Path Length. It is found that in those molecules with geometrical angles which are not consistent with the model of directed valence, the bond paths are not coincident with the internuclear axes between the bonded pairs of atoms. Instead, where the models predict strained or bent bonds,[5] the bond paths are outwardly curved from the perimeter of a three- or four-membered ring or from the edges of a cage structure. Identification of the bond with the bond path for equilibrium strutures implies that the bond length should be equated not to the geometrical distance separating a bonded pair of nuclei, but to the actual and somewhat longer length of the bond path which links the nuclei, the bond path length. As the geometrical interpretation of bond length is well established, the bond path length is reported as another property of a bond. Listed in Table III are the bond path lengths and their ratios with the corresponding bond lengths for bonds in some highly strained molecules. Also tabulated is the perpendicular distance d separating the (3,-1) critical pint of the bond path from the internuclear axis.

As a consequence of the curvature of a bond path, the charge density is not distributed so as to maximize the force of attraction it exerts on the nuclei. As is to be illustrated later, this effect leads to a weakening of the bond in spite of the fact that such strained bonds, in general, exhibit internuclear distances which are shorter than normal. Bond paths which are not curved in the molecular graph for an equilibrium geometry become so when the system is displaced from this configuration of minimum energy. In the equilibrium geoometry of ethylene the CH bond paths are coincident with the corresponding internuclear axes; i.e., the HCH bond path angle equals the HCH geometrical angle. When the HCH angle is decreased, the bond path angle exceeds the geometrical angle as the CH bond paths are now outwardly curved (see Figure 1). The relaxation of ρ induced by this motion, as reflected in the curvature induced in the bond paths, is such as to exert a restoring force on the protons to return them to their equilibrium positions. Thus the energy increase caused by a displacement away from an equilibrium configuration is reflected in the appearance of curvatures in the bond paths, corresponding to the physical picture of straining the links between the atoms.

It has been previously noted that information paralleling the relaxation of $\rho(\mathbf{r})$ caused by a change in bond angle, whether it facilitates or retards such a motion, is built into the static charge

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(5) C. A. Coulson and W. E. Moffitt, *Phil. Mag.*, **40**, 1 (1949).

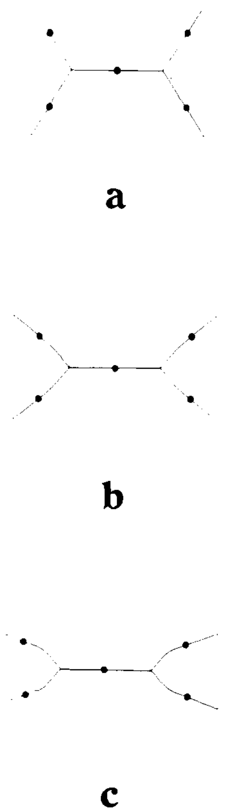

Figure 1. Molecular graphs for ethylene: (a) in its equilibrium geometry, HCH = 115.6°; (b) HCH = 85.6°, 45 kcal/mol higher in energy than (a); (c) HCH = 58.8°, 189 kcal/mol higher in energy than (a). The HH separation in (c) is 2.01 au, the smallest internuclear separation in this geometry. The values of $R_{CC} = 2.468$ au and $R_{CH} = 2.045$ au are the same in all structures. Bond critical points are denoted by solid circles.

distribution via the curvature of the bond paths.[6] An early demonstration of the incomplete following of a bending mode by $\rho(\mathbf{r})$ was provided by Chang et al.[7] for the methyl radical through displays of the CH bonding orbital densities for various out-of-plane bending angles. Nakatsuji et al.[8] make similar conclusions regarding the behavior of $\rho(\mathbf{r})$ in the bending of NH_3, NH_3^+, and CH_3^+ through an interpretation of density difference maps and the forces exerted on the nuclei. It has been suggested by Wiberg and Wendoloski[9] that the curvature of the CH bond path obtained in a bending mode of acetylene makes a significant contribution to the dipole moment derivative determining the infrared intensity of this motion.

A molecular graph is not trivial in the sense that it is not necessarily obtained by linking nearest neighboring atoms. While the structures of equilibrium geometries may correspond to this situation, even a significant displacement from such a configuration does not necessarily lead to a change in structure if the original structure is energetically stable. Even a large decrease in the HCH angle of ethylene, for example, while resulting in an increased curvature of the CH bond paths, does not result in the formation of a new bond path between the protons (Figure 1). Such a structural change could be obtained only at the expense of a very large increase in the energy of the system. Thus the energetic stabilities of structures as anticipated on the basis of physical models of bonds is reflected in their corresponding structural stabilities as defined in terms of the generic properties of the associated molecular graphs.

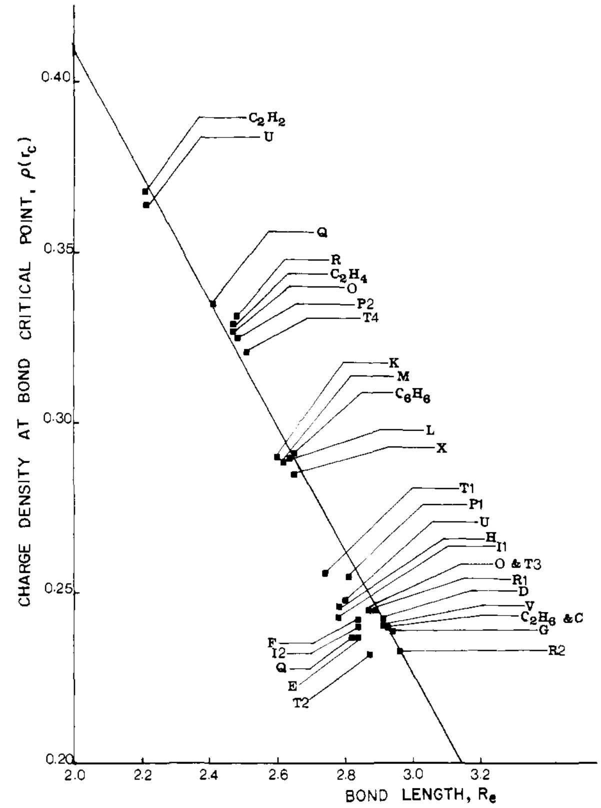

Figure 2. Bond-order–bond-length relationship for CC bonds in hydrocarbons. The bond order is characterized by the value of the total charge density at the CC bond critical point. The values of $\rho(r_c)$ and R_e are in au. The molecules whose points are used to determine the linear relationship expressed in eq 2 are labeled by their chemical formulas. The other points are labeled by a letter or a letter and a number as referenced in Figur 2 of the preceding paper.[2] The point labeled X is for the conflict structure of $C_2H_5^+$, Figure 3I. The points for the strained bonds of order 1.0 and 1.5 are all displaced closer to the line if $\rho(r_c)$ is plotted vs. the bond path length rather than the bond length. Point F for cyclopropane, for example, is then displaced by only 0.02 au from the line, the width of one solid square.

Definition of Bond Order. To attain the situation of zero force necessary for the formation of a bond requires that electronic charge be accumulated in the internuclear region in an amount greater than that obtained by the overlap of the undistorted atomic densities.[10] This accumulation of charge is necessary to balance both the large values of the nuclear repulsive force found for values of the internuclear separation R in the neighborhood of its equilibrium value R_e and the force resulting from any polarization of the charge density into antibinding regions. Thus it is to be anticipated that for a pair of atoms which can exhibit a number of characteristic bond lengths, a situation rationalized in terms of the Lewis model by the possibility of "multiple bonds", the value of the charge density at the bond critical point, $\rho(\mathbf{r}_c)$, will increase as the bond length decreases. This conjecture is found to be true and is illustrated for the CC bonds of hydrocarbons in Figure 2, and by the values of $\rho(\mathbf{r}_c)$ given in Table I. The variation of $\rho(\mathbf{r}_c)$ with R_e for the CC bonds in ethane, benzene, ethylene, and acetylene is best represented (in terms of the STO-3G model) by the linear relationship (expressed in au)

$$\rho(\mathbf{r}_c) = -0.184R_e + 0.777 \tag{1}$$

as indicated by the heavy line in the figure. Equation 1 exhibits a root-mean-square deviation of 0.003. This behavior of $\rho(\mathbf{r}_c)$ is similar to that of Coulson's bond-order parameter which was to provide a measure of the π-bond order of CC bonds in Hückel theory.[11] The relationship expressed in eq 1 is a generalization of the bond-length–bond-order relationship, and, while it is em-

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(6) G. R. Runtz, R. F. W. Bader, and R. R. Messer, *Can. J. Chem.*, **55**, 3040 (1977).

(7) S. Y. Chang, E. R. Davidson, and G. Vincow, *J. Chem. Phys.*, **52**, 5596 (1970).

(8) H. Nakatsuji, S. Kanayama, S. Harada, and T. Yonezawa, *J. Am. Chem. Soc.*, **100**, 7528 (1978).

(9) K. B. Wiberg and J. J. Wendoloski, *J. Comput. Chem.*, **2**, 53 (1981).

(10) R. F. W. Bader, "An Introduction to the Electronic Structure of Atoms and Molecules", Clarke Irwin, Toronto, 1970.

(11) C. A. Coulson, *Proc. R. Soc. London, Ser. A* **169**, 413 (1939).

pirical, it is based on a property of the *total* observable charge density. This linear relationship between $\rho(\mathbf{r}_c)$ and R_e persists for densities obtained using basis sets of better quality.[12]

The first important observation to be made regarding Figure 2 is that the points are clustered into four groups. Thus there are four observed relatively narrow ranges of CC bond lengths and correspondingly, four (potentially) observable and equally narrow ranges of values of $\rho(\mathbf{r}_c)$. In terms of the Lewis model these four groupings correspond to formal bond orders of 1, 1.5, 2, and 3. Within each cluster of points the percentage variation in the value of $\rho(\mathbf{r}_c)$ is equal to the percentage variation in the value of R_e. Thus the prediction of the Lewis model regarding the existence of four kinds of CC bonds is reflected not only in the observation of characteristic bond lengths, but also in a property of the distribution of charge found for the equilibrium geometry. These characteristic values for $\rho(\mathbf{r}_c)$ and R_e are found for CC bonds in a wide range of differing equilibrium structures, neutral and charged, strained and unstrained.

For structurally related molecules, such as ethane, propane, and isobutane, the values of $\rho(\mathbf{r}_c)$ for the CC bonds are essentially constant (Table I). The next to largest value of $\rho(\mathbf{r}_c)$ for the bonds of order 1 and the next to lowest value for bonds of order 2 are found for the corresponding bonds in 1,3-*trans*-butadiene, a result not unanticipated on chemical grounds. The largest value of $\rho(\mathbf{r}_c)$ for single bonds is found for the relatively short bridging bond in benzvalene. In those cases where the bond is noticeably curved or strained and the bond critical point is displaced from the internuclear axis, the value of the charge density at the critical point again retains the value characteristic of that order. Since the bond lengths for strained bonds of order 1 and 1.5 are shorter than normal, the points for these bonds fall below the line determined by the normal unstrained bonds. If these same values of $\rho(\mathbf{r}_c)$ are plotted vs. their corresponding (and somewhat longer) bond path lengths (Table III), they fall on the line or are displaced closer to it. For example, the point T1 is then almost coincident with P1, and the points R1 and V fall on the line. The point K for $C_3H_3^+$ is then nearly coincident with the point for benzene.

The invariance in the values of R_e and $\rho(\mathrm{r}_c)$ for CC bonds of a given order are quite remarkable when viewed in terms of the substantial reorganization of the charge density over which the invariance is observed to occur. Compare, for example, the very different positionings of the CC bond critical points in C_3H_8 and $C_3H_7^+$ (Figure 1[2]). In spite of this difference, their values of $\rho(\mathbf{r}_c)$ are almost the same.

The cyclopropenium and tropylium cations (Figure 2[2]) satisfy the Hückel $4m + 2$ rule for aromatic character. Unlike benzene, neither of these cations possesses the number of π electrons required to yield a formal CC bond order of 1.5. However, the values of $\rho(\mathbf{r}_c)$ for their CC bonds are the same as the value found for benzene (Table I). Assuming CH bond orders of unity, $C_3H_3^+$ would have a formal CC bond order of 1.33. Instead, charge density is transferred from the hydrogens to the carbons in an amount sufficient to yield values of $\rho(\mathbf{r}_c)$ for the CC bonds and a net charge on the carbons (+0.06 e, Table VI) equal to the corresponding values found in benzene. Correspondingly, the values of $\rho(\mathbf{r}_c)$ and $R_C(H)$ for the CH bonds in $C_3H_3^+$ are the smallest of all the values listed in Table II, and the net positive charge on the hydrogens in this cation is the largest for all of the systems studied (Table VI). The same effects are found for the hydrogens and the CH bonds in $C_7H_7^+$, but they are less pronounced as the number of valence electrons in this cation is sufficient to yield a formal CC bond order of 1.43. Hückel's prediction that the presence of certain numbers of π electrons in a cyclic hydrocarbon will yield CC bonds with particular properties is borne out by the properties of the total charge density.[13]

In all of the hydrocarbons reported in Table II, every CH bond has a formal bond order of 1 and the values of R_e vary by $\sim 2\%$ about a mean value of 2.035 au. Correspondingly, the values of $\rho(\mathrm{r}_c)$ for the nearly 50 different CH bonds found in these molecules deviate by only $\pm 2\%$ from a value of 0.265 au. There are two exceptions. For a CH bond in $C_3H_7^+$ and as referred to above, for the CH bonds in $C_3H_3^+$, the values of $\rho(\mathrm{r}_c)$ lie between 0.25 and 0.26 au. The value of $\rho(\mathrm{r}_c)$, equal to 0.136 au, for the two bonds linking the bridging H in edge-protonated cyclopropane (Figure 3k[2]), is approximately one-half of the value observed for CH bonds of order 1.

The relationship between R_e and $\rho(\mathrm{r}_c)$ illustrated in Figure 2 shows that a knowledge of the bond lengths of a hydrocarbon molecule infers a knowledge of the values of the charge density at each of its bond critical points. Bonds of a given order are, in general, not chemically equivalent. The CH bonds in Table II range from acetylenic systems where H bears a net positive charge to saturated systems where it bears a net negative charge.

Other properties of $\rho(\mathbf{r})$ at (3,-1) or bond critical points provide further characterizations of the interactions between atoms. The negative and positive eigenvalues of the Hessian matrix of $\rho(\mathrm{r})$ (a matrix of the nine second derivatives of ρ) at a (3,-1) critical point determine the curvatures of the charge density at this point in directions perpendicular to parallel to the bond path, respectively. The trace of the Hessian matrix, the sum of its eigenvalues, equals $\nabla^2\rho(\mathbf{r}_c)$.

For molecules which form bound molecular states with little or no charge transfer, "covalent binding", the value of $\rho(\mathbf{r}_c)$ is relatively large and exceeds the value obtained by the corresponding overlap of the undistorted atomic densities.[4,10] The accumulation of charge in the binding region leads to a lessening of the curvature of the charge density along the internuclear axis. There is also a general contraction of the charge toward the axis in directions perpendicular to it, and hence the two negative eigenvalues are large in magnitude. Thus covalent binding is characterized by the charge density exhibiting large negative curvatures perpendicular to the bond and a relatively small positive curvature along the bond at the position of the (3,-1) critical point.[14] Consequently, $\nabla^2\rho(\mathrm{r}_c) < 0$. For example, the values of $\nabla^2\rho(\mathrm{r}_c)$ obtained from near-Hartree–Fock densities for H_2 ($^1\Sigma_g^+$), N_2 ($^1\Sigma_g^+$), and CH ($^2\Pi_r$) are respectively −1.379, −3.050, and −1.039 au. In contrast to the formation of a bound molecular state, the approach of two closed-shell atoms to yield an unbound state results in the removal of charge density from the region between the nuclei, the binding region. The values of $\rho(\mathrm{r}_c)$ for Ne_2 and He_2, for example, are relatively low in value and less than the value obtained by the corresponding overlap of the undistorted atomic densities.[10] This removal of charge density from the binding region

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(12) The values of $\rho(\mathbf{r}_c)$ for the CC bonds of the same molecules at the same molecular geometries, for densities obtained from wave functions expanded in terms of the 6-31G basis set, while slightly different from the STO-3G values, yield an even better linear relationship with R_e. These data yield $\rho(\mathrm{r}_c) = -0.283R + 1.043$ with a root-mean-square deviation of 1.6×10^{-3}. The values (au) of $\rho(\mathrm{r}_c)$ for the 6-31G model are: 0.2219 (C_2H_6), 0.2915 (C_6H_6), 0.3443 (C_2H_4), 0.4189 (C_2H_2). The value of $\rho(\mathrm{r}_c)$ for the CC bond in C_2H_6 obtained from a wave function close to the Hartree–Fock limit and at the corresponding minimum energy geometry ($R_{CC} = 2.9159$ au) is 0.2086 au.

(13) The value of $\rho(\mathrm{r})$ is invariant to any unitary transformation of the set of molecular orbitals used in the representation of the state function. For a particular choice of representation, a (3,−1) critical point may be contained in one or more of the nodal surfaces generated by the molecular orbitals. Since all orbitals of a given set and their densities are coupled by the self-consistent field, the presence of an orbital mode at r_c does not imply that $\rho(\mathrm{r}_c)$ is unaffected by the degree of occupation of that orbital. For example, vertical ionization of an electron from the π orbital of OH ($X^2\Pi$) at R_e to form OH^+ ($X^3\Sigma^-$) causes $\rho(\mathrm{r}_c)$ to decrease from 0.376 to 0.364 au. Similarly, electron attachment to form OH^- ($X^1\Sigma^+$) causes $\rho(\mathrm{r}_c)$ to change to 0.367 au. These changes in the occupation number of the π orbital result in substantial changes in the total charge density, the changes in the "σ-like" region along the axis being as large as the changes in the "π-like" regions. (See P. E. Cade, R. F. W. Bader, and J. Pelletier, *J. Chem. Phys.*, **54**, 3517 (1971) for density difference maps illustrating these reorganizations of $\rho(\mathrm{r})$.) These changes in $\rho(\mathrm{r})$ result in the creation of net repulsive (in OH^+) and net attractive (in OH^-) forces acting on the nuclei. The reorganizations of the charge distributions required to reestablish electrostatic equilibrium, i.e., to obtain the distributions characterizing the bonds in OH^+ and OH^-, are reflected in the final values of $\rho(\mathrm{r}_c)$. The values (au) of R_e and $\rho(\mathrm{r}_c)$ are: OH^+ (1.944, 0.306), OH (1.834, 0.376), and OH^- (1.781, 0.397), the value of $\rho(\mathrm{r}_c)$ increasing with the number of "bonding" π electrons. **Note Added in Proof**: The point for $C_5H_5^-$ (another six π electron system), is nearly coincident with that for benzene in Figure 2. For $C_5H_5^-$, $\rho(\mathbf{r}_c) = 0.292$ au, $R_e = 2.636$ au.

(14) R. F. W. Bader and H. J. T. Preston, *Int. J. Quantum Chem.*, **3**, 327 (1969).

Table IV. Hydrocarbon Bond Energies

	CH bonds			CC bonds				thermo-chemical[b] strain/ CC bond
molecule	bond	N(C,H)	B(C,H), kcal/mol	bond	N(C,C)	B(C,C), kcal/mol	strain energy[a]	
methane	CH	1.904	105.1					
ethane	CH	1.913	105.0	CC	3.316	90.8		
propane	CH(CH_3)	1.913	105.0					
	CH(CH_3)	1.912	105.0	CC	3.375	92.1		
	CH(CH_2)	1.920	105.5					
isobutane	CH(CH_3)	1.908	104.7					
	CH(CH_3)	1.908	104.8	CC	3.476	94.9		
	CH(CH)	1.931	105.3					
isopropyl cation	CH(CH_3)	1.794	98.3					
	CH(CH_3)	1.758	96.0	CC	3.371	97.0		
	CH(CH)	1.680	87.8					
cyclobutane	CH(exo)	1.910	104.7	CC	3.119	83.6	7.2	6.8
	CH(endo)							
cyclopropane	CH	1.888	104.6	CC	2.885	82.8	8.0	9.3
bicyclo[1.1.1]pentane	CH(CH_2)	1.900	103.5	CC	3.076	83.5	7.3	(10)
	CH(CH)	1.867	101.8					
bicyclo[1.1.0]butane	CH(CH_2)	1.888	104.0	CC (b)[c]	2.776	71.2	19.6	13
	CH(CH_2)	1.881	103.2	CC	2.837	77.4	13.4	
	CH(CH)	1.838	102.6					
tetrahedrane	CH	1.802	102.1	CC	2.463	73.6	17.2	(21.2)

[a] Strain energy is calculated relative to B(C,C) of ethane as zero strain energy. [b] Estimated from thermochemical data, ref 15. Values in parentheses are estimates based on theoretical calculations of energy changes, ref 15. [c] Bridge.

leads to steep gradients in $\rho(\mathbf{r})$ along the internuclear axis in the neighborhood of the critical point. Thus for these molecules $\nabla^2\rho(\mathbf{r}_c) > 0$ since its value is dominated by the relatively large positive curvature of $\rho(\mathbf{r})$ at the critical point.[14] For He_2 ($^1\Sigma_g^+$) and Ne_2 ($^1\Sigma_g^+$) both for $R = 3.0$ au the values of $\nabla^2\rho(\mathbf{r}_c)$ are +0.250 and +1.354 au.

The idealized model of ionic bonding is based upon the properties of a charge distribution in which it is assumed that essentially all of the valence charge of one atom is transferred to the other to yield two closed-shell ions. The initial force of attraction between the oppositely charged ions is, for some value of the internuclear separation, balanced by the repulsion resulting from the close approach of the two closed-shell ions. One anticipates that the properties of the charge densities at the (3,-1) critical points for such molecules should be similar to those observed above for the approach of two closed-shell atoms. This is found to be the case for molecules such as LiF, NaF, and NaCl, for example. The values of $\rho(\mathbf{r}_c)$ are small,[4] in the range 0.05 to 0.08 au, and the values of $\nabla^2\rho(\mathbf{r}_c)$ are all greater than zero.

The values of $\nabla^2\rho(\mathbf{r}_c)$ reported in Tables I and II are all less than zero with small positive curvatures for $\rho(\mathbf{r}_c)$ along the bond axis as is characteristic of covalent binding. In addition, the values of $\nabla^2\rho(\mathbf{r}_c)$ fall into ranges characteristic of bonds of a given order. The magnitude of $\nabla^2\rho(\mathbf{r}_c)$ increases along with the bond order as a result of the positive curvature at $\rho(\mathbf{r}_c)$ decreasing as the amount of charge accumulated in the binding region increases. The eigenvalues of the Hessian of $\rho(\mathbf{r}_c)$ for the CC bond of C_2H_6, for example, are −0.40, −0.40, and +0.16 au, while for C_2H_4 they are −0.57, −0.33, and +0.004 au. The "π-like" nature of the charge distribution of a bond of order 2 is reflected in the differing curvatures of $\rho(\mathbf{r})$ perpendicular to the internuclear axis, the curvature in the direction perpendicular to the plane of the nuclei being of smallest magnitude.

Bond Energy. The atomic statement of the hypervirial theorem relates an atomic property (the average of an operator over the basin of the atom) to an integral over the surface of the atom.[3] Since every bonded pair of atoms shares a common interatomic surface, this theorem enables one to relate a sum of atomic properties for each such pair to a corresponding surface integral. It has been shown[3] that the sum of the atomic averages of the commutator $[H,r^2]$, where H is the Hamiltonian and r is the radial distance from the nucleus, for a bonded pair of atoms yields the surface integral

$$N(\mathrm{A,B}) = \mathbf{R}_{ab}\cdot\oint S(\mathbf{r})\rho(\mathbf{r})\mathbf{n}_a(\mathbf{r}) \qquad (2)$$

where $\mathbf{R}_{ab}$ is the vector from the nucleus of A to that of B and $\mathbf{n}_a$ is the unit vector normal to the surface, outwardly directed from A. When the length of $\mathbf{R}_{ab}$ equals the bond length, N(A,B) is a measure of the number of electrons involved in the formation of a bond between A and B as determined by the changes in their gradient vector fields, from their radial forms in the free atoms for which the surface integral vanishes, to their distorted forms in the molecule which result from the formation of an interatomic surface.[3]

If one inserts the units determined by the commutator $[H,r^2]$ into eq 2, then N(A,B) has the dimensions of energy·length,[2] the dimensions of $(\hbar^2/m)$. Thus division of N(A,B) by R_{ab}^2 should yield a quantity proportional to the change in energy resulting from the formation of an interatomic surface, i.e., the formation of a bond between A and B. Accordingly we define a bond energy B(A,B) as

$$B(\mathrm{A,B}) = \alpha N(\mathrm{A,B})/R_{ab}^2 \qquad (3)$$

where α is a dimensionless proportionality factor. In this study, we shall restrict the discussion to deal primarily with CH and CC bonds of the saturated hydrocarbons for which all bonds are of order 1. The total dissociation energy of methane[15] is used to determine a value for α in eq 3 which will apply to all hydrocarbon CH and CC bonds of order 1 for an STO-3G charge density.

The CH and CC bond energies obtained in this manner are listed in Table IV. They bear a striking similarity to the "average bond energies" found in the literature. Perhaps their most interesting use in these examples is in the discussion of bond strain. A bond between two carbon atoms in a ring or cage structure is defined to be strained if the bond path which links the nuclei is not coincident with the corresponding internuclear axis and is outwardly curved with respect to the geometrical perimeter of the ring or cage. The data in Tables III and IV show that as the extent of the geometrical bond strain increases, as measured by the curvature of the bond, the corresponding bond energy decreases. Listed in Table IV are empirical estimates as given by Newton[16] of the strain energies in CC bonds in a number of cyclic hydrocarbons based on thermochemical data using Franklin's[17] group equivalents for strain-free molecules. In an adjoining column we list the strain energy of a CC bond measured relative to the CC

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(15) R. M. Pitzer, *J. Chem. Phys.*, **46**, 4871 (1967).

(16) M. D. Newton, "Electronic Structure Theory", Vol. III, H. F. Schaefer, Ed., Plenum, New York, 1977, pp 223–276.

(17) J. L. Franklin, *Ind. Eng. Chem.*, **41**, 1070 (1949).

Table V. Energies of Isodesmic Reactions Calculated from Bond Energies

	ΔE, kcal/mol	
	calcd	exptl[a]
(1) $CH_3CH_2CH_3 + CH_4 \rightarrow 2CH_3CH_3$	+3.3	+1.5[b]
(2) $(CH_3)_3CH + 2CH_4 \rightarrow 3CH_3CH_3$	+10.2	+7.1[c]
(3) $\overline{CH_2CH_2CH_2} + 3CH_4 \rightarrow 3CH_3CH_3$	−25.8	−23.5[b]
(4) $\overline{CH_2CH_2CH_2CH_2} + 4CH_4 \rightarrow 4CH_3CH_3$	−30.6	−20.0[c]
(5) bicyclo[1.1.0]butane + $C_2H_6 \rightarrow 2\overline{CH_2CH_2CH_2}$	−30.5	− 7.4[c]

[a] Corrected for zero-point energy differences. [b] From ref 18. [c] From data in ref 15.

Table VI. Atomic Net Populations

molecule	q(C) × 1000	q(H) × 1000
CH_4	+250	−62
C_2H_6	+228	−76
C_2H_4	+104	−52
C_2H_2	−60	+60
C_4H_8	+161	−80 (exo) −81 (endo)
C_3H_6	+98	−49
C_4H_4	−39	+39
C_6H_6	+58	−58
$C_3H_3^+$	+60	+273
$C_7H_7^+$	+67	+76

bond energy in ethane. The two sets of values are in reasonable agreement. The thermochemical method equates the total strain to just the CC bonds. In the highly strained systems, one must correct for the weakened CH bonds in the theoretical calculation of the strain energy for their comparison with the thermochemical values. This adds 2.5 kcal/mol per CC bond in C_5H_8 and 2 kcal/mol per CC bond in C_4H_4. The CH bond energies show less variation overall. They deviate from the value of 105 kcal/mol only for the highly strained systems.

To provide a quantitative test of the bond energies reported here we calculate the energy changes for some isodesmic reactions (Table V).[18] The positive values for ΔE in the first two reactions are consistent with the fact that stability increases with branching in the paraffins. From the bond energies listed in Table V this increase in stability results primarily from an increase in the CC bond energies. From eq 2 and 3, a bond energy is proportional to the total amount of charge contained in its interatomic surface. The interatomic surface integrals of $\rho(\mathbf{r})$ for the CC bonds in C_2H_6, C_3H_8, and i-C_4H_{10} have the values 1.14, 1.17, and 1.21 e/a_0, respectively, and account for this increasing stability.

The strain present in cyclopropane and cyclobutane is evident in the negative values of ΔE obtained for reactions 3 and 4. Comparison with the corresponding experimental values suggests that the estimated CC strain energy in C_3H_6 is reasonable, but for C_4H_8 it is too large by approximately 2 kcal/mol per CC bond. The sign of ΔE for reaction 5 is correct but the magnitude is too large, suggesting that the strain energy in bicyclobutane is overestimated. The total dissociation energy of ethane has been estimated to be 1.133 au or 711.0 kcal/mol.[19] Using the bond energies listed in Table V one estimates this quantity to be 721.3 kcal/mol. With seven bonds in this molecule there is an average error of 1.4 kcal/mol per bond.

III. Atomic Properties

Atomic Populations. An atom's average electron population N(A) is determined by an integration of $\rho(\mathbf{r})$ over the atomic basin. The net atomic charge $q(A) = Z_A - N(A)$, where Z_A is the nuclear charge. Net charges are listed in Table VI, and for molecules with inequivalent atoms they are displayed in Figure 3. (All net charges are multiplied by a factor of 1000.) H bears a negative charge when bonded to a saturated or to an ethylenic C and a net positive charge when bonded to an acetylenic C. Wiberg and Wendoloski[9] have determined the net charges of the H atoms (as defined here) in CH_4, C_2H_4, and C_2H_2 using the 6-31G** basis set[20] which includes polarization functions. Their values for these three molecules are respectively −65, −47, and +120. These directions of charge transfer agree with the STO-3G results, and the magnitudes, with the exception of the result for acetylene, are in reasonable agreement.

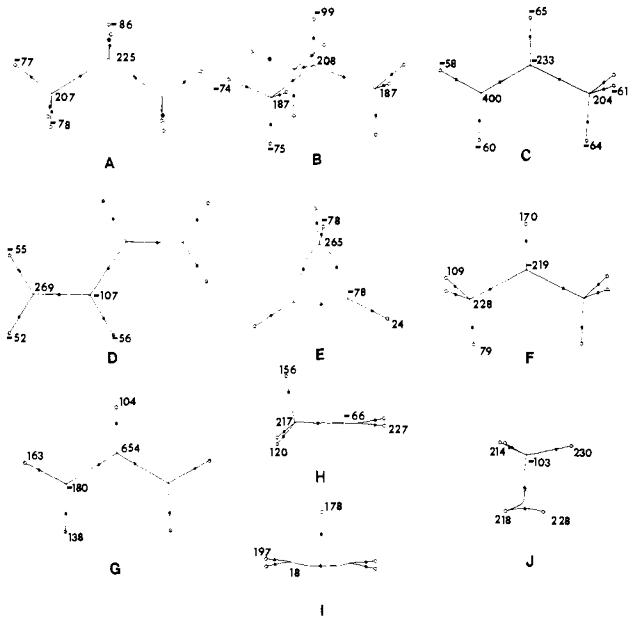

Figure 3. Molecular graphs for hydrocarbons showing net atomic charges. Each charge is multiplied by 1000: (A) propane, (B) isobutane, (C) propene, (D) *trans*-1,3-butadiene, (E) cyclopropene, (F) 2-propyl cation, (G) allyl cation, (H) $C_2H_5^+$, (I) $C_2H_5^+$ (conflict structure), (J) CH_5^+.

The net charges in the saturated series CH_4, C_2H_6, C_3H_8 (Figure 3A), and i-C_4H_{10} (B) lead to the following observations. H is more effective than CH_3 at withdrawing electrons from C, as q(C) decreases through this series, and, correspondingly, the magnitude of q(H) for H attached to this C increases with increasing substitution: −62, −76, −86, −99. The STO-3G charge distribution for C_3H_8 correctly predicts the dipole moment of this molecule.[21] The direction of the dipole parallels the direction determined by the net charges on the CH_3 (−26) and CH_2 (+52) groups in this molecule. The net charge on a methylenic H in cyclobutane, −81, is slightly less than that for a corresponding H in propane. In the more strained cyclopropane its magnitude is further decreased, and in the very strained C_4H_4 the H bears a net positive charge (Table VI).

Substitution of H by CH_3 in ethylene causes a substantial polarization of the charge density in the bond of order 2 (Figure 3C). The C bearing CH_3 is negatively charged, and the net positive charge on the second ethylenic C is increased approximately fourfold. Relative to CH_3 in C_2H_6 or C_3H_8, the hydrogens of CH_3 in C_3H_6 (C) donate charge to the remainder of the system, and the methyl group bears a net positive charge of +18. A similar polarization of charge density of a bond of order 2 is observed in 1,3-*trans*-butadiene (Figure 3D).

In benzene the charge transfer is from C to H (Table VI). As previously discussed, the cyclopropenium and tropylium cations while lacking the required number of valence electrons to yield formal CH and CC bond orders of 1 and 1.5, respectively, do satisfy the Hückel 4m + 2 rule and they exhibit a CC bond order equal to that of benzene. This is accomplished by a transfer of charge from H to C sufficient to yield net charges on C in $C_3H_3^+$

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(19) R. M. Pitzer and W. N. Lipscomb, *J. Chem. Phys.*, **39**, 1995 (1963).

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(21) L. Radom, W. A. Lathan, W. J. Hehre, and J. A. Pople, *J. Am. Chem. Soc.*, **93**, 5339 (1971).

and $C_7H_7^+$ very similar to that found in benzene. The large magnitude of $q(H)$ in $C_3H_3^+$ is indicative of the driving force underlying this transfer of charge.

The atomic net charges in the cations $C_3H_7^+$ (Figure 3F), $C_3H_5^+$ (Figure 3G), and $C_2H_5^+$ (Figure 3H) can be rationalized by viewing them as protonated carbenes, i.e., as carbenium ions.[22] In this model, the carbons bearing the negative charges are the corresponding carbene carbons. Thus $C_3H_7^+$ is protonated $(CH_3)_2C$: and $C_3H_5^+$ is the average of the protonated form of $CH_2{=}CHCH$: and its mirror image. In terms of the values of $q(C)$ for propene (Figure 3C), its protonation should initially yield the cation $CH_3CH_2CH_2^+$ (Figure 3f[2]), which rearranges to the more stable structure 3F by the migration of a proton. Structure 3I for $C_2H_5^+$ is the transition state for the migration of a hydrogen in this system as described in the preceding paper.[2] In the reactant 3H, the "carbene" carbon bears a net negative charge. The value of $\rho(\mathbf{r}_c)$ at the CC critical point is 0.238 au, within the range of values of CC bonds of order 1. The value of $\rho(\mathbf{r}_c)$ for the CH bond to the proton which migrates is low in value, 0.245 au. The transition state or conflict structure, 3I, is best described as protonated ethylene. The CC bond has a bond order of 1.5 (Table I, X) and the value of $\rho(\mathbf{r}_c)$ for the bond to the transitional hydrogen atom, 0.146 au, is approximately one-half the value for a CH bond of order 1. The structures encountered during the migration of a methyl group in $CH_3CH_2CH_2^+$ (Figure 3f of preceding paper[2]) exhibit similar charge and bond-order changes. In the reactant, the "carbene" carbon again bears a net negative charge, of amount −134. The value of $\rho(\mathbf{r}_c)$ for the CC bond to the CH_3 group is 0.183 au, substantially less than the value for a CC bond of order 1, while $\rho(\mathbf{r}_c)$ for the second CC bond is 0.262 au. In the transition state for this reaction, the ring structure Figure 3h,[2] the $H_2C{-}CH_2$ bond has a bond order of 1.5, $\rho(\mathbf{r}_c) = 0.289$ au, while the bonds to the CH_3 group have values of $\rho(\mathbf{r}_c) = 0.122$ au. The CH_5^+ cation, with five bonds and four valence electron pairs, is electron deficient. There is a contraction of the charge density on to the carbon (Figure 3J) which bears a net negative charge. Only four bond paths terminate at C. The values of $\rho(\mathbf{r}_c)$ for the bonds to the methyl protons are similar to those found for CH bonds of order 1. The values of $\rho(\mathbf{r}_c)$ for the long CH and HH bonds are ~50 and 60%, respectively, of the values for corresponding bonds of order 1.

Atomic Energies. The energy of an atom in a molecule is defined by the atomic statement of the virial theorem[3]

$$E(\mathrm{A}) = T(\mathrm{A}) + V(\mathrm{A}) \qquad (4)$$

where $T(\mathrm{A})$ is the average electronic kinetic energy of atom A and $V(\mathrm{A})$ is the virial of all the forces exerted on the electronic charge of the atom, its potential energy. The various statements of the virial theorem

$$E(\mathrm{A}) = -T(\mathrm{A}) \text{ and } -2T(\mathrm{A}) = V(\mathrm{A}) \qquad (5)$$

are satisfied for all molecular geometries. For a molecule in an equilibrium geometry, as is of interest here, the sum of $V(\mathrm{A})$ for all the atoms in a molecule equals the total potential energy of the molecule, the nuclear–electron, electron–electron, and nuclear–nuclear potential energies,

$$\sum_{\mathrm{A}} V(\mathrm{A}) = V_{\mathrm{ne}} + V_{\mathrm{ee}} + V_{\mathrm{nn}} = V \qquad (6)$$

The sum of the atomic energies over a molecule equals the total energy of the molecule,

$$\sum_{\mathrm{A}} E(\mathrm{A}) = E \qquad (7)$$

The energy $E(\mathrm{A})$ is also given by the integral over an atom, of the trace of a single particle stress tensor $\sigma(\mathbf{r})$[3]

$$E(\mathrm{A}) = (1/2)\int_{\mathrm{A}} Tr\sigma(\mathbf{r})\,\mathrm{dr} \qquad (8)$$

The stress tensor is determined by the one-electron density matrix $\Gamma^{(1)}(\mathbf{r},\mathbf{r}')$ whose trace determines the charge density $\rho(\mathbf{r})$. If the properties of $\Gamma^{(1)}(\mathbf{r},\mathbf{r}')$ in the neighborhood of its diagonal elements $\mathbf{r} = \mathbf{r}'$ are identical over the basin of a given atom in two different molecular systems, then the atoms's distribution of charge will be identical in the two systems as will its spatial distribution of energy. *In such a case the atom will appear identical in the two systems and will contribute identical amounts to the total energies of both systems.*

Underlying an atomic additivity relationship for a property in a series of structurally related molecules is the requirement that the property itself be expressible as a sum of atomic contributions over any given individual molecule. The atom as defined here possesses the two necessary properties to account for and explain additivity relationships: (a) a molecular property is expressible as a sum of atomic contributions, as in eq 7; (b) the atomic or group properties are constant throughout a series of molecules to the extent that the charge distributions of the atom or group are unchanged throughout the series.

The energies of hydrocarbon molecules are known to exhibit such an additivity relationship.[23] The energies calculated from STO-3G wave functions do not satisfy the virial theorem with sufficient accuracy to justify their use in illustrating the constancy of group energies in the hydrocarbons. We have, however, recalculated the wave functions for ethane and propane using the 6-31G basis set at the STO-3G geometries and have scaled the CH bond lengths to satisfy the V/T ratio to four figures after the decimal, leaving the CC bond lengths and all bond angles unchanged. The scaling resulted in energy increases of 0.0019 au in C_2H_6 and 0.0015 au in C_3H_8. The average electronic kinetic energies of the C and H atoms in C_3H_8 were obtained by integration of the kinetic energy densities over their atomic basins to obtain the average kinetic energy of the CH_3 group. Because of the atomic virial theorem, $E(CH_3) = -T(CH_3)$. One finds $E(CH_3)$ to be −39.598 au in ethane and −39.611 au in propane. These two energies differ by 8 kcal/mol. This is a small difference and it is obtained without a full geometry optimization in the search for a configuration which yields $E = -T$ for this approximate wave function. It illustrates that an atom or grouping of atoms may be transferred between molecules with little change in its properties. With accurate wave functions for a number of standard hydrocarbon molecules, the definition of an atom in a molecule makes it possible to determine absolute energies for a group additivity relationship and thereby provide, as well, explanations for any observed deviations.

All calculations reported in this paper were performed using programs developed in this laboratory and previously described.[24,25]

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Registry No. Cyclobutane, 287-23-0; cyclobutene, 822-35-5; cyclopropane, 75-19-4; bicyclo[1.1.1]pentane, 311-75-1; benzvalene, 659-85-8; bicyclo[1.1.0]butane, 157-33-5; tetrahedrane, 157-39-1; cyclopropene, 2781-85-3; cyclopropenium cation, 19553-81-2; methane, 74-82-8; ethane, 74-84-0; propane, 74-98-6; isobutane, 75-28-5; isopropyl cation, 19252-53-0; propene, 115-07-1; *trans*-1,3-butadiene, 106-99-0; allyl cation, 1724-44-3; $C_2H_5^+$, 14936-94-8; CH_5^+, 15135-49-6; C_2H_4, 74-85-1; C_2H_2, 74-86-2; C_4H_4, 1120-53-2; C_6H_6, 71-43-2; $C_3H_3^+$, 19553-81-2; $C_7H_7^+$, 26811-28-9; $C_3H_7^+$, 19252-52-9; C_4H_{10}, 106-97-8.

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