[1.1.1]propellane account for the fact that this molecule is susceptible to acetolysis, while the same properties for the [2.2.2] molecule dictate that it be unreactive.

The ellipticity of the bridgehead bond in [2.1.1]propellane is so great and the charge distribution so close to the formation of a singularity and rupture of the bond that the instability present in the static distribution dominates the properties of this molecule. This molecule, in fact, does not survive above a temperature of 50 K.[75] In [2.2.1]propellane the symmetric transition density is lowest in energy and of moderate relative intensity, and this fact, coupled with the relatively large ellipticities of all three bonds of the three-membered ring in this structure, may be used to rationalize its observed thermal instability, which is similar to that observed for the [2.1.1] molecule.

Figure 6 also gives the orbital ordering for bicyclo[1.1.0]butane, another molecule which exhibits a very intense low-frequency absorption.[74] The bonding and antibonding characters of the HOMO and of the symmetric and antisymmetric virtual orbitals are the same as in the propellanes. The excitation energies for the SS and AS transition densities are close in value, with the SS density lying lowest. While the symmetric motion is predicted to be slightly favored in terms of the $\Delta\epsilon$ values, it is clear from the contour plot for ρ_{SS} that it will be of low intensity, because the dipolar component of this transition density is small and tends to cancel out. The transition dipole arising from the ρ_{AS} transition density is, however, very large, and the antisymmetric bridgehead stretch of B_1 symmetry should be a very intense band. These predictions are in agreement with experiment,[74] which shows this molecule to have a weak, low lying symmetric stretch at 422 cm^{-1} and a very strong antisymmetric stretch at 735 cm^{-1}. The chemistry of bicyclobutane, like that of [1.1.1]propellane, is dominated by the properties of the charge density in the bridgehead region. Both molecules exhibit nonbonded concentrations of charge on the bridgehead carbons, and these concentrations are enhanced by the very pronounced asymmetric polarization of the bridgehead density induced by the antisymmetric skeletal stretch.

VI. Summary

It is the purpose of this work to demonstrate that molecular structures can be assigned and their relative stabilities and reactivities understood in terms of global and local properties of the electronic charge density. In the following companion paper, the atomic *averages* of the charge and energy densities are used to account for energy additivity in the homologous series of acyclic alkanes and for the deviations from this scheme that are observed for molecules containing small ring structures, deviations which give rise to the concept of strain energy.

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Theoretical Analysis of Hydrocarbon Properties. 2. Additivity of Group Properties and the Origin of Strain Energy

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Abstract: The theory of atoms in molecules is used to obtain electron populations and energies for the atoms in the same set of molecules studied in the preceding paper. Hydrogen is more electronegative than carbon in hydrocarbons with no geometrical strain, and the order of the relative electron-withdrawing abilities of the groups is H > CH_3 > CH_2 > CH > C. The electronegativity of a carbon increases with an increase in geometrical strain as measured by the decrease in its bond path angles from the normal value. In cyclopropane 0.05 fewer electrons are transferred from carbon to hydrogen than in the standard CH_2 group. The bridgehead carbons in the propellanes and in the most strained of the bicyclic molecules withdraw charge from CH_2 and H, and there is a flow of charge from the peripheral groups to the bridgehead region with increasing strain in these molecules. It is found that the charge distribution of a CH_3 or CH_2 group as defined by theory can appear unchanged as a transferable unit throughout a homologous series of molecules. When this occurs, the contribution of the group to the total energy of the molecule is also unchanged, and these groups account for the additivity of energy. The transfer of charge from H to C in CH_2 that occurs as C is subjected to geometric strain leads to a decrease in the energy of C but to an even greater increase in the energy of H, and the net result is a strain energy equal to the increase in energy of CH_2 relative to that of the standard. The more strained a bridgehead carbon, the greater its stability relative to its neighboring groups from which it withdraws charge, causing their energies to increase above the standard values and thereby resulting in a strain energy.

I. Introduction

This paper illustrates the relationship between the spatial form of an atom and its properties. In particular, it is demonstrated that when the distribution of charge over an atom or some functional group is the same in two different molecules, then the atom or group makes the same contribution to the total energy in both systems.[1] This property of an atom is exemplified for the homologous series of acyclic hydrocarbons whose experimental heats of formation exhibit group additivity.[2] The atomic properties are also used to obtain an understanding of the closely related quantity of strain energy.[3] This energy is defined in terms of the difference between the observed heat of formation and that predicted on the basis of group additivity. The same sets of acyclic,

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cyclic, bicyclic, and propellane molecules whose charge distributions and structures were studied in the preceding paper[4] form the basis of this investigation.

II. Atomic Properties

A number of atomic properties, including average populations and energies, are given in Table I. Every atomic property is expressed in terms of a corresponding three-dimensional density distribution which is then integrated over the basin of the atom to obtain its average value.[5] The program PROAIM which determines the properties of atoms in molecules has been previously described.[6] The average electron population of atom Ω, $N(\Omega)$ for example, is obtained by numerical integration of the charge density over the basin of the atom. The net charge of atom Ω, $q(\Omega)$, is obtained by subtracting $N(\Omega)$ from the nuclear charge, $q(\Omega) = Z_\Omega - N(\Omega)$. In all but a few cases, the integrations were performed over every atom in a molecule.[7] Their accuracy may be gauged by comparing the sums of the integrated atomic populations and energies with the total number of electrons and the total computed energy as quoted in Table II. In general, the error in the total electron population is less than ±0.01 e and that in the energy less than ±2.0 kcal/mol. As a consequence of a hydrogen atom having but a single interatomic surface and this being determined by slowly curving trajectories terminating at a single bond critical point, the errors in the values of the properties of a hydrogen atom are less than these total errors, their populations being correct to ±0.001 e. A carbon atom, with four interatomic surfaces, is more difficult to integrate. The four surfaces bounding a bridgehead carbon in bicyclo[1.1.1]pentane, for example, are determined by the trajectories which terminate at four bond critical points and originate at three ring critical points and one cage critical point. The accuracy of individual atomic integrations may be judged in terms of the integral of $\nabla^2\rho$, an integral which, because of the zero flux surface condition, should vanish (eq 1 of the preceeding paper[4]). The extent to which this condition is satisfied is a direct test of how well the surfaces of zero flux have been approximated. The quantity $-(\hbar^2/4m)\nabla^2\rho$ is the local difference between two expressions for the kinetic energy density, and it also appears in the local form of the virial theorem, eq 2 of the preceding paper.[4] Its integrated value, denoted by $L(\Omega)$ in Table I, is a measure of error in the average kinetic energy and virial theorem. It is generally smaller than 1×10^{-4} au or 0.06 kcal/mol for a hydrogen atom. To obtain populations and energies which sum correctly to the total values, the population and kinetic energy of the carbon atom with the largest value for $L(\Omega)$ within a given molecule, an atom denoted by an asterisk in Table I, are obtained by subtraction. These corrections will equal the corresponding differences between the totals and the sums of integrated values listed in Table II or be less than these if the starred atom is a member of an equivalent set.

III. Atomic Populations

As is to be expected, the atomic populations exhibit a basis set dependence.[8] Because the atom is defined in terms of a property of the charge distribution, $N(\Omega)$ changes in an ordered and understandable way with changes in the basis set. The transfer of charge between carbon and hydrogen is relatively small, and even a minimal basis set without polarizing functions, but balanced in its makeup, yields populations similar to those obtained by using a larger set. Thus the STO-3G[9] and 6-31G**[10] basis sets are equally balanced, the former having no polarization functions and the latter having such functions on both carbon and hydrogen. Table III shows that the net charges on H in a number of saturated hydrocarbons differ by 0.003 ± 0.001 between the two sets, the larger set giving the larger net charge. Corresponding to the larger charge, the distance of the C–H bond critical point from the proton is slightly greater for the larger basis set. The basis set used in the present study,[4] 6-31G*,[10] is unbalanced in that it contains no polarization functions on hydrogen. As a consequence, the position of the bond critical point (as recorded in Table I of the preceding paper[4]) is found closer to the proton when this basis is used than when the 6-31G** basis is used by 0.0225 ± 0.0007 Å, both sets of results being for 6-31G* geometries. Methane, for which the difference is only 0.0211 Å, is an exception. While the absolute charges obtained with the 6-31G* set are smaller than those for the 6-31G** set, the differences between the two sets of charges are remarkably constant. The average difference in the hydrogen atom populations equals 0.055 ± 0.002 e for the wide range of molecules listed in Table III, from acyclic to very strained molecules, its variation being close to the uncertainty of ±0.001 e in the integrated value of $N(\mathrm{H})$. Because of this near constancy in the difference between the two sets of populations, the changes in population as a function of structure are nearly independent of the basis set, and the single star results may be converted to the more accurate double star results by adding 0.055 e to the hydrogen populations and adjusting the $N(\mathrm{C})$ values accordingly. This same behavior is found to be true even between systems where H is replaced by F. Wiberg and Wendoloski[8] found the decreases in $N(\mathrm{H})$ between methane and methyl fluoride to be 0.024, 0.025, and 0.021 e for the 6-31G**, 4-31G+BF, and 4-31G basis sets, respectively, and 0.024 e for a correlated GVB function using the largest of the above basis sets.

Since the effect of switching from the single to the double star basis set is to shift the C–H interatomic surface slightly closer to carbon, all of the changes in populations occur within each functional group, and one has the important result that the charges on the functional groups are the same for the two basis sets. For example, the net charges on the methyl group in the normal alkanes propane to hexane for the double star and a single star basis sets are −0.018 and −0.017 e, respectively. The same result is obtained even in the very strained systems. The net charge on a methylene group in [1.1.1]propellane differs by only 0.001 e between the two basis sets, and hence the bridgehead carbon in this same molecule is also assigned the same charge within the integration error.

Reference to Table I shows hydrogen to be more electronegative than carbon in all of the acyclic hydrocarbons. Hydrogen has its most negative charge in the CH group of isobutane, followed by its values in CH_2, and exhibits its least negative values in CH_3 of normal alkanes. However, a hydrogen atom becomes less electronegative relative to carbon as the carbon is subjected to increasing geometric strain. Thus the hydrogen in cyclopropane has a small positive charge, a slightly larger one when attached to the bridgehead carbon of bicyclobutane, and its largest net charge in tetrahedrane. This trend of a decreasing population for H with increasing geometric strain is identical with that obtained by using the 6-31G** basis, but the net charge on hydrogen is positive only in the most highly strained systems because of the difference of 0.055 e in populations between the two sets.

Since hydrogen withdraws charge from carbon in the acyclic hydrocarbons, the relative group-electron-withdrawing ability is in the order $CH_3 > CH_2 > CH > C$. A methyl group linked to a methylene group withdraws an almost constant amount of charge from CH_2, as $q(CH_3) = -0.0165 \pm 0.0005$ e in propane through hexane, Table IV. The methylene group in propane is linked to two methyls, and its net charge of +0.034 e is, within integration error, twice that of a methylene linked to a methyl and a second

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(7) Structure **17** possesses an unstable intersection of gradient paths associated with two ring critical points, a situation PROAIM has not been programmed for. The gradient vector field behaves in an extreme manner within the basins of a bridgehead carbon in **18** and **22**. The populations and energies for these atoms were obtained by difference.

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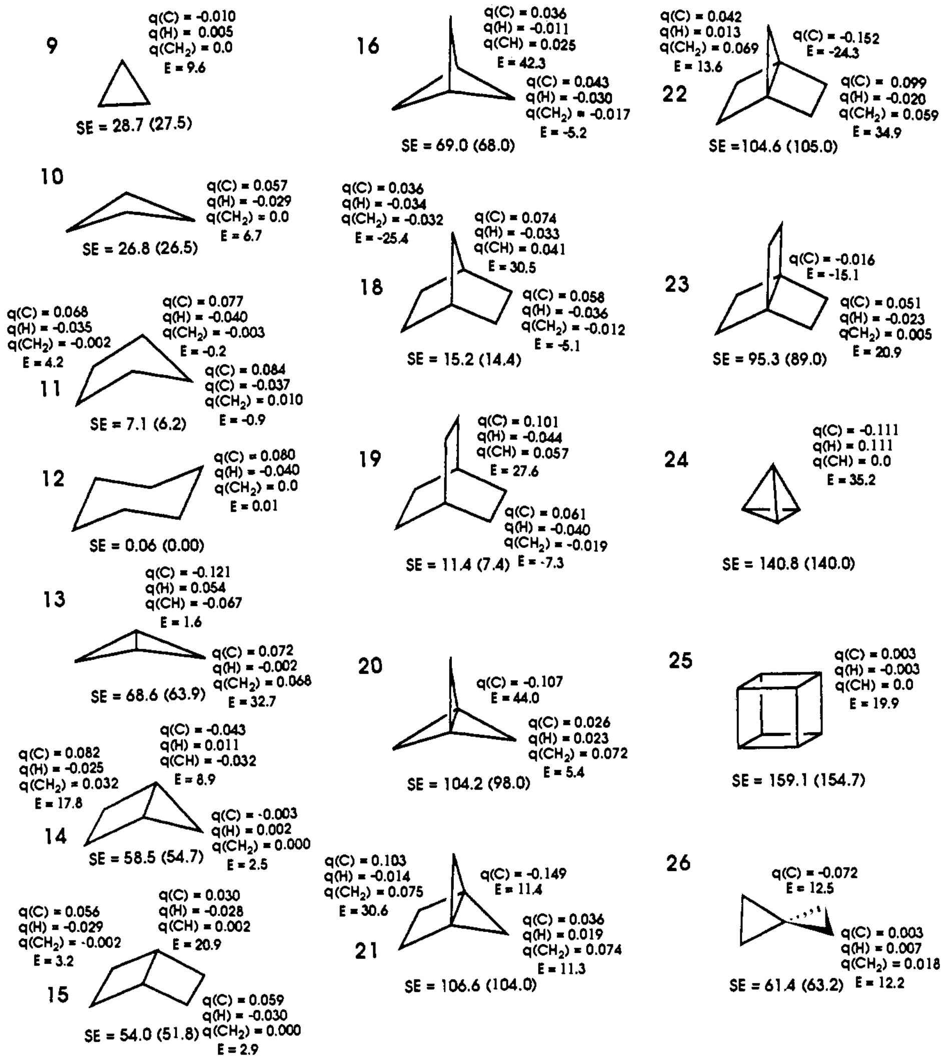

Figure 1. Carbon skeletal structures of strained molecules. Opposite each CH_2, CH, or C group is given the net charge on C, the average net charge on the H atoms, the net charge for the group, and the strain energy (*E*) for the group in kcal/mol. The total calculated strain energy, also in kcal/mol, is given below each structure followed by the experimental value in parentheses.

methylene, as found in butane through hexane. A methylene linked only to other methylenes as found in pentane and hexane has a zero net charge, Table IV. Thus the inductive transfer of charge from methylene to methyl is a nearly constant quantity, equal to 0.017 e per methyl, and this transfer is damped by a single methylene group, as a CH_2 group once removed has a zero net charge.

The net charges on the individual atoms in these groups also exhibit a similar constancy. The H atom of methyl in the plane of the carbon framework has a charge of −0.025 e, 0.003 e smaller in magnitude than that of the two other H atoms of methyl. The H of CH_2 linked to a single methyl bears a charge of −0.040 e, while that for a H on a carbon linked only to other methylenes has a charge of −0.043 e. The values of the charge density at the positions of the nuclei are also included in Table I, and one notes that these values also reflect the constancies in the average populations of the methyl and methylene groups in the normal alkanes, to within 1 part in 1×10^5 for the carbons of the methyl groups, for example. One correctly anticipates that these constancies in average populations are a result of essentially constant distributions of charge over corresponding atoms in these molecules and that this will in turn result in essentially constant contributions to their total energies. The central methylene groups in hexane and the single such group in pentane have essentially zero net charge, and their energies are found to be equal to the additive contribution per methylene group in the energy additivity scheme for the normal alkanes. These groups will be taken to define the properties of the "standard" CH_2 group for comparison with the methylene groups of the cyclic and bicyclic hydrocarbons.

When three methyls are attached to a single carbon as in isobutane, each withdraws significantly more electronic charge than when bonded to methylene. This effect is further enhanced in neopentane. The net charges on the carbon atoms in CH_3, CH_2 (linked only to methylenes), CH_2 (linked to one methyl), CH, and C are respectively +0.065, +0.085, +0.097, +0.129, and +0.137 e.

There is a dramatic decrease in the average population of a hydrogen atom when it is linked to a carbon atom in a system with ring strain. Figure 1 gives net atomic and group charges for all cyclic structures. By symmetry, a CH_2 group of the three-, four- and six-membered cyclic molecules has zero net charge as does the standard methylene group of the acyclics defined above. Compared to the hydrogens of this standard group, the hydrogens of cyclopropane have 0.048 fewer electrons (0.046 fewer at the 6-31G** level). In cyclobutane this difference has decreased to 0.014 e, and in cyclohexane the average of the axial and equatorial H populations is only 0.003 e less than that in the standard methylene group. Correspondingly, the average electron population of a carbon atom in these molecules increases with increasing strain, the net charge of a C atom in the six-, five-, four-, and three-membered cyclics being +0.086, +0.077(average), +0.057, and −0.010 e, respectively. The value for cyclohexane which may be considered to be strain free is within 0.006 e of the standard value. The bridgehead carbon atoms in bicyclobutane **13** and in the propellanes **21** and **22** bear the largest negative charges of all the carbon atoms, and the order of electron-withdrawing ability

Table I. Atomic Properties in Hydrocarbons[a]

molecule		$N(\Omega)$	$L(\Omega)$, au	$T(\Omega) = -E(\Omega)$, au	$V_{neo}(\Omega)$,[b] au	$\rho(0)$,[c] au
1, methane	C1	5.9668	-0.00017	37.73936	-89.55023	117.9958
	H2	1.0083	0.00007	0.61395	-1.29140	0.4252
2, ethane	C1	5.9249	0.00040	37.73323	-89.47475	117.9993
	H3	1.0248	0.00007	0.62711	-1.31048	0.4298
3, propane	C1	5.9373	-0.00070	37.75004	-89.53348	118.0234
	*C2	5.8924	-0.00477	37.72485	-89.42062	118.0078
	H4	1.0248	-0.00002	0.62640	-1.31006	0.4294
	H5	1.0275	0.00013	0.62735	-1.31202	0.4293
	H7	1.0367	0.00006	0.63826	-1.32562	0.4338
4, butane	C1	5.9350	-0.00012	37.74948	-89.52894	118.0218
	*C2	5.9043	0.00053	37.73827	-89.46767	118.0265
	H5	1.0251	0.00017	0.62734	-1.31094	0.4298
	H6	1.0281	0.00010	0.62804	-1.31299	0.4297
	H8	1.0397	0.00020	0.63902	-1.32760	0.4334
5, isobutane	*C1	5.9433	-0.00058	37.76337	-89.57491	118.0450
	C2	5.8706	-0.00041	37.71128	-89.37296	118.0176
	H5	1.0275	0.00009	0.62776	-1.31251	0.4295
	H6	1.0296	0.00010	0.62759	-1.31290	0.4287
	H7	1.0452	0.00039	0.64825	-1.33740	0.4369
6, pentane	C1	5.9343	0.00024	37.74725	-89.52447	118.0224
	*C2	5.9047	0.00072	37.74062	-89.47012	118.0262
	C3	5.9142	0.00069	37.75732	-89.53001	118.0470
	H6	1.0251	0.00008	0.62702	-1.31087	0.4298
	H7	1.0280	0.00009	0.62790	-1.31260	0.4295
	H9	1.0399	0.00011	0.63884	-1.32732	0.4332
	H11	1.0430	0.00011	0.63949	-1.32916	0.4327
7, neopentane	C1	5.9460	0.00005	37.77488	-89.59899	118.0642
	*C2	5.8626	-0.00163	37.69291	-89.35801	118.0287
	H6	1.0295	-0.00008	0.62845	-1.31412	0.4294
8, hexane	C1	5.9357	0.00051	37.74940	-89.52884	118.0196
	*C2	5.9044	0.00223	37.73837	-89.46315	118.0228
	C3	5.9136	0.00086	37.75598	-89.52404	118.0399
	H7	1.0249	0.00008	0.62660	-1.31021	0.4294
	H8	1.0280	0.00009	0.62775	-1.31247	0.4294
	H10	1.0400	0.00010	0.63926	-1.32777	0.4334
	H12	1.0427	0.00011	0.63977	-1.32940	0.4329
9, cyclopropane	*C1	6.0102	0.00035	37.78234	-89.76484	117.9648
	H4	0.9949	0.00009	0.61866	-1.28992	0.4307
10, cyclobutane	*C1	5.9434	0.00028	37.75930	-89.56237	118.0458
	H5	1.0289	0.00008	0.63220	-1.31694	0.4324
	H9	1.0277	0.00009	0.63252	-1.31613	0.4318
11, cyclopentane	*C1	5.9160	0.00185	37.75849	-89.54247	118.0532
	C2	5.9241	0.00077	37.75620	-89.53876	118.0506
	C3	5.9308	0.00040	37.74861	-89.53831	118.0435
	H6	1.0326	0.00009	0.63551	-1.32195	0.4333
	H7	1.0416	0.00044	0.64224	-1.33123	0.4348
	H8	1.0407	0.00010	0.64200	-1.33093	0.4350
	H9	1.0386	0.00013	0.63691	-1.32338	0.4339
	H10	1.0338	0.00004	0.63861	-1.32508	0.4344
	H11	1.0369	0.00010	0.64088	-1.32805	0.4349
12, cyclohexane	*C1	5.9202	0.00024	37.75803	-89.53898	118.0411
	H7	1.0361	0.00009	0.63708	-1.32445	0.4330
	H8	1.0437	0.00010	0.63965	-1.32954	0.4326
13, bicyclo[1.1.0]butane	C1	6.1210	0.00017	37.86024	-90.15791	117.9854
	*C2	5.9283	0.00208	37.74152	-89.47624	118.0013
	H5	0.9463	0.00006	0.59296	-1.24273	0.4233
	H6	0.9976	0.00008	0.61878	-1.29218	0.4318
	H7	1.0068	0.00011	0.62233	-1.29753	0.4319
14, bicyclo[2.1.0]pentane	C1	6.0433	0.00136	37.82717	-89.92775	118.0263
	C2	5.9160	0.00001	37.74429	-89.46929	118.0412
	C5	6.0063	-0.00034	37.79396	-89.78073	117.9951
	H6	0.9893	-0.00003	0.61440	-1.28320	0.4296
	H9	1.0288	0.00009	0.63150	-1.31610	0.4324
	H10	1.0211	-0.00007	0.63070	-1.31205	0.4324
	H12	0.9941	0.00007	0.61707	-1.28832	0.4296
	H13	1.0027	0.00009	0.61985	-1.29386	0.4297
15, bicyclo[2.2.0]hexane	C1	5.9696	-0.00123	37.78665	-89.66826	118.1042
	C2	5.9408	0.00100	37.76071	-89.55634	118.0571
	C3	5.9444	-0.00020	37.76075	-89.56513	118.0571
	H7	1.0284	0.00020	0.63593	-1.32088	0.4356
	H8	1.0275	0.00008	0.63420	-1.31812	0.4333
	H9	1.0317	0.00010	0.63527	-1.32133	0.4338
	H10	1.0269	0.00012	0.63391	-1.31764	0.4333
	H11	1.0307	0.00009	0.63506	-1.32055	0.4335
16, bicyclo[1.1.1]pentane	*C1	5.9644	-0.00286	37.76700	-89.60721	118.1198
	C2	5.9570	-0.00002	37.77870	-89.60816	118.1069
	H6	1.0108	0.00006	0.62135	-1.29980	0.4321
	H7	1.0298	0.00009	0.63215	-1.31847	0.4335

Table I (Continued)

molecule		$N(\Omega)$	$L(\Omega)$, au	$T(\Omega) = -E(\Omega)$, au	$V_{neo}(\Omega)$,[b] au	$\rho(0)$,[c] au
17, bicyclo[2.1.1]hexane	C1					118.1144
	C2					118.0573
	C5	5.9722	−0.004 31	37.789 35	−89.664 34	118.0999
	H7	1.0233	0.000 78	0.632 24	−1.316 72	0.4358
	H8	1.0341	0.000 10	0.637 81	−1.325 00	0.4345
	H13	1.0365	−0.000 04	0.636 54	−1.325 63	0.4346
	H14	1.0257	0.000 09	0.632 32	−1.316 74	0.4329
18, bicyclo[2.2.1]heptane	C1	5.9264		37.769 91		118.1025
	C2	5.9418	0.001 20	37.767 87	−89.594 28	118.0642
	C7	5.9641	−0.001 74	37.808 57	−89.715 16	118.1034
	H8	1.0326	−0.000 08	0.637 34	−1.324 84	0.4328
	H9	1.0356	0.000 10	0.638 08	−1.324 97	0.4334
	H10	1.0349	0.000 10	0.636 90	−1.323 95	0.4330
	H13	1.0344	0.000 11	0.633 34	−1.320 77	0.4309
19, bicyclo[2.2.2]octane	*C1	5.8991	0.004 25	37.765 59	−89.533 94	118.0823
	C2	5.9389	−0.002 41	37.764 53	−89.594 38	118.0552
	H9	1.0441	0.000 11	0.646 31	−1.336 29	0.4366
	H10	1.0400	0.000 15	0.640 99	−1.329 57	0.4341
20, [1.1.1]propellane	*C1	6.1076	0.001 36	37.806 19	−89.708 68	118.4066
	C2	5.9744	−0.000 84	37.799 98	−89.872 18	118.1019
	H6	0.9770	0.000 10	0.613 13	−1.277 67	0.4329
21, [2.1.1]propellane	*C1	6.1494	0.001 59	37.858 21	−90.114 57	118.2880
	C2	5.8969	−0.000 17	37.729 70	−89.409 91	118.0267
	C5	5.9640	−0.000 63	37.789 28	−89.671 26	118.0640
	H7	1.0138	0.000 07	0.628 13	−1.306 39	0.4328
	H11	0.9835	0.000 10	0.613 73	−1.277 17	0.4311
	H12	0.9786	0.000 10	0.613 76	−1.280 79	0.4316
22, [2.2.1]propellane	C1	6.1523		37.915 03		118.0866
	C2	5.9009	0.000 44	37.717 59	−89.366 16	118.0406
	C7	5.9584	0.000 90	37.776 66	−89.623 00	118.0122
	H8	1.0232	0.000 09	0.631 98	−1.314 18	0.4338
	H9	1.0168	0.000 10	0.629 53	−1.309 30	0.4328
	H16	0.9867	0.000 11	0.618 22	−1.286 19	0.4323
23, [2.2.2]propellane	*C1	6.0156	0.001 92	37.900 48	−89.988 33	118.1432
	C2	5.9494	0.001 10	37.744 31	−89.536 55	118.0572
	H9	1.0227	0.000 09	0.628 55	−2.611 13	0.4304
24, tetrahedrane	C1	6.1112	−0.000 02	37.836 69	−90.064 53	117.9035
	H5	0.8889	−0.000 09	0.562 98	−1.186 73	0.4138
25, cubane	*C1	5.9966	0.001 02	37.809 32	−89.736 40	118.1552
	H9	1.0034	0.000 06	0.614 81	−1.288 69	0.4266
26, spiropentane	*C1	5.9969	0.001 20	37.782 13	−89.726 72	117.9752
	C3	6.0718	0.001 15	37.856 33	−90.114 41	117.8755
	H6	0.9926	0.000 14	0.616 58	−1.286 52	0.4296

[a] Numbering of structures and of atoms is as given in Table I of the preceding paper.[4] Also see Figure 1 of this paper. [b] $V_{neo}(\Omega)$ is the potential energy of interaction of the nucleus of atom Ω with the electronic charge of Ω. [c] $\rho(0)$ is the value of the charge density at the nuclear maximum. This is shifted slightly off the nuclear position ($\sim 3 \times 10^{-2}$ au) for a proton for a basis set which does not contain polarizing functions on hydrogen. A Gaussian basis set was used in these calculations, and such functions do not satisfy the nuclear cusp condition on ρ.

found in the unstrained acyclic molecules is reversed. In the strained molecules the CH and C groups withdraw charge from the CH_2 groups. These observations indicate that a carbon becomes more electronegative as it is subjected to more angular strain. This fact is of primary importance in understanding the gross effects of geometrical constraints on the charge distribution and its energy.

Orbital theories relate an increase in the electronegativity of a carbon atom relative to that of a bonded hydrogen to an increase in the s character of its bonding hybrid orbital.[11] Thus the decrease in bond length and pK_a and the increase in force constant and bond dissociation energy for C–H through the series cyclohexane, ethylene, and acetylene is accounted for by a change in hybridization on carbon from sp^3 to sp^2 to sp, respectively. The increasing electron populations of these carbons to yield net charges of +0.080, −0.035, and −0.177 e, respectively (see Table III), quantify the accompanying increase in electronegativity. An empirical expression has been proposed to relate the C–H coupling constant $J(^{13}C–H)$ to the percent s character of the bond,[12] and the values of this constant for cyclohexane, ethylene, and acetylene (123, 156, and 249 Hz,[13] respectively) yield values of 25%, 31%, and 50% for the s character.

The hybridization model also predicts that the smaller bond angles found in a system with angular strain should result in an increase in the p character of the strained C–C bonds and hence to an increase in the s character of the associated C–H bonds.[14,15] In this way one can account for the increase in the electronegativity of carbon relative to hydrogen which, as noted above, accompanies the introduction of strain into a cyclic system. The validity of this model can be demonstrated by showing that the properties of the CH_2 group in cyclopropane resemble those for ethylene, a point emphasized by Coulson and Moffitt.[14] The C–H bond length and HCH bond angle, both observed and calculated at the 6-31G* level, are similar for the CH_2 groups in cyclopropane and ethylene, the observed values being 1.082 and 1.090 Å and 116.6° and 116.5°, respectively. The similarity in properties extends to the C–H coupling constants, the value for cyclopropane being 161 Hz, the C–H force constant, and the bond dissociation energies as well as to their pK_a values[16] of 46 and 44, with ethylene being

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(11) Coulson, C. A. *Valence*, 2nd ed.; Oxford University: Oxford, 1961; p 218.

(12) Shoolery, J. N. *J. Chem. Phys.* **1959**, *31*, 1427. Muller, N.; Pritchard, D. E. *J. Chem. Phys.* **1959**, *31*, 1471. Results based on the expression percent s = $0.2J(^{13}C–H)$.

(13) Levy, C. G.; Lichter, R. L.; Nelson, G. L. *Nuclear Magnetic Resonance Spectroscopy*, 2nd ed.; Wiley-Interscience: New York, 1980.

(14) Coulson, C. A.; Moffitt, W. E. *Philos. Mag.* **1949**, *40*, 1.

(15) Walsh, A. D. *Nature (London)* **1947**, *159*, 167, 712.

(16) March, J. *Advanced Organic Chemistry*, 3rd ed.; Wiley-Interscience: New York, 1985; p 222.

Table II, Total Energies and Errors in Integrated Atomic Energies and Populations

molecule	E(6-31G*/ 6-31G*), au	$E - \sum_\Omega E(\Omega)$, kcal/mol	$N - \sum_\Omega N(\Omega)$	$\gamma - 1$[c]
1, methane	−40.195 17	−0.02	0.0000	1.000 301
2, ethane	−79.228 76	0.22	0.0011	1.000 364
3, propane	−118.263 65	−1.97	−0.0033	1.000 358
4, butane	−157.298 41	1.06	0.0032	1.000 320
5, isobutane	−157.298 96	1.90	−0.0016	1.000 314
6, pentane	−196.333 03	2.49	0.0035	1.000 261
7, neopentane	−196.333 82	1.81	−0.0001	1.000 254
8, hexane	−235.367 79	1.29	0.0065	1.000 362
9, cyclopropane	−117.058 86	0.07	0.0022	1.000 488
10, cyclobutane	−156.097 03	−0.59	0.0012	1.000 347
11,[a] cyclopentane	−195.162 66	1.00	−0.0064	1.000 280
12, cyclohexane	−234.208 02	0.34	0.0025	1.000 378
13, bicyclo[1.1.0]butane	−154.871 69	−0.02	0.0037	1.000 397
14, bicyclo[2.1.0]pentane	−193.926 97	−0.14	0.0034	1.000 312
15,[a] bicyclo[2.2.0]hexane	−232.965 20	−0.15	0.0001	1.000 360
16, bicyclo[1.1.1]pentane	−193.905 68	−1.69	−0.0037	1.000 054
17,[a] bicyclo[2.1.1]hexane[b]	−232.989 29			1.000 400
18, bicyclo[2.2.1]heptane[b]	−272.061 15			1.000 372
19, bicyclo[2.2.2]octane	−311.103 58	−0.54	−0.0021	1.000 235
20, [1.1.1]propellane	−192.691 10	−2.34	0.0008	0.999 810
21, [2.1.1]propellane	−231.721 88	−1.12	0.0034	1.000 054
22, [2.2.1]propellane[b]	−270.759 56			1.000 544
23, [2.2.2]propellane	−309.809 07	1.57	0.0089	1.000 396
24, tetrahedrane	−153.597 88	0.48	−0.0005	1.000 544
25, cubane	−307.393 70	−0.38	0.0062	1.000 293
26, spiropentane	−193.917 53	−0.16	0.0032	1.000 612

[a] 6-31G*/4-31G. [b] See footnote 7. [c] $\gamma = -V/T$.

Table III. Effect of Basis Set on Atomic Populations[a]

molecule	q(C)			q(H)			
	STO-3G	6-31G**	6-31G*	STO-3G	6-31G**	6-31G*	Δ[b]
CH_4	0.250	0.244	0.039	−0.062	−0.061	−0.008	−0.053
C_2H_6	0.228	0.237	0.075	−0.076	−0.079	−0.025	−0.054
$\mathit{CH}_3\mathrm{CH_2CH_3}$	0.207	0.225	0.063	−0.077	−0.079	−0.025	−0.054
				−0.078	−0.082	−0.028	−0.054
$\mathrm{CH_3}\mathit{CH}_2\mathrm{CH_3}$	0.225	0.220	0.110	−0.086	−0.092	−0.037	−0.055
$\mathit{CH}_3\mathrm{CH(CH_3)_2}$	0.187	0.218	0.057	−0.074	−0.082	−0.028	−0.054
				−0.075	−0.084	−0.030	−0.054
$\mathit{CH}\mathrm{(CH_3)_3}$	0.208	0.193	0.129	−0.099	−0.102	−0.045	−0.057
$\mathit{CH}_3\mathrm{(CH_2)_2CH_3}$		0.224	0.065		−0.079	−0.025	−0.054
					−0.082	−0.028	−0.054
$\mathrm{CH_3(}\mathit{CH}_2\mathrm{)_2CH_3}$		0.210	0.096		−0.095	−0.040	−0.055
$\mathit{CH}_3\mathrm{(CH_2)_3CH_3}$		0.227	0.066		−0.080	−0.025	−0.055
					−0.082	−0.028	−0.054
$\mathrm{CH_3CH_2(CH_2)_2CH_3}$		0.209	0.095		−0.095	−0.040	−0.055
$\mathrm{CH_3CH_2(}\mathit{CH}_2\mathrm{)CH_2CH_3}$		0.196	0.086		−0.098	−0.043	−0.055
$\mathrm{C(}\mathit{CH}_3\mathrm{)_4}$		0.214	0.054		−0.084	−0.030	−0.054
$\mathit{C}\mathrm{(CH_3)_4}$		0.151	0.137				
C_3H_6	0.098	0.104	−0.010	−0.049	−0.052	0.005	−0.057
[1.1.1]propellane							
CH_2		0.137	0.026		−0.033	0.023	−0.056
C		−0.105	−0.107				
C_2H_4		0.082	−0.035		−0.041	0.017	−0.058
C_2H_2		−0.121	−0.177		0.121	0.177	−0.056

[a] Results are from STO-3G/STO-3G, 6-31G**/6-31G*, and 6-31G*/6-31G* calculations. [b] Δis the difference in hydrogen populations, double star–single star results.

Table IV, Net Charges on Methyl and Methylene Groups and Their Energies Relative to Standard Values[a] 6-31G*/6-31G*

molecule	$q(CH_3)$, e	$q(CH_2)$, e	$q(CH_2)$,[b] e	$\Delta E(CH_3)$, kcal/mol	$\Delta E(CH_2)$, kcal/mol	$\Delta E(CH_2)$,[b] kcal/mol
methane	+0.032					
ethane	+0.000					
propane	−0.017	+0.034		−10.5	+21.0	
butane	−0.016	+0.016		−11.6	+11.6	
pentane	−0.016	+0.016	+0.000	−9.9	+10.3	−0.7
hexane	−0.017	+0.016	+0.001	−10.7	+11.2	−0.5

[a] $E(CH_3)$ in ethane = A = −39.614 38 au. $E(CH_2)$ = B = −39.034 78 au. [b] This CH_2 is bonded only to other methylenes.

more acidic. The carbon is negatively charged in both molecules, slightly more so in ethylene. Similarly, the properties for the C–H bridgehead group in bicyclo[1.1.0]butane and the still larger net negative charge on this carbon are understood by noting that its properties approach those observed for the same group in acetylene. A value of 205 Hz for J(CH) correlates with 41% s character. The C–H bond length of 1.070 Å, while larger than the value of 1.057 Å in acetylene, is less than that found in ethylene. Since bicyclobutane reacts with phenyllithium (benzene pK_a is 43), the pK_a of this bicyclic molecule is probably less than 40, which makes it more acidic than ethylene or cyclopropane but less acidic than acetylene itself, which has a pK_a of 25. The atomic charges for the cyclic molecules are considered in detail below in the discussion of the origin of strain energy and its variation with structure throughout this series of molecules. The ultimate argument for an increase in electronegativity with increasing s character is, of course, based on energy, an s electron being more tightly bound than a p electron. As described below, one indeed finds that the energy of a carbon atom decreases as the s character of its hybrids to dissimilar neighboring atoms increases. The bridgehead carbon atom in bicyclobutane, for example, is found to be only 9.5 kcal/mol less stable than the carbon in acetylene.

IV. Atomic Energies

Since the atoms are quantum subsystems, the virial theorem applies, and through this theorem the total energy of the electrons in an atom in a molecule, the quantity $E(\Omega)$, may be defined.[5,17,18] The atomic energies sum to yield the total electronic energy of the molecule, eq 1. The virial theorem gives the following re-

$$E = \sum_{\Omega} E(\Omega) \qquad (1)$$

lationships between the kinetic ($T(\Omega)$), potential ($V(\Omega)$), and electronic ($E(\Omega)$) energies of an atom in a molecule:

$$E(\Omega) = -T(\Omega); \quad 2T(\Omega) = -V(\Omega) \qquad (2)$$

where $E(\Omega) = T(\Omega) + V(\Omega)$. For a molecule in an equilibrium geometry, the energy $V(\Omega)$, which is the virial of the forces acting on the electrons (the virial of the Ehrenfest force[19]), equals the total potential energy as it is usually defined, that is, as the sum of the electron–nuclear energy V_{en}, the electron–electron energy V_{ee}, and the nuclear–nuclear energy V_{nn}. Under these conditions the sum of the electronic energies, $E(\Omega)$, equals the total energy of the molecule.[20] The average kinetic energy of an atom in a molecule is readily obtained by integration of a corresponding density over the basin of the atom, and the first of the equations given in (2) is used to obtain the energy $E(\Omega)$. The virial theorem is not exactly satisfied at the 6-31G* level of calculation, and the ratio $-V/T$, with V equal to the sum of the potential energies as stated above, differs slightly from the correct value of 2 for an equilibrium geometry. This can be seen from Table II, where this ratio is listed under the heading $\gamma - 1$. To correct for the error in the virial, each atomic kinetic energy is multiplied by the factor $\gamma - 1$ to obtain a set of atomic energies that correctly sum to the total energy of the molecule. The factor $\gamma - 1$ is in every case close to unity, the value it should equal for an equilibrium geometry.

Acyclics and Group Additivity. It is possible to fit the experimental heats of formation of the members of the homologous series $CH_3(CH_2)_mCH_3$, starting with $m = 0$, with the expression $2A + mB$, where A is the contribution from the methyl group and B that from the methylene group.[21] The generally accepted value of B at 25 °C is −4.93 kcal/mol while $A = -10.12$ kcal/mol. Wiberg[22] has shown that the correlation energy correction, the zero-point energies, and the change in ΔH_f on going from 298 to 0 K are well represented by group equivalents. This is borne out by the calculated 6-31G*/6-31G* energies which refer to the vibrationless molecules at 0 K. These can be fitted to the relationship $E = 2A + mB$, with $A = -39.61438$ and $B = -39.03478$ au. These constants reproduce the calculated energies with a maximum error of 0.05 kcal/mol. This means that the calculated state functions, energies, and charge distributions contain the necessary information to account for the additivity observed in this homologous series of molecules.

It is clear from the group populations given in Table IV that the methyl group in ethane is not identical with the corresponding group in the other members of the homologous series, and similarly, the methylene group differs slightly, depending on whether it is bonded to one methyl or to two other methylenes. The small differences in populations found for these groups are to be anticipated as their environments change by correspondingly small amounts in these cases. In ethane methyl is bonded to methyl, while in the other molecules it is bonded to methylene from which it withdraws charge. Table IV also lists the energies of the methyl groups relative to the constant A, the energy of a methyl group in ethane. To within the accuracy of the numerical integrations, the energy and populations of methyl are constant when it is bonded to methylene, and the CH_3 group is the same in all members of the homologous series past ethane. The methyl group in these molecules is more stable relative to methyl in ethane by an amount $\Delta E = -10.7 \pm 0.9$ kcal/mol, and its electron population is greater by an amount $\Delta N = 0.0165 \pm 0.0005$ e. The charges and energies obtained by using 6-31G**/6-31G* wave functions behave in an identical manner, their values of ΔE and ΔN being -10.5 ± 0.5 kcal/mol and 0.018 ± 0.001 e,[23] respectively. The charge and energy gained by methyl are taken from the methylene groups. What is more remarkable, and what accounts for the additivity observed in these molecules, is that the energy gained by methyl is equal to the energy lost by methylene. Table IV lists the energies of the methylene groups relative to the energy increment B. One finds that in propane, where it is bonded to two methyls, the energy of the methylene group is $B - 2\Delta E$ and its net charge is $+2\Delta N$. In butane, a methylene is bonded to a single methyl, its energy is given by $B - \Delta E$, and its charge is given by $+\Delta N$. The corresponding CH_2 groups in pentane and hexane, those bonded to a single methyl, have the same properties as the CH_2 groups in butane. Thus the central methylene in pentane and the two such groups in hexane, those bonded only to other methylenes, should have an energy equal to the increment B and a zero net charge. This is what is found to within the uncertainties of the integrated values. Therefore, methylene groups bonded only to other methylenes, as found in pentane and in all succeeding members of the series, possess zero net charge and contribute the standard increment B to the total energy of the molecule.

The group additivity scheme for the energy in hydrocarbons is not the result of methyl and methylene groups having the same energies in every molecule in spite of small changes in their environments. Instead, their properties do change with changes in environment to give two kinds of methyl groups and three kinds of methylene groups. There are only three different CH_2 groups because the change in environment is damped by a single such group. The underlying reason for the observation of additivity in the face of these small differences is the fact that the change in energy for a change in population, the quantity $\Delta E/\Delta N$, is the same for both the methyl and methylene groups. Thus the small amount of charge shifted from methylene to methyl makes the same contribution to the total energy. Reference to Table I shows that nearly all of this small shift in charge and its accompanying change in energy are restricted to the carbon atoms of the methyl and methylene groups, the properties of corresponding hydrogen atoms remaining essentially unchanged. This is to be expected as it is the carbons that are bonded and share a common interatomic surface, and the charge transfer is accomplished by a small shift in this surface. This shift is reflected in the movement of the C–C bond critical point 0.003 or 0.004 Å in the counter direction of the charge transfer (Table I of preceding paper[4]). The bonded radius of the methyl carbon is slightly greater than that for the methylenic carbon. Since the transfer of charge occurs between chemically similar atoms, the resulting change in energy is zero. It is also necessary that the change in correlation energy

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(17) Srebrenik, S.; Bader, R. F. W. *J. Chem. Phys.* **1975**, *63*, 3945.

(18) Srebrenik, S.; Bader, R. F. W.; Nguyen-Dang, T. T. *J. Chem. Phys.* **1978**, *68*, 3667. Bader, R. F. W.; Srebrenik, S.; Nguyen-Dang, T. T. *J. Chem. Phys.* **1978**, *68*, 3680.

(19) Bader, R. F. W. *J. Chem. Phys.* **1980**, *73*, 2871.

(20) The electronic energy defined by the virial theorem equals the total energy of the system as usually defined plus the virial of the net forces exerted on the nuclei. When these forces are zero, as they are in an equilibrium geometry, the electronic energy equals the usual total energy.

(21) Prosen, E. J.; Johnson, W. H.; Rossini, F. D. *J. Res. Natl. Bur. Stand. (U.S.)* **1946**, *37*, 51.

(22) Wiberg, K. B. *J. Comput. Chem.* **1984**, *5*, 197.

(23) Bader, R. F. W. *Can. J. Chem.* **1986**, *64*, 1036.

for a change in population be the same for both groups if one is to account for the experimental observation of group additivity of the energy.[24]

Reference to Table I indicates that the energy of a hydrogen atom decreases as its average population increases. This is in general not true for the more complex electronic distribution of a carbon atom. The carbon of the standard methylene group as found in pentane and hexane, for example, has a smaller average electron population than the carbon in the repeating methyl group, yet it is 5 kcal/mol more stable. The charge density is slightly more contracted in the carbon of CH_2 than in that of CH_3, as is reflected in their values of $\rho(0)$ at the nuclei, Table I.

The data in Table V illustrate the basis for the observation of group properties in chemistry—that the properties of a group are determined only by the total force acting on it and not by the individual contributions to this total force.[1,5] The atoms considered to exemplify this property are the hydrogens and carbons of the methyl groups in propane to hexane. All quantities are referenced to the values for the hexane molecule. The total atomic populations and kinetic energies, the latter equalling minus the atomic energy, are all remarkably constant for each kind of atom. If the distribution of charge is the same for each type of atom, then the quantity $V_{eno}(\Omega)$, the potential energy of interaction of the nucleus of atom Ω with its own charge distribution, should also be the same. This is indeed the case, the largest difference being 0.4 kcal/mol for a hydrogen and the carbons exhibiting a variation of ± 2.6 kcal/mol about the mean. The interaction of all the nuclei in the molecule with the charge in atom Ω, the quantity $V_{ne}(\Omega)$, increases by very large amounts with the removal of each CH_2 group, changing by 1.5×10^3 kcal/mol for H and by 9.2×10^3 kcal/mol for carbon from hexane to propane. The repulsion of the electrons in atom Ω by the other electrons in the molecule, the quantity $V_{ee}(\Omega)$, and the contribution of the nuclear–nuclear repulsion energy to the energy of Ω, the quantity $V_{nn}(\Omega)$, on the other hand, decrease by large amounts with the removal of each CH_2 group.[25] The sum of all three contributions to give $V(\Omega)$, the total potential energy of the atom, is however, the same for each kind of atom through the series. This must be, since $V(\Omega)$ is equal to twice the total energy of the atom by the virial theorem. $V(\Omega)$ is the total virial, the virial of all the forces—electron–nuclear, electron–electron, and nuclear–nuclear—acting on atom Ω. This quantity is conserved along with the kinetic energy when the distribution of charge of the atom remains unchanged.

The reason for the total virial remaining unchanged in spite of the large changes in its individual components lies in the fact that the incremental decreases in the electron–electron and nuclear–nuclear repulsive energies are both one-half of the magnitude of the incremental increase in the electron–nuclear attractive energy. Thus the removal of each CH_2 group causes changes of increasing magnitude in all contributions to $V(\Omega)$ for each atom of the methyl group (the changes occur closer to the methyl with the removal of successive methylenes), but the changes sum to zero for each atom. For example, the sums of the incremental changes in $^1/_2V_{en}$, V_{ee}, and V_{nn} for one of the two equivalent hydrogens in CH_3 for the removal of all three methylene groups to change hexane into propane are +1.2018, −1.2018, and −1.2010 au, respectively.

The branched molecules isobutane and neopentane are more stable than their normal isomers by 1.9 and 5.1 kcal/mol, respectively, in terms of their ΔH_f values at 25 °C and by 1.6 and 3.8 kcal/mol in their vibrationless state at 0 K.[26] The 6-31G*/6-31G* calculated energies predict increased stabilities of only 0.4 and 0.5 kcal/mol, respectively, indicating that the change in correlation energy for a change in population of the CH and C groups is different from that for the CH_3 and CH_2 groups. As noted above, the relative electron-withdrawing abilities of the hydrocarbon groups are in the order $CH_3 > CH_2 > CH > C$. Thus the charges on the methyl groups in the branched isomers are greater than those found in the normal alkanes, and they are correspondingly more stable. Relative to methyl in ethane the ΔE and ΔN values for methyl in isobutane are −21.6 kcal/mol and −0.028 e, and in neopentane the corresponding values are −28.8 kcal/mol and −0.034 e. Nearly all of the increase in stability of the methyl groups in isobutane and neopentane resides in their carbon atoms, which are 20.1 and 25.8 kcal/mol more stable, respectively, than C in ethane. The carbon atoms at which the branching occurs are less stable than C in ethane by 17.9 and 23.1 kcal/mol, respectively. It follows that the actual energies of the C–H and C groups in the branched molecules are less than the values assigned to them in the additivity scheme.

Strain Energy. To discuss and compare theoretically defined strain energies with those defined in terms of the experimental heats of formation for the cyclic, bicyclic, and propellane molecules, we shall define group energies in the same manner as is done by using the experimental heats of formation except that they will not be referenced to the standard states of the elements. The strain energy of a given group in a molecule is obtained by subtracting from its energy the energy of the corresponding standard group. The energies of the standard methyl and methylene groups are the constants A and B reported above. The energies of the standard methyne and C groups are obtained by subtracting 3 and 4 times the value of A, respectively, from the total energies of isobutane and neopentane. This yields $E(\mathrm{CH}) = -38.45582$ and $E(\mathrm{C}) = -37.87630$ au.[27] The strain energies calculated in this manner are given in kcal/mol opposite CH_2, CH, and C groups for the structures shown in Figure 1. The sum of the group strain energies for a given structure is also given, followed in brackets by the experimental value[3] determined by using the Franklin group equivalents.[2] While there are small differences between the theoretical and experimental values for the strain energy, the overall agreement is rather good, the largest errors being found for [1.1.1]- and [2.2.2]propellane.

Cyclic Molecules. As noted above, the relative order of the electronegativities of H and C is reversed from that found in the standard methylene group when carbon is subjected to the geometrical strain encountered in the formation of the small ring cyclic compounds because of the accompanying increase in s character of the C–H bonds. Thus, relative to its population in the standard CH_2 group, each hydrogen in cyclopropane transfers 0.048 e to carbon. This leads to an increase of 15.5 kcal/mol in the stability of the carbon but also to a 12.6 kcal/mol decrease in the stability of each of the two hydrogens relative to their values in the standard group. Overall the transfer of charge within the CH_2 group leads to a 9.6 kcal/mol decrease in its stability relative to the standard value and to a total strain energy 3 times this, 28.8 kcal/mol, in good agreement with the generally accepted value.[28] The CH_2 group in cyclopropane is only 2.3 kcal/mol more stable than the same group in ethylene, and in terms of the charge transfer within the group and its energy, it resembles the ethylene fragment more than it does the standard methylene group.

If one takes the s character in the C–H bonds to carbon in the standard methylene group to be 25%, in ethylene to be 33.3%, and in acetylene to be 50%, then the energy of this carbon varies

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[24] In density functional theory the correlation energy is expressed as a functional of the charge density. [For a review, see: Williams, A. R.; von Barth, U. *Theory of the Inhomogeneous Electron Gas*, Lundquist, S., March, N. H., Eds.; Physics of Solids and Liquids; Plenum: New York, 1983.] When ρ remains unchanged for a given group in different molecules, the group's contribution to the correlation energy will also remain unchanged.

[25] The nuclear–nuclear repulsion energy for atom Ω, $V_{nn}(\Omega)$, is the virial of the Hellmann–Feynman forces exerted on the charge density in the atom by all of the nuclei in the molecule.

[26] Fliszar, S. *Charge Distribution and Chemical Effects*; Springer-Verlag: Berlin, 1983.

[27] The standard energies for the CH and C groups are obtained by ignoring the transfer of charge from these groups to their attached methyl groups as actually occurs in isobutane and neopentane. Because of this, the standard CH and C groups are more stable than the actual groups by 64.7 and 113.1 kcal/mol, respectively.

[28] The use of the double star basis set leads not only to the same group charges but also to the same charge transfers within a group and to the same changes in energy relative to the standard groups. This was noted above for the methyl and methylene groups in the acyclic molecules and remains true for the strained systems. The double star results for cyclopropane yield a charge transfer of 0.044 e from H to C over that in the corresponding standard CH_2 group and a contribution of 9.2 kcal/mol to the strain energy.

in a linear manner with the s character of this bond, the energy decreasing by 3.0 kcal/mol with each percentage increase in s character. In all of these molecules the charge transfer is between C and H, and the functional group has no net charge. The population of carbon in cyclopropane is slightly smaller than that of the carbon in ethylene, and its energy is correspondingly greater, by 7.9 kcal/mol, yielding ≈31% s character. While the carbon of ethylene is more stable than the carbon in the standard CH_2 group, the CH_2 fragment in ethylene is less stable than the standard, as is the same fragment in cyclopropane. In both cases the hydrogens are destabilized more than the carbon is stabilized by the transfer of charge within the CH_2 group.

In the less strained cyclobutane, the transfer of charge from H to C relative to the populations in the standard CH_2 group is reduced to 0.014 e. Correspondingly, carbon has an energy only slightly lower than the standard value and, in terms of the above linear relationship, a 26% s character. In agreement with this, the value of the C–H coupling constant,[13] 134 Hz, is only slightly greater than the value for methylene in cyclohexane, and the relationship between J(C–H) and s character[12] yields a value of 27%. Similarly, the bond length, the stretching force constant, and the HCH bond angle for the CH_2 group in this molecule suggest only a small increase in s character over that found in the standard CH_2 group. Thus the stability of C is increased by only 1.0 kcal/mol over the standard value while the stabilty of each hydrogen is decreased by 3.9 kcal/mol with each CH_2 group in cyclobutane being 6.7 kcal/mol less stable than the standard. The total strain energy is calculated to be 26.8 (experimental 26.5) kcal/mol.[29]

The populations and energies of the atoms in the methylene group of cyclohexane differ little from their values in the standard group. The small differences which are present lead to a total calculated strain energy of 0.06 kcal/mol compared to an anticipated value of zero for a system with no geometrical strain. The results for cyclopentane refer to but one configuration of a molecule which undergoes a rapid ring-puckering motion. The results are, however, intermediate between those for its neighbors. Two of the methylene groups have almost zero net strain while the third is less stable by 4.2 kcal/mol. The total strain energy for this one geometry is calculated to be 7.1 kcal/mol compared to the conformationally averaged experimental value of 6.2 kcal/mol.

The relative degree of geometric strain in these molecules can be measured in terms of the departure of the C–C–C bond path angles from the tetrahedral value (Table II of preceding paper[4]). As a carbon atom is subjected to an increasing amount of geometric strain as determined in this way, an increasing amount of charge is transferred from H to C in CH_2 relative to the populations in the standard methylene group. This redistribution of charge within the methylene group leads to a stabilization of the carbon atom and to an even greater destabilization of the hydrogen atoms. The overall result is a strain energy equal to the increase in the energy of the group relative to that of standard methylene. These observations, obtained from the theory of atoms in molecules, may be related to and rationalized in terms of the orbital model of electronic structure by assuming that the s character of the C–H bonds increases along with the increase in the geometric strain to which the carbon atom is subjected. We shall continue to use this orbital model to account for the relative energies and populations found for the atoms in the bicyclic molecules which are discussed next.

Bicyclic Molecules. Bicyclo[1.1.0]butane (**13**) is the most strained of the bicyclic molecules. The magnitude of the net charge of −0.121 e on the bridgehead carbon of this molecule, which possesses an inverted geometry, is exceeded only by that for the bridgehead carbons in [2.1.1]- and [2.2.1]propellane. This carbon withdraws charge from its bonded hydrogen and from the two methylene groups. Its energy is only 9.5 kcal/mol above that of carbon in acetylene, suggesting a considerable degree of s character in its hybrid bonds to the groups from which it withdraws charge. Orbital analyses indicate that the bridgehead bond is essentially pure p,[30] and hence all the s character is in the hybrids directed at H and the CH_2 groups. The ^{13}C coupling constant for the bridgehead C–H bond yields 41% s character, leaving ≈30% for each of the hybrids to the methylene groups. The coupling constants for the C–H bonds in these CH_2 groups average to the same value as found for cyclopropane, giving them 32% s character. This implies that each of the hybrids directed at the bridgehead carbons has 18% s character, considerably less than that of the hybrids directed from the bridgehead carbons. While admittedly approximate, the analysis indicates that in the bonds between a bridgehead and a methylenic carbon there is considerably more s character in the hybrids from the former than from the latter. Therefore, the bridgehead carbons should withdraw charge from the methylene carbons as well as from the bridgehead hydrogens. Thus what at first might appear as an anomoly—the most strained carbon atom possessing the most negative total energy—follows directly from the orbital model. It predicts the hybrids from the bridgehead carbons to be relatively rich in s character and for these atoms to be the most electronegative and hence the most stable in the molecule.

As noted above,[27] in assigning the group energy to CH it is assumed that there is no transfer of charge from this group to the three attached methyl groups, whereas it bears a charge of +0.084 e in isobutane. As a result, the group energy for the standard CH group is 60 kcal/mol more stable than its actual energy in the isobutane molecule. Even so, because of the very electronegative nature of the bridgehead carbon and its similarity with the energy of carbon in acetylene, the energy of the bridgehead CH groups differs from the standard value by only 1.6 kcal/mol. Thus essentially all of the strain energy in this molecule, when computed with standard group energies, has its origin in the charge distributions of the methylenic groups. The charges and energies of the methylenic hydrogens are very similar to those for cyclopropane, as is the average of the ^{13}C coupling constants for the C–H bonds. Thus the increase in the strain energy for the methylenic groups in this molecule over that found in cyclopropane comes from the further transfer of charge from the methylenic to the bridgehead carbons. Each CH_2 group has a net charge of +0.068 e and is calculated to be 32.7 kcal/mol less stable than the electrically neutral standard CH_2 group. The total calculated strain energy is 68.6 (63.9) kcal/mol.

In the progression through the bicyclic series from the most strained bicyclobutane **13** to the least strained bicyclo[2.2.2]octane (**19**), the populations of the bridgehead carbons undergo a continuous decrease and the CH group becomes positively charged. The populations of the bridging methylene groups, on the other hand, increase through the same series, and they become negatively charged. The group energies parallel these changes in populations in a nearly linear manner, with the methylene groups becoming more stable through the series and the methine group, its charge approaching that of the CH group in isobutane, becoming less stable and the principal source of strain energy. Thus as the strain at the bridgehead carbon is decreased, the s character in its hybrids directed at the hydrogen and at the methylene carbons decreases as does its electronegativity, and the relative electron-withdrawing ability reverts to the normal order with CH_2 withdrawing charge

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[29] This analysis of the strain energy in these two molecules agrees with and substantiates the observations made in the preceding paper[4] regarding the greater stability of the carbons in cyclopropane over those in cyclobutane. This results from the delocalized concentration of charge over the interior of the three-membered ring where it is shared by and binds all three ring nuclei. Thus one finds the value of V_{neo}(C), the attractive energy of interaction of the carbon nucleus with its own charge distribution, to be 127 kcal/mol more negative for a carbon in cyclopropane than for one in cyclobutane. This is the source of the extra stabilization that causes a carbon of cyclopropane to be 14.5 kcal/mol more stable than a carbon in cyclobutane. The greater charge and stability of C in cyclopropane are a result of the greater s character in its bonds to hydrogen. This increase in stability, therefore, appears in a relatively large C–H bond dissociation energy for cyclopropane, 106 kcal/mol, a value only 2 kcal/mol less than that for ethylene (Baghal-Vayjooee, M. H.; Benson, S. W. *J. Am. Chem. Soc.* **1979**, *101*, 2838).

[30] Newton, M. D.; Schulman, J. M. *J. Am. Chem. Soc.* **1972**, *94*, 767. Finkelmeier, H.; Lüttke, W. *J. Am. Chem. Soc.* **1978**, *100*, 6261.

Table V. Properties of H and C Atoms in CH_3 Relative to CH_3 in Hexane[a]

atom	molecule	$N(\Omega)$, e	$T(\Omega) = -E(\Omega)$	$V_{eno}(\Omega)$	$V_{en}(\Omega)$	$V_{ee}(\Omega)$	$V_{nn}(\Omega)$	$V(\Omega) = 2E(\Omega)$
H1	hexane	1.025	0.6266	−1.3102	−9.3780	4.3442	4.3503	−1.2532
	pentane	0.000	+0.3	−0.4	356.4	−178.7	−178.5	−0.6
	butane	0.000	+0.4	−0.4	791.9	−396.5	−396.6	−0.8
	propane	0.000	−0.1	+0.0	1343.0	−671.7	−671.2	+0.2
H2	hexane	1.028	0.6278	−1.3125	−10.5354	4.6370	4.6429	−1.2555
	pentane	0.000	−0.1	−0.1	381.4	−190.8	−190.8	+0.2
	butane	0.000	+0.1	−0.3	894.1	−445.7	−448.8	−0.2
	propane	0.000	−0.3	+0.3	1508.3	−754.1	−753.6	+0.6
C	hexane	5.936	37.7494	−89.5288	−138.1137	37.6551	24.9598	−75.4988
	pentane	−0.001	−1.3	−2.7	2333.6	−1166.4	−1164.5	+2.7
	butane	−0.001	+0.1	−0.1	5349.0	−2672.7	−2676.4	−0.2
	propane	+0.001	+0.4	−2.9	9157.3	−4580.3	−4577.8	−0.8

[a] The energies for hexane are given in au, and for the other compounds the differences with respect to hexane are given in kcal/mol.

from the CH groups.

These observations are illustrated for bicyclo[1.1.1]pentane (**16**), for which the CH coupling constants are known. The total strain energy and the contribution to the strain energy from the CH group attain their maximum values for the bicyclic series in this molecule. The coupling constant for the bridgehead C–H bond, 160 Hz,[13] yields 32% s character for this carbon hybrid and thus 23% for each of the hybrids directed toward the methylene carbons. The methylene coupling constant, 144 Hz, yields 29% s character for the C–H bonds, thereby leaving 21% s character for the hybrids directed at the bridgehead carbons. Hence the hybrids making up the C–C bonds are essentially evenly matched in s character, and the groups revert to their normal relative electronegativities, with methylene withdrawing charge from methyne. The CH_2 groups, since they are negatively charged, are stabilized relative to the standard, electrically neutral methylene group, and they contribute −5.6 kcal/mol each to the strain energy.

The methyne group has a large net negative charge in **13**, has about half this value in **14**, is neutral in **15**, and exhibits its first positive charge in bicyclo[1.1.1]pentane (**16**). Correspondingly, the group becomes progressively less stable, and its strain energy contribution attains its largest value in the bicyclic series for **16**, even though its net positive charge continues to increase through the remainder of the series to a value of +0.057 e in bicyclo[2.2.2]octane (**19**). Structure **16** has no bridging bond, and it is for this reason that there is a sharp increase in the methyne strain energy at this point in the bicyclic series. In terms of the orbital model, a bridging bond is mostly p in character, leaving an increased percentage of s character for the bonds from the bridgehead carbon to its dissimilar neighbors. With the loss of the bridgehead–bridgehead bond, the bridgehead carbon becomes less electronegative relative to its neighbors, and there are, in addition, four rather than three such neighbors. In terms of the potential energy contributions to the atomic energy, there is a sudden relative increase in the repulsive contributions to the energy of the bridgehead carbon in **16**. The energies of the bridgehead carbon atoms are essentially the same in the structures without a zero bridge, **16**, **18**, and **19**, in spite of a decrease in their electron populations. Because of this decrease in $N(\Omega)$, the contribution to the energy of the atom from the attractive interaction of the carbon nucleus with its own charge density is 46 kcal/mol more stable in **16** than in **19**. The fact that the total energies of these two bridgehead atoms are identical necessarily means that the repulsive forces make a relatively larger contribution to the external virial, i.e., to the potential energy of the atom arising from its interactions with the remainder of the system, in **16** than in **19**. Such a result is in accord with the classical idea of a significant nonbonded repulsion between the bridgehead atoms which decreases from **16** to **19**. It also shows what was emphasized in the previous paper:[4] the presence or absence of a bond path between the bridgehead nuclei has direct physical consequences. In the zero-bridged structures **13** through **15**, the charge density in the bridgehead internuclear region exerts net attractive forces on the bridgehead nuclei, and their virials lower the energy of the system.[31] In the structures without zero-carbon bridges, there is no accumulation of electronic charge to give a line of maximum charge density linking the bridgehead nuclei, repulsive forces dominate, and their virials raise the total energy.

There is a further correlation to be noted. This is one between the electronegativity and energy of the methylenic carbon and the degree of relaxation of the geometric strain as measured by $\Delta\alpha$, the difference between the bond path and geometric angles (Table II of preceding paper[4]). The greater the relaxation as measured by $\Delta\alpha$ the greater the stability of the atom. Compare the carbon in the one-carbon-bridge methylene in **14** with that in **13**. While their geometric angles are nearly identical, $\Delta\alpha$ is 5° greater for the carbon in **14**, and its population and stability are greater than for the carbon in **13**. The methylene group in **14** is in fact very similar in its properties, including the value of $\Delta\alpha$, to that in cyclopropane. The two-carbon-bridge methylene in **14** is under less strain, its relaxation is smaller, and there is a substantial charge transfer to the bridgehead carbons. Because of this loss of charge, its strain energy is considerably greater than that for a methylene group in cyclobutane. In **18**, where the relative electronegativity has reverted to the normal order, the one-carbon-bridge methylene has a larger population and is more stable that the two-carbon-bridged methylenes. In addition to having a larger value for $\Delta\alpha$, the one-bridged carbon can withdraw charge from both bridgehead groups.

In **19**, the final member of the bicyclic series, the bond angles are all fairly normal, leading to normal hybridization. As a result, the methylenes should withdraw charge from the CH groups. The effect should be similar to isobutane but not as large since a methylene is not as electronegative as a methyl. The choice of a methylene attached to a CH group in a branched structure as a reference group would yield a more direct measure of the source of strain in these molecules. The present values are obtained by comparing energies with those of groups which are physically unrelated to the molecules in question. Thus in **19**, methylene is found to be more stable than its standard (the standard CH_2 has a zero net charge) while the CH group is correspondingly less stable, and the final strain energy is obtained as a difference rather than as a sum of group contributions.

The relative electronegativity of the carbon in the CH groups in the cage structures cubane and tetrahedrane again parallel the percent s character. The s character in the CH group of tetrahedrane must be considerably greater than for the bridgehead CH in bicyclobutane because of the increased geometric strain. The linear relationship between s character and energy of the carbon in neutral CH_2 and CH groups yields a value of 42% for the carbon in tetrahedrane. The relaxation as measured by $\Delta\alpha$ is also a maximum for this molecule. As a result the carbons are more electronegative than the bridgehead carbons in bicyclobutane, **13**. Unlike the CH group in **13**, which possesses a net negative charge, this group in tetrahedrane has a zero net charge, as the charge transferred to carbon is necessarily taken from the hydrogen. As with the methylene group, a transfer of charge from hydrogen to carbon raises the energy of the group, and each CH group has a strain energy of 35.2 kcal/mol. The energy of a CH group in

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(31) Bader, R. F. W.; Essen, H. *J. Chem. Phys.* **1984**, *80*, 1943.

tetrahedrane is in fact only 5.9 kcal/mol greater than its value in acetylene. The energy of a carbon atom in cubane predicts a 36% s character, while the ^{13}C coupling constant predicts 31%. The charge transfer from C to H is much reduced from that found in tetrahedrane, and the strain energy per CH group is reduced to 19.9 kcal/mol to give a total value of 159.1 kcal/mol. Taking into account the −0.055-e correction to the population of a hydrogen atom relative to carbon to obtain the more realistic absolute charges of the 6-31G** basis, the tetrahedron cage is bounded by hydrogens bearing net positive charges of 0.056 e while in cubane, the carbon cage is bounded by hydrogens bearing net negative charges of almost equal magnitude, the value being −0.058 e.

The percent s character at the central carbon in spiropentane, **26**, is 25% by symmetry. The methylene groups should be similar to those in cyclopropane, with 32% s character in the C–H bonds and 18% in the C–C bonds. Therefore, the central carbon has more s character in its contribution to the C-C bonds and is more electronegative than are the carbons of methylene. Thus the central carbon withdraws charge from the methylenes and is 12.5 kcal/mol less stable than the standard C group while the methylenes with a net positive charge have a strain energy one-third again as large as that for cyclopropane. The energy of the methylene group in **26** follows the nearly linear energy vs. net charge relationship observed for this group in the bicyclics.

Propellanes. The unusual structures possessed by the propellanes give atomic charges and energies that do not yield to the rationalizations based on percent s character in the hybrid bonds that were found to apply to the cyclic and bicyclic systems. The theory of atoms in molecules can, of course, still be used to obtain the energies and populations of the atoms, and these are found to follow the major observation established above—the more strained the carbon atom, the greater its electronegativity. The bridgehead carbons in propellanes **20** through **23** all bear net negative charges, being largest in magnitude for the two mixed members **21** and **22** and smallest for the least strained member **23**. These atoms, together with the bridgehead carbon in bicyclobutane, have the lowest energies of all the atoms in this series of molecules. The strain energies reported in Figure 1 for the bridgehead carbons in the propellanes are computed by comparing their atomic energies with the energy assigned to the standard C group. This standard group is considerably more stable than the actual C atom in neopentane,[27] and thus the bridgehead group contributes to the strain energy in two of the propellanes in spite of their large negative charges and low energies. The bridgehead carbon in [2.1.1]propellane, whose average electron population exceeds that of the actual C group in neopentane by 0.268 e, has an energy that is about 100 kcal/mol lower. Of the bridgehead carbons, those in [1.1.1]propellane are the least stable, and relative to the standard energy, each contributes 44.0 kcal/mol to the strain energy of this molecule. The next most stable are those in [2.1.1]propellane, each of which is 11.4 kcal/mol higher in energy than the standard C group. The smallest bond angles formed with the bridgehead bond in the propellanes are those with the bonds of the three-membered rings, all of which are about 60°. The extent of relaxation of charge density about this angle is about the same for the three such angles in [1.1.1]propellane as it is for the two such angles in [2.1.1]propellane, with $\Delta\alpha$ equal to 10° (Table II[4]). The extent of relaxation of strain is, however, considerably greater for the single such angle in [2.2.1]propellane, where $\Delta\alpha$ equals 16°. This carbon has the largest net negative charge and is the most stable of all the bridgehead carbons. Its energy is lower than that of the standard group by 24.3 kcal/mol. A bridgehead carbon in [2.2.2]propellane is less strained and has smaller relaxations in its bond angles. It thus has a smaller net negative charge, and its energy is 15.1 kcal/mol lower than that of the standard C group.

The three- and four-membered-ring methylene groups in the propellanes behave in different ways in the manner of their charge loss to the bridgehead carbons. Their energies do not correlate with their net charges in the nearly linear manner found for the bicyclics. In keeping with the basic observation that the electronegativity of a carbon increases with the extent of its geometric strain, the atomic populations for the carbons in the propellanes decrease in the order bridgehead, one-bridged methylenic carbon, and two-bridged methylenic carbon. Charge is transferred to the bridgehead carbons from both the carbon and the hydrogen atoms of a three-membered-ring methylenic group. The net charge on these CH_2 groups is essentially the same in **20**, **21**, and **22**, but an increasing fraction of it resides on the carbon atom. The strain energy increases in parallel with the increasing positive charge on carbon, 5 to 11 to 14 kcal/mol. It is important to note that the middle two members of this series possess the largest strain energies. The 6-31G*/6-31G* calculations are in good agreement with the values for these two molecules, but they overestimate the strain energies in both [1.1.1]- and [2.2.2]propellane by 6 kcal/mol.[32]

The methylenic carbon in a four-membered ring bears the largest positive charge in these molecules. It is $\approx$+0.1 e in both [2.1.1]- and [2.2.1]propellane and decreases to half this value in the less strained [2.2.2]propellane. The hydrogens are negatively charged in these methylenic groups. Because these carbons suffer the largest loss of charge to the bridgehead carbons, they are the least stable carbons in the propellanes, and the methylenic groups of the four-membered rings make larger contributions to the strain energy than do those of the three-membered rings. Whatever standards are used to determine the strain energies, the same order for the relative stabilities of the propellane carbons will be obtained: bridgehead C more stable than methylenic C of a three-membered ring more stable than methylenic C of a four-membered ring. This order of stabilities is a consequence of the flow of charge within the molecules—from the methylenic carbons to the bridgeheads, with the largest loss occurring for the carbons of the four-membered rings. This will result in each of the propellanes exhibiting a relatively large quadrupole moment.

The propellane structures are unusual and do not fit any of the standard hybridization models. In [2.2.2]propellane the bridgehead bond path angles, or bond angles (Table II of preceding paper[4]), predict sp^2 hybridization for the bridgehead carbon, giving a bridgehead bond of pure p which is in agreement with the form of the SCF orbital. The energy of the bridgehead carbon is, however, 66 kcal/mol more stable than that of the sp^2 carbon in ethylene, but the reason for this is easy to understand. In ethylene the pure p hybrid on each carbon forms a π-bond, while in the propellane the pure p hybrid forms a σ-bond with the second bridgehead carbon with a bond order of 1.26.[4] In [1.1.1]propellane the bond path angles formed at a bridgehead carbon are very close to those required for sp^3 hybrids to be directed at the bridging methylenes. This model then describes the bridgehead bond as resulting from the overlap of the tails of two sp^3 hybrid orbitals on the bridgehead carbons. These models account for the bridgehead carbons of [2.2.2]propellane being lower in energy than those in [1.1.1]propellane. It is difficult to rationalize the larger net charge on the bridgehead carbons in the latter molecule and to rationalize the charges and energies of the two intermediate members of this series in terms of the orbital model.

V. Discussion

The charge distribution of a methyl or a methylene group defined and bounded by a surface of zero flux in the gradient of ρ can appear essentially unchanged as a transferable unit throughout a homologous series of molecules. When this occurs, the contribution of the group to the total energy of the molecule is also unchanged, and the groups defined in this manner account for the additivity of the energy. Following on this observation, if the charge distribution of a group does change when it is transferred to another system, then its contribution to the total energy will be different, and one may relate its change in energy to the changes in the group's charge distribution as induced by its new environment. Aside from the fact that the atoms and their

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[32] The 6-31G**/6-31G* results for [1.1.1]propellane are very similar, yielding strain energies for the CH_2 and C groups of 4.5 and 44.7 kcal/mol, respectively, and a total strain energy of 103 kcal/mol.

properties are defined by quantum mechanics, the ultimate justification for identifying them with the chemical atoms is this very observation—that their properties change in direct proportion to the changes in their distribution of charge. Thus whether the form of an atom changes by a little or by a lot, its energy and other properties change by a corresponding amount.

Examples have been given in which the methylene group can be transferred without change, with little change, or with substantial change. The standard methylene group is identified with the transferable repeating unit as found in the central positions of pentane and hexane. The nearly identical group is found in cyclohexane, and correspondingly, the energy of the group in this molecule is nearly unchanged from that of the standard. The strain energy of this molecule is thus zero, in agreement with experiment. Since the energy of the standard CH_2 group is independently fixed by the theory, the fact that the energy of cyclohexane is 6 times the energy of the standard group is very much a consequence of the atomic theory.

The methylene group as it appears in cyclopropane differs significantly from the standard. We have here the first evidence of what initially might seem surprising in terms of prevailing ideas on the origin of strain—that the "strained" atom is stabilized at the expense of the hydrogens. Thus when carbon is subjected to angular strain, the result is an increase in its relative electronegativity, an increase in its average electron population, and, hence, an increase in its stability. The more strained the atom, as measured by the departure of its bond path angles from the tetrahedral value, the greater its electronegativity and the greater its relative stability. Thus the bridgehead carbon in bicyclo[1.1.0]butane is more stable than the methylenic carbon from which it withdraws charge. This way of reasoning accounts for the relative values of the strain energies calculated for the individual groups in the cyclic, bicyclic, and propellane molecules. In the case of the cyclic and bicyclic molecules these observations can be accounted for in terms of the orbital model. This model predicts, through hybridization arguments based on geometries and ^{13}C coupling constant data, that the s character percentage of the hybrids from carbon to dissimilar neighboring groups increases as the carbon is subjected to an increasing degree of geometric strain. This results in an increase in both the electronegativity and stability of the strained carbon relative to its bonded neighbors. It should be borne in mind that the atomic charges defined by theory have a direct physical and spatial significance. Thus there is a physical flow of charge from the peripheral groups to the bridgehead region in the bicyclics and propellanes as the geometrical strain in the molecule is increased.

In 1967, Bader, Henneker, and Cade[33] proposed that a particular outer contour of the charge density could be used to define the shape of a molecule for its nonbonded interaction with other molecules. In particular, they showed that the 0.002-au contour of the density provided a good approximation to the van der Waals' envelope of a molecule.[33,34] Their Hartree–Fock-based envelope models of the diatomic molecules N_2, O_2, and F_2 were, and still are, being used in the elucidation of the crystal structures of the various solid phases of these systems.[35] It is clear that good van der Waals' envelopes can be constructed for hydrocarbons of any chain length from the charge distributions of the standard repeating methyl and methylene groups defined in this study. As suggested some time ago[36] and recently illustrated,[37] the multipole moments of the atoms defined by theory, moments calculated by the program PROAIM,[6] may be used in a multipole moment expansion to quickly and efficiently obtain the electrostatic field in the neighborhood of a molecule. What is particularly appealing about the use of the atomic moments is that they are the most transferable moments that one can define. The electrostatic field in the neighborhood of a saturated hydrocarbon can readily be constructed by using the moments obtained here for the standard repeating methyl and methylene units.[38]

Theory and observation have uncovered the transferable atoms of chemistry, and in those cases where transferability is essentially complete, as in the homologous series of hydrocarbons, these pieces can be used to replicate molecules and their properties. Clearly the next step is to learn to predict the manner in which the atoms respond to a change in environment. Then one will be able to use the theory to make molecules from atoms rather than from bare nuclei and electrons as we now do.

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Registry No. **1**, 74-82-8; **2**, 74-84-0; **3**, 74-98-6; **4**, 106-97-8; **5**, 75-28-5; **6**, 109-66-0; **7**, 463-82-1; **8**, 110-54-3; **9**, 75-19-4; **10**, 287-23-0; **11**, 287-92-3; **12**, 110-82-7; **13**, 157-33-5; **14**, 185-94-4; **15**, 186-04-9; **16**, 311-75-1; **17**, 285-86-9; **18**, 279-23-2; **19**, 280-33-1; **20**, 35634-10-7; **21**, 36120-91-9; **22**, 36120-90-8; **23**, 36120-88-4; **24**, 157-39-1; **25**, 277-10-1; **26**, 157-40-4.

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(38) It should be noted that all properties, including the charge distribution, of the methyl and methylene groups exhibit the same transferability and constancy in values as reported herein for their electron populations and energies. Table I of the preceding paper[4] illustrates the constancy in the charge distribution in terms of the transferability in the values of the charge density, its curvatures, and the ellipticity of corresponding bond critical points and in the values of the associated bonded radii. It is demonstrated again by the transferability in the values of $V_{neo}(\Omega)$ and of $V(\Omega)$ for corresponding atoms by the data in Table V of this paper. A future publication will demonstrate that in addition to these properties, the methyl and methylene groups exhibit transferable moments, atomic volumes (as determined by the space enclosed by the intersection of the atomic surface and the 0.001- or 0.002-au density envelope), and correlation energies expressed as functionals of the charge density. The observation of variations of 1 kcal/mol or less in the atomic kinetic and correlation energies for atoms with identical net charges provides a more stringent test of the transferability of an atom's charge distribution than can be obtained from any pictorial display in terms of comparisons of density or density difference maps. The kinetic energy is a complicated functional, including gradients, of the single-particle density matrix while correlation energies are expressed as functionals of its diagonal elements, the charge density. The observations that have been made so far suggest that it should be possible to prove that chemically similar atoms (i.e., atoms with the same nuclear charge) with the same average electron populations and kinetic energies will have identical charge distributions.