into the core, resulting in the increase of ϵ. Griffith et al.[19] proposed a model of penetration of water molecules into a lipid bilayer. Müller and Birkhahn[22,23] suggested penetration of water molecules in the core of a micelle from ^{19}F NMR chemical shifts. Therefore, it is reasonable to consider that penetration of water molecules is responsible for the large a_N.

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Deviations from Bond Additivity in Compton Profiles: The Relation to Strain Energy in Hydrocarbons

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Abstract: Strained cyclic hydrocarbons and unsaturated hydrocarbons show a characteristic deviation of their theoretical Compton profiles from bond additivity of computed carbon-hydrogen and carbon-carbon single bond Compton profiles. For both classes of molecules we tentatively attribute this deviation from bond additivity to strain.

Introduction

In a Compton scattering experiment on molecules, the probability distribution of frequency shifts of X-rays[1,2] or γ-rays[3,5] scattered through a fixed angle is measured. Under the impulse approximation[5] this distribution of photon frequency shifts is interpreted as the Compton profile, $J(q)$, the probability distribution of a molecular electron momentum in the direction of photon momentum change. A comprehensive review of research on electron momentum distributions and their relation to chemical bonding has been provided by Epstein.[6]

It was pointed out by Coulson[7] and by Epstein[8] that the molecular electronic kinetic energy can be computed from an experimental Compton profile. Because of the relation through the virial theorem of the kinetic energy to the total energy, it is possible to compute total energy from Compton profiles. Thus changes of Compton profiles attributable to strain energy can, in principle, be employed to compute the strain energy.

Since 1920 there have been published a number of empirical methods to express the heat of atomization ΔH_a of a hydrocarbon as a sum of bond contributions.[9,10] For example:

$$\Delta H_a = n_{CH}E_{C-H} + n_{CC}E_{C-C} \qquad (1)$$

where n_{CH} is the number of C-H bonds and n_{CC} is the number of C-C bonds in the hydrocarbon. Both E_{C-H} and E_{C-C} are empirical bond energy terms. To improve such empirical methods, terms for bond interactions[11,12] were subsequently added. Other quite accurate empirical schemes to predict heats of formation of hydrocarbons employ group increments, where the groups are CH_3, CH_2, CH, and C.[13,14] If the parameters of these empirical methods of predicting reaction heats are fixed on acyclic, "unstrained", saturated hydrocarbons, then when they are applied to predict heats of formation of strained, saturated, cyclic hydrocarbons, the stability of the strained molecules is predicted to be greater than is observed. The discrepancy in the heat of formation is referred to as strain energy. Generally saturated, cyclic molecules are found to be strained when the angles between vectors to atoms bonded to a carbon deviate greatly from the tetrahedral angle of 109.47°.

Ethylene is occasionally looked upon as a highly strained two-member ring, cycloethane,[15] in which two tetrahedrally hybridized carbon atoms are joined by highly bent bonds as originally described by Pauling.[16]

It was first suggested by Hicks[17] that the various types of chemical bonds in hydrocarbons may have characteristic Compton profiles from which the molecular profiles can be constructed additively.

Guided by the success of empirical methods by chemists, Eisenberger and Marra[18] used experimental Compton profiles to develop $J_{C-H}(q)$ and $J_{C-C}(q)$ for an electron in a C-H bond and C-C single bond, respectively. They also generated an empirical Compton profile $J_{C=C}(q)$ for an electron in a carbon-carbon double bond (C=C). The three empirical Compton profiles were taken to fit experiments on methane (CH_4), ethane (C_2H_6), and ethylene (C_2H_4). It was found that by adding these bond Compton profiles the measured Compton profiles of the unstrained hydrocarbons propylene, benzene,

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cyclohexane, and n-hexane could be predicted within the experimental error of 1% at $q = 0$ and 5% at $q = 2$ au. However, the empirical C-C single bond Compton profile agrees less well with the observed Compton profile of diamond.[19] Subsequent theoretical work using localized molecular orbitals has supported the concept that hydrocarbon Compton profiles are an additive sum of characteristic bond profiles[20] but have disagreed on the requirement of distinct profiles for carbon-carbon multiple bonds.[21]

Cade et al. found bond additivity for Compton profiles computed from Hartree-Fock wave functions for a series of linear molecules.[22]

This paper will attempt to show that theoretical Compton profiles for strained hydrocarbons differ in a characteristic way from the prediction of bond additivity of empirical bond Compton profiles derived from theoretical Compton profiles for methane, ethane, and ethylene. These empirical-theoretical bond Compton profiles accurately predict theoretical Compton profiles for larger unstrained saturated hydrocarbons such as butane and neopentane, and give a good prediction of the experimental Compton profile of diamond.[19] Second, we will show that the deviation from bond additivity of unsaturated hydrocarbon computed Compton profiles, if they are regarded as composed of C-H and C-C bonds, is very similar in form to that exhibited by strained cyclic saturated hydrocarbons.

Theoretical Background

The spherical average Compton profile $J(q)$ of an n-electron molecule is expressible as an integral of the momentum density $\rho(\boldsymbol{p})$ for a molecular electron:

$$J(q) = n \int_{|q|} \frac{1}{2} p \int_0^{2\pi} \int_0^{\pi} \rho(\boldsymbol{p}) \sin\theta_p \, d\theta_p \, d\phi_p \, dp \qquad (2)$$

where the momentum density $\rho(\boldsymbol{p})$ is given in terms of the electronic wave function in momentum space $\psi(\boldsymbol{p})$:

$$\rho(\boldsymbol{p}) = \int \psi^*(\boldsymbol{p}) \, \psi(\boldsymbol{p}) \, dp_2 dp_3 \ldots dp_n \qquad (3)$$

The wave function in momentum space $\psi(\boldsymbol{p})$ is given by a Dirac transform[23] of the wave function in position space $\psi(\boldsymbol{r})$:

$$\psi(\boldsymbol{p}) = (2\pi)^{-3n/2} \int e^{-i\boldsymbol{r}\cdot\boldsymbol{p}} \psi(\boldsymbol{r}) \, d\boldsymbol{r} \qquad (4)$$

where $\boldsymbol{r}\cdot\boldsymbol{p}$ is given by

$$\boldsymbol{r}\cdot\boldsymbol{p} = \boldsymbol{r}_1 \cdot \boldsymbol{p}_1 + \boldsymbol{r}_2 \cdot \boldsymbol{p}_2 + \boldsymbol{r}_3 \cdot \boldsymbol{p}_3 \ldots \qquad (5)$$

Coulson[24] noted that the form of a wave function is not changed by the Dirac transformation, so that corresponding to every computable quantity in position space there is a conjugate quantity in momentum space.[6]

It is fortunate that high-quality determinantal wave functions are available in position space,[25] for it has proven most convenient to generate momentum space wave functions by the Dirac transformation. Computational experience has shown that a Hartree-Fock or SCF-MO determinantal wave function in an adequate basis provides a good representation of the position space charge density. When transformed to momentum space a corresponding high-quality representation of the momentum density is expected.

In the computational studies of Compton profiles in this paper, we have employed a SCF-MO determinantal wave function of molecular orbitals $\phi(\boldsymbol{r})$ in position space for the closed-shell molecules of interest:

$$\psi(\boldsymbol{r}) = \frac{1}{\sqrt{n!}} |\phi_a(\boldsymbol{r}_1) \, \phi_a(\boldsymbol{r}_2) \ldots \phi_{n/2}(\boldsymbol{r}_n)| \qquad (6)$$

which transforms to

$$\psi(\boldsymbol{p}) = \frac{1}{\sqrt{n!}} |\phi_a(\boldsymbol{p}_1) \, \phi_a(\boldsymbol{p}_2) \ldots \phi_{n/2}(\boldsymbol{p}_n)| \qquad (7)$$

where the molecular orbital $\phi_a(\boldsymbol{p})$ in momentum space is the Dirac transform of $\phi_a(\boldsymbol{r})$.

For $\psi(\boldsymbol{p})$ of determinantal form for a closed-shell molecule, with each molecular orbital occupied by a pair of electrons of opposite spin, the momentum density $\rho(\boldsymbol{p})$ is the mean of the molecular orbital momentum densities.

$$\rho(\boldsymbol{p}) = \frac{2}{n} \sum_{i=1}^{\frac{n}{2}} \phi_i^*(\boldsymbol{p}) \, \phi_i(\boldsymbol{p}) \qquad (8)$$

and the spherical average Compton profile is the sum of twice the individual molecular orbital Compton profiles $J_i(q)$

$$J(q) = \sum_{i=1}^{\frac{n}{2}} 2J_i(q) \qquad (9)$$

where

$$J_i(q) = \int_{|q|}^{\infty} \frac{1}{2} p \int_0^{2\pi} \int_0^{\pi} \times \phi_i^*(\boldsymbol{p}) \, \phi_i(\boldsymbol{p}) \sin\theta_p \, d\theta_p \, d\phi_p \, dp \qquad (10)$$

We note that if the molecular orbitals $\phi_i(\boldsymbol{r})$ are subjected to a unitary transformation to localized molecular orbitals corresponding to "bonds" of the molecule,[20,26] the Compton profile becomes a sum of "bond" Compton profiles. This is the theoretical analogue to an empirical analysis of experimental Compton profiles into a sum of bond profiles.

Computed Compton Profiles for Hydrocarbons

In the computational work reported here we have employed previously computed[25] SCF-MO position space wave functions in a "double-ζ" basis of Gaussian orbitals. The basis used consists of two "contracted" functions per atomic orbital of a minimum basis set.[27] Each of the functions represents an inner or outer region, respectively, and variation of the relative coefficients of these permits expansion and contraction of atomic wave functions in the molecular environment. This flexibility makes possible approximate conformity to the virial theorem without variation of basis function exponents. This basis has been applied without contraction to methane, ethane, and cyclopropane, with no significant change in the results reported here. The basis used has been detailed in other publications,[25,27] and will not be repeated here.

Valence electron Compton profiles for hydrocarbons computed in this work are presented in Table I. These are given on a per valence electron basis for easy comparison. In Figure 1 are plotted the Compton profiles per valence electron for unsaturated acyclic molecules of this study as well as the theoretical C-H and C-C bond Compton profiles. Here the C-H bond Compton profile is defined to be $^1/_8$ the valence electron Compton profile of methane. The theoretical C-C bond Compton is defined to be $^1/_2$ the ethane profile − 6 (C-H) bond Compton profiles. These definitions correspond to those used by Eisenberger and Marra[18] in empirical analysis of hydrocarbon Compton profiles. Figure 2 depicts the computed Compton profiles per valence electron for strained cyclic and unstrained saturated hydrocarbons of this study.

Eisenberger and Marra[18] measured the Compton profile of a number of saturated and unsaturated hydrocarbons including methane, ethane, ethylene, propene, benzene, cyclohexane, and n-hexane. They found that the observed Compton profiles could be fitted as a sum of three characteristic profiles for C-H, C-C, and C=C bonds. These bond Compton profiles are listed in Table II along with our computed theoretical analogues. The theoretical C=C Compton profile is $^1/_4(J_{C_2H_4} - J_{CH_4})$. The theoretical C-C and C=C bond Compton profiles are both larger at $q = 0$ than the experimental profiles. In part this may be a consequence of systematic experimental problems such as multiple scattering.[19]

Table I. Computed Valence Electron Compton Profiles of Hydrocarbons

q	$J(q)^a$									
	acetylene	allene	ethylene	butadiene	cyclopropene	bicyclobutane	cyclopropane	neopentane	butane	ethane
0.0	0.572	0.559	0.573	0.556	0.551	0.543	0.554	0.557	0.559	0.571
0.1	0.566	0.554	0.567	0.551	0.546	0.538	0.549	0.552	0.554	0.566
0.2	0.549	0.539	0.551	0.536	0.531	0.524	0.533	0.538	0.539	0.550
0.3	0.521	0.515	0.523	0.511	0.507	0.501	0.509	0.514	0.515	0.524
0.4	0.481	0.480	0.485	0.477	0.474	0.470	0.477	0.480	0.482	0.489
0.5	0.433	0.437	0.439	0.435	0.433	0.432	0.437	0.439	0.441	0.445
0.6	0.380	0.387	0.387	0.386	0.387	0.389	0.392	0.393	0.394	0.395
0.7	0.324	0.334	0.332	0.335	0.337	0.342	0.342	0.343	0.344	0.341
0.8	0.272	0.281	0.279	0.284	0.287	0.293	0.291	0.292	0.292	0.286
0.9	0.223	0.232	0.229	0.236	0.239	0.246	0.242	0.243	0.242	0.234
1.0	0.181	0.188	0.185	0.192	0.195	0.201	0.196	0.197	0.195	0.188
1.2	0.116	0.119	0.116	0.122	0.124	0.127	0.122	0.121	0.119	0.114
1.4	0.073	0.073	0.070	0.074	0.075	0.076	0.072	0.070	0.069	0.067
1.6	0.045	0.045	0.042	0.044	0.045	0.044	0.042	0.040	0.040	0.039
1.8	0.029	0.028	0.026	0.027	0.027	0.026	0.025	0.023	0.023	0.023
2.0	0.019	0.018	0.016	0.017	0.017	0.016	0.016	0.015	0.015	0.014
2.5	0.009	0.008	0.007	0.007	0.008	0.007	0.007	0.007	0.007	0.006
3.0	0.005	0.004	0.004	0.004	0.005	0.005	0.004	0.004	0.004	0.004
3.5	0.003	0.003	0.003	0.003	0.003	0.003	0.003	0.002	0.002	0.002
4.0	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.001
4.5	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001
5.0	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001

[a] Per valence electron.

Table II. Theoretical and Experimental Empirical Bond Compton Profiles of Hydrocarbons[a]

q	$J_{C-H}(q)$		$J_{C-C}(q)$		$J_{C=C}(q)$		$J_{C=C}(q) - J_{C-C}(Q)$	
	theor	exptl	theor	exptl	theor	exptl	theor	exptl
0.0	0.590	0.585	0.462	0.412	0.539	0.516	0.077	0.104
0.1	0.584	0.578	0.457	0.410	0.533	0.510	0.077	0.100
0.2	0.568	0.558	0.444	0.410	0.516	0.498	0.072	0.088
0.3	0.540	0.525	0.431	0.408	0.490	0.475	0.059	0.067
0.4	0.500	0.484	0.421	0.400	0.456	0.444	0.034	0.044
0.5	0.450	0.434	0.415	0.391	0.417	0.408	0.002	0.017
0.6	0.393	0.380	0.404	0.374	0.374	0.368	−0.030	−0.006
0.7	0.334	0.325	0.382	0.352	0.329	0.326	−0.053	−0.026
0.8	0.276	0.271	0.348	0.324	0.285	0.284	−0.063	−0.040
0.9	0.223	0.221	0.302	0.291	0.241	0.243	−0.060	−0.048
1.0	0.177	0.176	0.251	0.255	0.201	0.205	−0.050	−0.050
1.2	0.108	0.106	0.154	0.181	0.133	0.134	−0.022	−0.047
1.4	0.064	0.064	0.086	0.112	0.083	0.087	−0.003	−0.025
1.6	0.038	0.042	0.046	0.063	0.051	0.057	+0.005	−0.006
1.8	0.023	0.031	0.026	0.034	0.032	0.041	+0.006	+0.007
2.0	0.014	0.022	0.016	0.024	0.021	0.030	+0.005	+0.006
2.5	0.006		0.009		0.010		+0.001	
3.0	0.003		0.006		0.006		0	
3.5	0.002		0.004		0.004		0	
4.0	0.001		0.002		0.002		0	
4.5	0.001		0.001		0.002		0	
5.0	0.001		0.001		0.001		0	

[a] Per valence electron.

Ab initio SCF-LCAO-MO wave functions for hydrocarbons have been transformed to localized molecular orbitals both by Epstein[20] and by Smith and Whangbo.[21] Epstein, who employed a minimum basis of Slater orbitals, found that average C-H and C-C single bond Compton profiles used in an additive way fit the theoretical Compton profiles of eight hydrocarbons.[20] However, Epstein concluded that carbon-carbon multiple bonds were well represented by a sum of C-C single bond profiles. Smith and Whangbo, who employed a double-ζ basis similar to that employed in this work, found the C=C Compton profile to be significantly different from that of C-C.[21] Their Compton profiles for C-C and C=C are very close to our theoretical empirical profiles given in Table II.

Deviations of Computed Hydrocarbon Compton Profiles from Bond Additivity

It is known that Eisenberger and Marra achieved a good fit of the observed Compton profiles. However, their collection of molecules excluded strained molecules. Comparable success is achieved when theoretical C-C and C-H Compton profiles are used to estimate the computed Compton profiles of unstrained saturated hydrocarbons such as butane and neopentane. The deviations of the computed butane and neopentane Compton profiles from the sum of theoretical C-H and C-C bond Compton profiles are given on a per C-C bond electron basis in Table III and as the lower two curves of Figure 4. The

Table III. Deviations from C-C and C-H Bond Additivity of Hydrocarbon Valence Electron Compton Profiles[a]

	$J(q)^2$								
q	acetylene	allene	ethylene	butadiene	cyclopropene	bicyclobutane	cyclopropane	neopentane	butane
0.0	0.097	0.065	0.077	0.055	0.051	0.025	0.020	−0.003	−0.003
0.1	0.097	0.067	0.077	0.055	0.052	0.026	0.020	−0.001	−0.002
0.2	0.093	0.067	0.072	0.054	0.051	0.027	0.021	+0.004	−0.000
0.3	0.078	0.059	0.059	0.046	0.043	0.024	0.018	+0.005	+0.000
0.4	0.048	0.039	0.034	0.028	0.026	0.013	0.009	−0.000	−0.001
0.5	0.007	0.009	0.002	0.002	0.002	−0.004	−0.003	−0.008	−0.004
0.6	−0.033	−0.023	−0.030	−0.025	−0.023	−0.020	−0.015	−0.012	−0.006
0.7	−0.064	−0.049	−0.053	−0.045	−0.042	−0.031	−0.023	−0.011	−0.006
0.8	−0.079	−0.062	−0.063	−0.053	−0.049	−0.033	−0.026	−0.005	−0.003
0.9	−0.078	−0.062	−0.060	−0.050	−0.047	−0.029	−0.023	+0.001	+0.000
1.0	−0.066	−0.052	−0.050	−0.040	−0.038	−0.020	−0.017	+0.005	+0.003
1.2	−0.032	−0.024	−0.022	−0.015	−0.015	−0.003	−0.003	+0.005	+0.004
1.4	−0.007	−0.003	−0.003	+0.009	+0.000	+0.005	+0.004	+0.002	+0.002
1.6	+0.005	+0.006	+0.005	+0.006	+0.006	+0.006	0.005	+0.001	+0.001
1.8	0.008	+0.007	+0.006	+0.006	+0.006	+0.005	0.004	+0.000	+0.001
2.0	0.006	+0.005	+0.005	+0.005	+0.005	+0.003	0.003	+0.000	+0.000

[a] Per C-C bond electron.

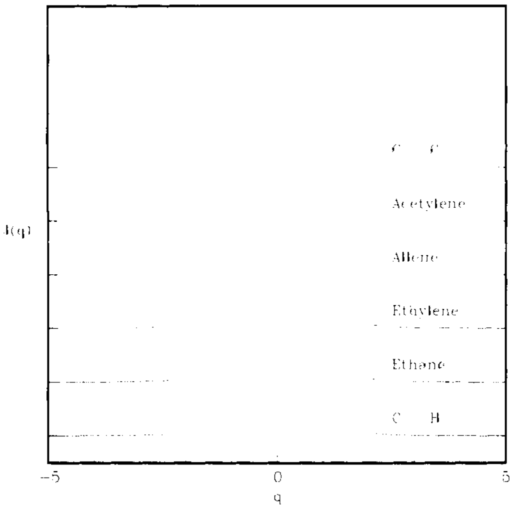

Figure 1. Computed bond and small hydrocarbon Compton profiles.

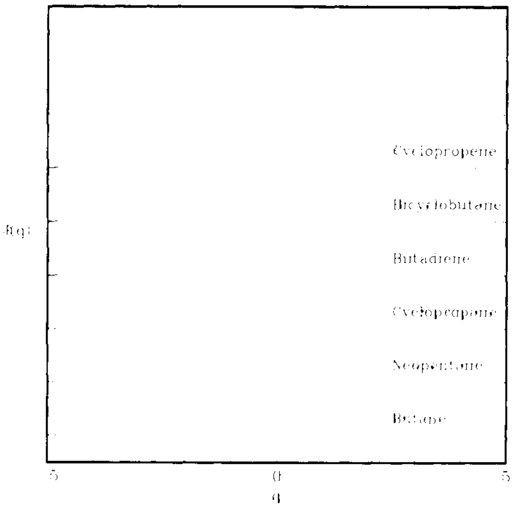

Figure 2. Computed Compton profiles for strained cyclic and unstrained saturated hydrocarbons.

deviations are less than 2% of the theoretical C-C bond profile.

The cyclic hydrocarbons cyclopropene, bicyclobutane, and

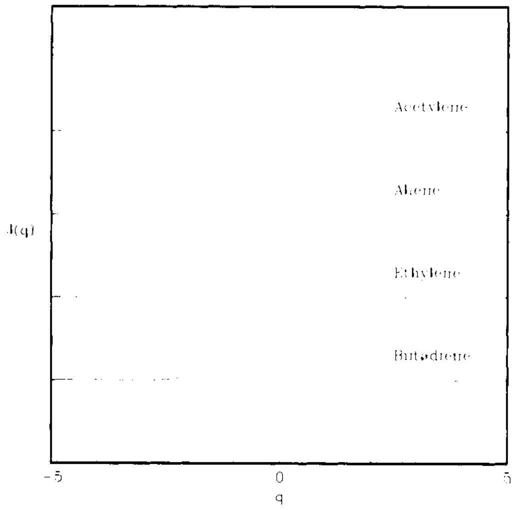

Figure 3. Deviation of unsaturated hydrocarbon computed Compton profiles from bond additivity. The ordinate scale corresponds to a 0.1 separation of curve base lines.

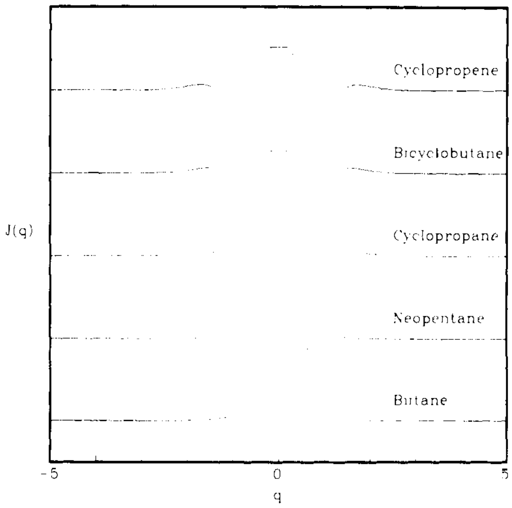

Figure 4. Deviation of strained cyclic hydrocarbon computed Compton profiles from bond additivity. The ordinate scale corresponds to a 0.1 separation of curve base lines.

cyclopropane are known from thermochemical heats of formation to be strained.[14,15] Their strain energies per carbon-carbon bond, estimated using empirical group increments for heat of formation, are 19.0, 13.3, and 9.4 kcal, respectively.[14] The deviations of their computed Compton profiles from C-C and C-H bond additivity are shown in Figure 4 and listed in Table III, on a per electron in C-C bond basis. The deviations have a characteristic shape. In strained molecules the probability of momentum values near zero is enhanced, and the probability of momentum near 1 au is decreased. The minima occur near ±0.8 au. There is also a slight increase of probability for momentum greater than 1.5 au.

It has been common in chemistry to propose that the double bond of ethylene consists of two highly strained single bonds.[15,16] Similarly the triple bond of acetylene has been regarded as consisting of three highly strained C-C bonds.[15,16] We have pursued this idea by computing the deviation of Compton profiles of unsaturated molecules from the Compton profile predicted from simple C-C and C-H bond additivity. Those deviations are given per C-C bonding electron in Figure 3 and Table III for acetylene, allene, ethylene, and butadiene. The characteristic deviation is an increased probability of low momenta, a decreased probability of momentum values near 1 au, and a small increase in probability for momentum beyond 1.5 au. The overall shape of the deviation is very similar to that exhibited by the strained cyclic hydrocarbons. The application of saturated hydrocarbon group increments to estimate the heats of formation of acetylene, allene, ethylene, and butadiene indicates their respective strain energies to be 19.5, 14.1, 11.4, and 8.2 kcal per carbon-carbon bond.

We have found the deviation from C-H and C-C bond additivity of the Compton profile of an ethylenic double bond to be about double the amplitude but of the same phase and form as in cyclopropane.

The difference between the Compton profiles of cyclopropane and propene, measured by Holt, Pattison, and Cooper[28] and computed theoretically by Hirst and Liebmann,[29] is close to the difference of the total deviations from additivity of cyclopropane and ethylene in this study. However, the effect of strain on the Compton profile of cyclopropane is better illustrated with a saturated reference compound.

Summary

There appears to be a common characteristic deviation of computed strained cyclic hydrocarbon and unsaturated hydrocarbon Compton profiles from their values predicted from additivity of theoretical carbon-hydrogen and carbon-carbon single bond Compton profiles. This characteristic deviation of computed Compton profiles from bond additivity appears to be associated with "strain energy".

However, it is possible that these deviations are associated with next-nearest-neighbor contributions to the Compton profile. For both cyclic hydrocarbons and unsaturated acyclic hydrocarbons the ratio of the number of carbon-hydrogen bonds to the number of carbon-carbon bonds is lower than in saturated acyclic hydrocarbons. For this reason the number and kind of next-nearest-neighbor contributions to the Compton profile also change, and may be responsible for the characteristic deviations from bond additivity noted here.[29]

We defer to a subsequent paper a study of the problems of computing strain energy from theoretical or experimental Compton profiles.

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