Theoretical Studies of Dodecahedrane. 2. Dodecahedrane, Inclusion Compounds, and Fluorine Derivatives

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Abstract: This paper describes extensions of our previous studies of the dodecahedrane molecule. In the present work, the orbital energies of dodecahedrane are determined using MINDO/3 and coupling constants for ^{13}C and ^{1}H nuclei are predicted by perturbation theory and hybridization arguments. The energetics of a variety of dodecahedrane inclusion compounds $C_{20}H_{20}X$ are studied with the INDO and CNDO methods where X = e^-, H, H^+, H^-, Li, Li^+, Be, Na^+, and H_2 within the carbon cavity. Finally, the charge distributions in polyfluorinated dodecahedranes are discussed.

I. Introduction

In a preliminary study[1] of dodecahedrane, $C_{20}H_{20}$ (Figure 1), we discussed various aspects of the molecule from the viewpoints of molecular orbital theory, group theory, and graph theory. The continuing efforts of several groups to synthesize dodecahedrane[2-5] have encouraged us to make additional studies both on the parent molecule and on various derivatives of it. The latter fall into the categories of (a) inclusion compounds of the formula $C_{20}H_{20}X$ where X = e^-, H^+, H, H^-, Li^+, Li, Be, Na^+, or H_2, and resides interior to the carbon dodecahedral cavity; and (b) fluorine substitution isomers of formula $C_{20}H_{20-n}F_n$ where n = 1, 2, 4, and 8. The investigation of $C_{20}H_{20}X$ inclusion compounds probes the interaction between an electron, atom, ion, or molecule and its saturated hydrocarbon clathrate. This type of interaction does not appear to have been considered previously in the literature. Because of the extremely large numbers of atoms and electrons involved the calculations are per force semiempirical, being of the INDO, CNDO, and MINDO/3 kinds. It should be noted that even the smallest calculation reported here involves 40 atoms and 100 basis functions in its valence set; the largest system studied was octafluorododecahedrane with 40 atoms and 124 basis functions.

II. Studies on Dodecahedrane

A. Energetics. The previously reported orbital energies of dodecahedrane were obtained using INDO approximate molecular orbital theory.[6] A subsequent study of cubane[7] using (1) INDO, (2) MINDO/3,[8] (3) SCF-Xα,[9] and (4) STO-3G ab initio methods[10] gave very similar orderings of the orbital energies for (2)-(4) while the ordering in method (1) was rather different. This implies, not unexpectedly, that MINDO/3 is preferable to INDO as a semiempirical method for calculating orbital energies, and we have therefore resolved the dodecahedrane molecular orbital problem using MINDO/3. The two sets of orbital energies are given in Table I where it can be seen that a significant reordering of the dodecahedrane levels has occurred, commencing with the $2a_g$ level.[11]

The results for dodecahedrane were obtained using the geometry of ref 1 where R_{CC} = 1.54 Å and R_{CH} = 1.09 Å. At this geometry the MINDO/3 ΔH_f(298 K) = 80.1 kcal/mol. When the dodecahedrane geometry was optimized using MINDO/3, maintaining I_h symmetry, the heat of formation decreased to 62.3 kcal/mol for R_{CC} = 1.56 Å and R_{CH} = 1.13 Å. This heat of formation of dodecahedrane is still considerably more positive than three previously reported values: −0.22 kcal/mol obtained by Engler, Androse, and Schleyer,[12a] 45.28 kcal/mol calculated by these same authors using the force field of Allinger and co-workers,[12b] and, most recently, 22.5 kcal/mol obtained by Allinger[12c] using a revision of his molecular mechanics method called MM2. The higher ΔH_f obtained here is consistent with the fact that MINDO/3 overestimates the heat of formation of so-called "globular" molecules; for example, ΔH_f of adamantane is in error by 35.1 kcal/mol.

Finally, it should be noted that a recent force field study by Ermer[13] has considered the question of whether dodecahedrane would have a symmetry lower than I_h and concluded that it would not.

B. Nuclear Spin–Spin Coupling Constants of Dodecahedrane. Semiempirical molecular orbital theory has proven useful for calculating the nuclear spin–spin coupling constants of hydrocarbons.[14] In a saturated molecule the Fermi contact term is much greater than the orbital and spin-dipolar terms.[15,16] Using the coupled Hartree–Fock version of the semiempirical method[15] we obtained the values given in Table II for all possible J_{CC}, J_{CH}, and J_{HH} couplings (where C = ^{13}C).

For the case of C–C coupling, the one-bond value, $^{1}J_{CC}$ = 37.2 Hz, is quite similar to the ethane value, 34.6 Hz.[17] A prediction of $^{1}J_{CC}$ can also be obtained from hybridizations since we have previously shown[18] that the one-bond constant for carbons C_A and C_B can be obtained from the equation

$$^{1}J_{C_AC_B} = 0.0621(\%\ s_A)(\%\ s_B) - 10.2\ \text{Hz} \qquad (1)$$

with a standard deviation from experiment of 2.4 Hz. The percent s characters in the bonding hybrids on C_A and C_B are obtained from INDO localized orbitals. Since localization of the dodecahedrane canonical molecular orbitals was prohibitively time consuming, we elected instead to simulate a dodecahedrane (tertiary) carbon with C_2 of isobutane, employing the dodecahedrane bond angles and bond lengths about C_2. This calculation furnished 27.6% s character in the CC hybrid emanating from C_2 to C_1 and $^{1}J_{CC}$ = 30.1 Hz when employed in eq 1 which is in reasonable agreement with the coupled Hartree–Fock value. Actually, there is some indication that the dodecahedrane $^{1}J_{CC}$ should indeed be smaller than the ethane value since $^{1}J_{CC}$ of cyclobutane is 29.8 Hz.[19]

The two-bond value, $^{2}J_{C_1C_3}$, = 0.2 Hz, is similar to the geminal constant in substituted butanes where $^{2}J_{CC}$ is generally less than 1 Hz.[20] However, this coupling constant is also a vicinal coupling constant (via the path $C_1C_{20}C_4C_3$), where the dihedral angle ϕ equals 0°. Since Barfield and co-workers[21] have calculated $^{3}J_{CC}$ to be ca. 5 Hz and $^{2}J_{CC}$ to be ca. −4 Hz at this angle, the present result, 0.2 Hz, may represent some compromise between a geminal and a vicinal value.

The three-bond coupling constant, $J_{C_1C_7}$ = 0.8 Hz, is in reasonable agreement with the vicinal coupling constants of

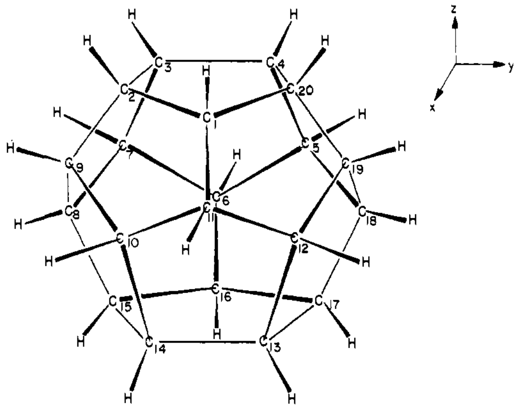

Figure 1. The dodecahedrane molecule and its numbering system.

alicyclic alcohols[21] where $^2J_{CC}$ is less than 0.4 Hz for a dihedral angle ϕ of 90°; in dodecahedrane ϕ has the value, 116.6°.

Turning to the J_{CH} values perturbation theory gives a $^1J_{CH}$ value of 102.7 Hz. This is significantly smaller than the observed methane value, $^1J_{CH} = 125$ Hz,[22] and somewhat surprising even though the perturbation method predicts a decreasing $^1J_{CH}$ in the aliphatic series methane (122.9 Hz), ethane (122.0 Hz), propane (119.4 Hz), and isobutane (114.2 Hz) at standard geometries.[14] The smallest $^1J_{CH}$ value yet observed appears to be the equatorial CH coupling constant of cyclohexane, 118.7 Hz,[23] and thus the value for dodecahedrane, 102.7 Hz, does seem unusually low.

An alternate estimate of J_{CH} can be obtained from our semiempirical equation[18]

$$^1J_{CH} = 5.7(\%\,s) - 18.4\ \text{Hz} \qquad (2)$$

with a standard deviation of 5.7 Hz from experimental values, where the percent s character in the INDO localized carbon hybrid is again required. Using the isobutane simulation of a dodecahedrane carbon as described previously we obtained 25.2% s character and $^1J_{CH} = 125.3$ Hz from eq 2. This value seems more plausible than the perturbation value since the dodecahedrane bond angles are very close to tetrahedral[1] and the effect of alkyl substitution on $^1J_{CH}$ is usually small. It should be noted that dodecahedrane is by no means the only molecule for which the hybridization eq 2 predicts a better $^1J_{CH}$ than INDO perturbation theory.

The two- and three-bond couplings, $^2J_{CH} = -5.3$ and $^3J_{CH} = 3.5$ Hz, are similar to $^2J_{CH}$ in ethane (−4.5 Hz[24]) and $^3J_{CH}$ in benzene (7.4 Hz[25]).

Finally, for the proton-proton coupling constants only the vicinal case, $^3J_{HH} = 11.3$ Hz, shows significant coupling. This value is somewhat similar to the theoretical value of Karplus for ethane with $\phi = 0°$, 8.2 Hz.[26]

III. Derivatives of Dodecahedrane

A. Inclusion Compounds. In this section we consider the energetics of the reaction

$$C_{20}H_{20} + X \rightarrow C_{20}H_{20}X \qquad (3)$$

where X = (e^-, H, H^+, He, Li, Li^+, Be, Na^+, or H_2) is infinitely separated from dodecahedrane on the left-hand side of eq 3 and is located within or proximate to the molecular cavity of 4.3 Å diameter on the right. This study thus probes an unusual hydrocarbon-X interaction, in which the former has available only σ bonding electrons. The literature on molecular macrocyclic inclusion compounds, while growing rapidly, is concerned almost exclusively with cavities having lone pairs. The results obtained here may be of value for hydrocarbons which contain channels and the problem of penetration or tunneling of X into the cavity is obviated.

Table I. Orbital Energies of Dodecahedrane[a]

orbital	MINDO/3 orbital energy	INDO orbital energy
$1a_g$	−1.71	−2.37
$1t_{1u}$	−1.43	−1.94
$1h_g$	−1.11	−1.54
$1g_u$	−0.87	−1.14
$1t_{2u}$	−0.72	−1.18[b]
$2a_g$	−0.71	−1.24
$1g_g$	−0.65	−0.87
$2t_{1u}$	−0.61	−1.02[b]
$2h_g$	−0.52	−0.82
$2t_{2u}$	−0.45	−0.59
$3h_g$	−0.41	−0.56
$2g_u$	−0.40	−0.50
$1h_u$	−0.37	−0.52
$2g_g$	−0.36	−0.45

[a] CC and CH bond lengths were 1.54 and 1.09 Å, respectively. The orbital numbering used here begins with the valence-shell molecular orbitals, whereas the C_{1s} furnish a_g, t_{1u}, h_g, g_u, t_{2u}, and g_g core molecular orbitals as well. [b] In ref 1 the energies of orbitals $1t_{2u}$ and $2t_{1u}$ were interchanged.

Table II. NMR Coupling Constants of Dodecahedrane[a]

atom pair (AB)	$^nJ_{AB}$, Hz	number of intervening bonds, *n*
	Carbon-Carbon[b]	
C_1C_2	37.2, 33.5[d]	1
C_1C_3	0.2	2 (or 3)
C_1C_7	0.8	3
C_1C_6	−0.2	4
C_1C_{16}	0.1	5
	Carbon-Proton[c]	
C_1H_1	102.7, 125.3[e]	1
C_1H_2	−5.3	2
C_1H_3	3.5	3
C_1H_7	0.0	4
C_1H_6	0.1	5
C_1H_{16}	0.0	6
	Proton-Proton[c]	
H_1H_2	11.3	3
H_1H_3	−0.2	4
H_1H_7	0.2	5
H_1H_6	0.0	6
H_1H_{16}	0.0	7

[a] From the coupled Hartree-Fock method, ref 9, except where indicated for $^1J_{CH}$ and $^1J_{CC}$. [b] Based on $S_C{}^2(0) = 3.54a_0{}^{-3}$. See ref 10. [c] Based on $S_C{}^2(0) = 4.0318a_0{}^{-3}$, $S_H{}^2(0) = 0.3724a_0{}^{-3}$. See ref 8. [d] Using eq 1. [e] Using eq 2.

It is worth noting in passing that while reaction 3 could presumably be carried out in the gas phase in a number of instances using mass spectrometry, ion cyclotron resonance spectroscopy, etc., a possible method of detecting $C_{20}H_{20}X$ in the liquid phase exists in magnetic resonance spectroscopy, i.e., the odd-electron X (e^-, ^1H, ^7Li) would presumably show EPR ^{13}C and ^1H hyperfine splittings while the even-electron X ($^1H^+$, ^3He, $^7Li^+$, and $^{23}Na^+$) could show ^{13}CX and ^1HX nuclear-nuclear spin-spin couplings.

The first set of calculations reported here has X at the dodecahedrane center referred to as 0 since this point can be taken as the origin in Figure 1. They are INDO closed-shell calculations for X = H^+, He, Li^+, Be, H_2; CNDO closed shell for Li^+ and Na^+; and INDO open shell for X = e^-, H·, Li. For He, which is not included in the standard INDO atom set, we employed the experimental values $I_s = 24.6$ eV, $A_s = 0.0$ eV,

Table III. Energies, Atomic Charges, and Spin Densities for $C_{20}H_{20}X$ with X at the Dodecahedrane Midpoint

X	energies ΔE, kcal/mol	charges			spin densities		
		P_X[b]	P_C[b]	P_H[b]	ρ_x[d]	ρ_c[d]	ρ_H[d]
e^-	149	*c*	0.03	−0.03			
H^+	−130	+0.81	−0.01	0.02			
H	−30	−0.04	+0.04	−0.04	0.934	0.001	0.002
H^-	−52	−0.81	0.08	−0.09			
He	+22	<0.01	0.03	−0.03			
Li^+	−162, −183[e]	−0.06	0.05	<0.01			
Li	+25	−0.12	0.05	−0.05	0.058	0.010	0.041
Be	−519	−0.31	0.07	−0.05			
Na^+	+420.3[e]	−0.69	+0.58	+0.27			
H_2	+48	−0.005	+0.04	−0.03			

[a] Energies are for X at the dodecahedrane midpoint 0 relative to X at infinite separation. [b] Atomic charges in electrons on nuclei X, C, and H; the atomic charges in dodecahedrane itself were $P_C = 0.03$, $P_H = -0.03$. [c] No center is associated with the extra electron. [d] Spin densities on X, H, and C from the open-shell INDO calculations on the $C_{20}H_{20}X$ radicals, X = H or Li, located at the dodecahedrane midpoint. [e] This is a CNDO/2 value. The CNDO value for Li^+ was computed as a check to determine whether that method and INDO would produce the same qualitative results as the Na^+ calculation could be done only as CNDO. [f] The H_2 molecule was located along the *z* axis with its midpoint at 0. The INDO equilibrium bond length, 0.746 Å, was employed.

and an interpolated $\beta^0 = -11$ eV ($\beta^0 = -16$ eV gave essentially the same results). Test calculations on the diatomic potential energy curves of HeH^+, He_2, and He_2^+ gave reasonable agreement with the corresponding ab initio calculations.

The results, given in Table III, suggest (1) possibly stable inclusion compounds for X = H^+ ($\Delta E = -130$ kcal/mol), Li^+ ($\Delta E = -162, -183$ kcal/mol), and Be ($\Delta E = -519$ kcal/mol); (2) weaker interactions for X = H ($\Delta E = -30$ kcal/mol), H^- ($\Delta E = -52$ kcal/mol), He ($\Delta E = +22$ kcal/mol), Li ($\Delta E = +25$ kcal/mol), and H_2 ($\Delta E = +48$ kcal/mol);[27] and (3) a destabilized extra electron ($\Delta E = +149$ kcal/mol). The last result probably arises from lack of provision of additional basis functions for the extra electron within the cavity (the desired matrix elements could not be adequately parametrized), thus forcing the electron into a strongly antibonding orbital of dodecahedrane. Table III also contains the atomic charge densities (core charge minus atomic population) of the atoms C, H, and X for each case. The transfer of charge (and spin density for the radicals as well) is very small, considering the short C-X separation of 2.16 Å, except in the cases of Li^+, Be, and Na^+, which are calculated to have *negative* atomic charges.

In $C_{20}H_{20}Li^+$ the 2s atomic orbital of Li has a population (diagonal density matrix element) of 0.25 electron. A large transfer of 0.27 electron into each of the Li 2p orbitals from the corresponding dodecahedrane orbitals of t_{1u} symmetry makes the Li of $C_{20}H_{20}Li^+$ a nearly neutral sp^3 atom. Thus, the hydrocarbon does appear capable of "solvating" the cation, even though it has no lone pair electrons. In order to ascertain whether this result is merely an artifact of INDO when applied to Li^+ complexes, its complex with H_2 was studied. The equilibrium geometry found for Li^+-H_2 agreed well with that of ab initio calculations and in this case the Li was positive to the extent of 0.8 electron.

A more dramatic example of charge transfer takes place in $C_{20}H_{20}Na^+$ where the sodium has an atomic charge of −0.62 electron, the 2s, 2p, and 3d populations being ca. 0.15, 0.51, and 1.03 electrons, respectively. Somewhat surprisingly, as seen from Table III, ΔE for reaction 3 with X = Na^+ is large and positive. Since the INDO method treats the core charges of H^+, Li^+, and Na^+ as +1, the adverse energetics are electronic in origin.

The most stable of all the inclusion compounds is $C_{20}H_{20}Be$ with an extraordinary $\Delta E = -519$ kcal/mol. Once again there is considerable charge transfer with the Be 2s and 2p atomic populations being 1.36 and 0.95 electrons vs. 2.0 and 0.0 in the Be atom. Clearly this case deserves more extensive study even if the predicted stability seems much too large. (Similar large stabilities are found also for the isoelectronic $C_{20}H_{20}B^+$.)

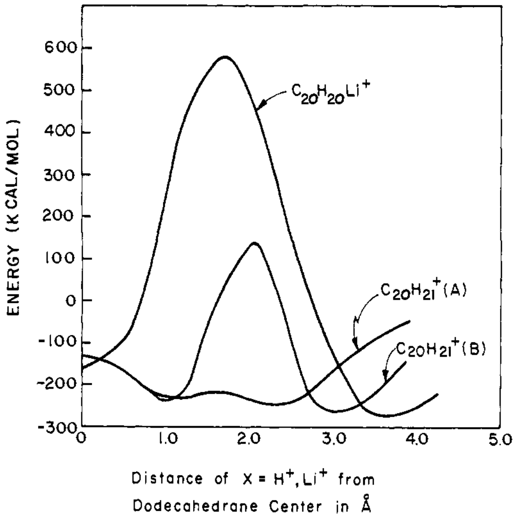

Figure 2. The total energy of $C_{20}H_{20}X$ for various X positions. $C_{20}H_{21}^+$ (A) designates positions of the proton along the positive *z* axis; similarly, Li is also located on the *z* axis in $C_{20}H_{20}Li^+$. For $C_{20}H_{21}^+$ (B) the proton is located along the ray connecting the dodecahedrane midpoint 0 with the midpoint of bond C_3C_4. The distance of X from the center 0 is the abscissa in each case.

Studies of the cases of H^+ and Li^+ at positions other than the dodecahedrane center 0 were also made. For protonated dodecahedrane we considered the energy of the complex for various proton positions along two rays (A and B) originating at 0 and penetrating the dodecahedron to emerge at the outside. The first ray, A, was the positive *z* axis of Figure 1. Two minima were found on it (Figure 2), a local minimum within the cavity at $z = 1.29$ Å ($\Delta E = -230$ kcal/mol) and an external minimum at $z = 2.35$ Å ($\Delta E = -246$ kcal/mol). They are separated by a relatively small barrier of 24 kcal/mol (relative to the external minimum) at $z = 1.74$ Å where ray A intersects the pentagon $C_1C_2C_3C_4C_{20}$. It is interesting that the two minima are comparable in energy and that the minimum inside the cavity is not at 0, as might have been thought from our previous discussion, but off center.

Ray B lies in the *xz* plane of Figure 1 and connects 0 with the midpoint of bond C_3C_4. It also contains two mimina, the internal one being at 1.05 Å ($\Delta E = -228$ kcal/mol) and an external minimum at 3.0 Å ($\Delta E = -260$ kcal/mol) as shown in Figure 2. Now, however, the two minima are separated by

Table IV. Dipole Moments and Relative Energies of Difluorododecahedranes[a]

isomer	point group	minimum number of intervening bonds	μ, D	rel energy, kcal/mol
F_1F_{16}	D_{3d}	5	0	0
F_1F_6	C_{2v}	4	1.5	0.03
F_1F_7	C_2	3	2.4	0.09
F_1F_4	C_σ	2	3.4	0.30
F_1F_2	C_{2v}	1	4.0	3.5

[a] Calculated by INDO approximate molecular orbital theory, based on the dodecahedrane I_h geometry with fluorines substituted at the indicated positions (CF bond lengths, 1.36 Å).

a large barrier of 406 kcal/mol, which occurs when the proton is located on the C_3C_4 bond. The internal minima on rays A and B are quite similar in both energy and distance from 0, ca. 1.25 Å. The external minima are different in that the deeper one on ray B corresponds to a nonclassical bridged carbonium ion with C_3H (and C_4H) distances of 2.4 Å. While no further search for inner and outer minima was undertaken, it might be noted that the interior of the carbon dodecahedron is a 120-fold replication of the elementary prism whose corners are at 0, C_3, the C_3C_4 midpoint, and the center of pentagon $C_1C_2C_3C_4C_{20}$, which indicates that a modest survey of the interior serves to characterize it.

A study of the energetics of protonated dodecahedrane along ray A was also made using MINDO/3. It furnished an external minimum of −94 kcal/mol at $z = 2.6$ Å and an inflection point rather than a minimum at the internal point $z = 1.52$ Å, $\Delta E = -78$ kcal/mol.

The energy of the Li^+-dodecahedrane complex was also studied along ray A using INDO and the resulting ΔE's, Figure 2, are qualitatively different from the protonated case. The internal minimum ($\Delta E = -162$ kcal/mol) now occurs with Li^+ at the dodecahedrane midpoint rather than off center as in $C_{20}H_{21}^+$, the external minimum ($\Delta E = -272$ kcal/mol) occurs farther out at $z = 3.6$ Å, and there is a strikingly large barrier of more than one atomic unit of energy when the Li^+ is in the top pentagonal face. To test whether these unusual results were due to the presence of the 2p lithium atomic orbitals we removed them and recomputed the energy. At all points proximate to dodecahedrane including the interior, the energy increased on the order of 1.5 au—some increase is of course required by the variational principle. Since the core repulsion energies are identical for $C_{20}H_{20}Li^+$ and $C_{20}H_{21}^+$ at the same geometries the difference in the barriers arises from differences in the electronic energies. We have not determined whether it is an increase in Coulomb repulsion for Li^+ relative to H^+ which gives the larger barrier for $C_{20}H_{20}Li^+$ or whether it is a loss of some of the negative core contribution to the electronic energy.

What is most noteworthy in both complexes is that the core repulsion energy increases by ca. 5000 kcal/mol in going from the exterior point $z = 3.4$ Å to 0 along ray A which shows that a comparable and therefore very large stabilization has been obtained through the $C_{20}H_{20}$-X interactions. And an even greater electron stabilization occurs with Be. Hydrocarbon inclusion compounds are thus real possibilities, although finding them will entail a careful balancing of bonding (overlap) and core repulsions.[27]

B. Fluorinated Dodecahedranes. Substitution of fluorine for one or more hydrogens in dodecahedrane was studied at the INDO level of approximation using the standard C–F bond length of 1.36 Å, without any other changes of geometry. The monofluorinated compound, $C_{20}H_{19}F$, exhibits the alternating charge distribution pointed out by Pople and Beveridge[6] in a discussion of CNDO/2 results in small fluorinated hydrocarbons; the effect is rather subdued in dodecahedrane, and the charge polarization between the fluorine and α-carbon atoms is greater. The fluorine atomic charge in $C_{20}H_{19}F$ is −0.277 and that of the α carbon is +0.264. The β, γ, and δ carbon atoms have charges of −0.01, +0.035, and +0.032, respectively, the latter value being very close to that in the parent dodecahedrane molecule. The attached hydrogen atoms have charges of −0.005, −0.028, and −0.030, respectively. The INDO dipole moment of $C_{20}H_{19}F$ is 2.108 D.

Table IV summarizes some results for the five difluorinated dodecahedranes. The atomic charges on the F and α-C atoms are essentially the same as in the monofluorinated compound, except for the F_1F_2 isomer, in which the charges are −0.257 and +0.231, respectively. The alternating charge effects are roughly additive; for example, in the F_1F_4 isomer, that carbon which is β to both fluorines (C_{20}) experiences almost exactly twice the charge shift relative to dodecahedrane which is found in the β carbon atom of the monofluorinated compound. Its charge is −0.053.

One tetrafluoro isomer was examined, $F_1F_7F_{14}F_{18}$, which possesses the unusual point-group symmetry T. This is enantiomeric with the $F_4F_9F_{12}F_{16}$ isomer. The F, α-C, β-C, and γ-C atomic charges are respectively −0.271, +0.264, −0.008, and +0.042, not substantially different from those of the monofluorinated compound.

The octafluorinated isomer $F_1F_4F_7F_9F_{12}F_{14}F_{16}F_{18}$ possesses the unusual point-group symmetry T_h. The proximity to the fluorinated positions (any α-C must be γ to three other F atoms) leads to a fluorine atomic charge which is intermediate between that of the monofluorinated and the F_1F_2 difluorinated compounds, −0.260, while the α-C attains the most positive charge found in any of the compounds studied, +0.277. Any β-C is, in fact, β to two fluorines and γ to two others, and its atomic charge is very close to that of C_{20} in the F_1F_4 compound, −0.05.

The occupied canonical molecular orbitals exhibit substantial mixing of fluorine tangential p orbitals with the framework, suggesting that "back-donation"[6] by F atoms is involved in the alternating charge effects, despite their reduced extent in dodecahedranes relative to those in simpler fluorinated hydrocarbons.

Because of the large positive charges on the α carbons of fluorinated dodecahedranes, we were interested in their possible further stabilizing effect on negative X moities. Accordingly, we calculated the energetics of the reaction

$$C_{20}H_{16}F_4 + H^- \rightarrow C_{20}H_{17}F_4^- \qquad (3')$$

for the tetrafluorinated dodecahedrane. The ΔE for this reaction is −84 kcal/mol, indeed smaller than the value obtained for the corresponding reaction 3 with X = H^- by 32 kcal/mol. This result suggests that another way to stabilize the included X is by replacement of the dodecahedrane hydrogens with suitable substituents.

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Localized Molecular Orbitals for Polyatomic Molecules. 6. Condensed Aromatic Ring Systems

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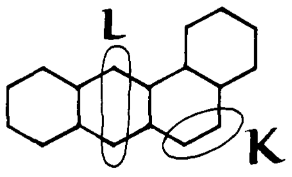
Abstract: Wave functions have been calculated in the approximation of partial retention of diatomic differential overlap (PRDDO) for the molecules naphthalene, anthracene, tetracene, pentacene, phenanthrene, triphenylene, chrysene, benzanthracene, pyrene, 1,2-benzopyrene, and 3,4-benzopyrene. The wave functions are examined in terms of both the canonical molecular orbitals and the localized molecular orbitals obtained using the Boys criterion. Dipole moments for these molecules are presented, along with energy differences for the various isomers. Ionization potentials for the π orbitals are compared with experiment and with those obtained from the simulated ab initio molecular orbital (SAMO) method. The reactivity index most useful for predicting the site of electrophilic attack is the population in the highest occupied molecular orbital. Bond overlap populations are presented and are found to correlate well with the experimental data. Localized molecular orbitals (LMOs) have been obtained for all electrons and for π electrons only. The complete LMOs correspond to Kekulé-type structures with alternating single bonds and pairs of τ bonds. Secondary maxima on the LMO hypersurface, found for certain molecules, are related to the Fries rule. A detailed analysis of these LMOs is presented and correlations between bond order and delocalization index are found. The π LMOs are in general two-center bonds that occur between centers which have τ bonds in the complete localizations. However, no multiple maxima are observed and the π LMOs tend to be significantly more delocalized than their τ-bond counterparts. Three-center π LMOs are found if there are symmetry-related maxima for the complete LMOs.

The approximate molecular orbital method PRDDO[1] (partial retention of diatomic differential overlap) is applied here to several polycyclic aromatic ring systems: benzene, naphthalene, anthracene, tetracene, pentacene, phenanthrene, triphenylene, chrysene, benzanthracene, pyrene, 1,2-benzopyrene, and 3,4-benzopyrene.

One area of biochemical interest is the possible relationship between charge density and carcinogenicity in some of these compounds. Pullman's calculations[2,3] by the Hückel method correlate carcinogenic activity with high π-electron density in the K region, while region L is deactivating, as shown in an example



(1)

and outlined in historical perspective by Herndon.[4] Recent theoretical studies of aromatic hydrocarbons include the use of graph theory[4,5] and of the SAMO (simulated ab initio molecular orbital) method,[6-8] which has given the best previously available wave functions for these molecules. The SAMO studies[6,7] have correlated a high π-bond order in the K region with carcinogenicity but have also indicated that other factors are involved in carcinogenicity. On the experimental side, the recently available photoelectron spectra[9] are particularly relevant to our study.

In this study of 12 aromatic molecules, eigenvalues obtained by the PRDDO method are compared with the photoelectron spectra and with the results of the SAMO method. Also, reactivity predictions[10] are discussed in terms of simple indexes such as group charges, bond overlap populations, HOMO (highest occupied molecular orbital) populations, and total π-orbital populations. In order to analyze the wave functions in simple chemical terms, we have obtained localized molecular orbitals (LMOs)[11] from the Boys criterion[12] using the Edmiston-Ruedenberg procedure[13] for all of the occupied orbitals, and also for the subset of occupied orbitals containing

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