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C_{60} Dihydrides And Fullerene Aromaticity. Insights From Calculations On Model Compounds

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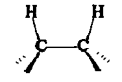
Abstract: Semiempirical MO calculations on model fullerene compounds reveal a connection with less and more curved aromatics, and allow, via comparisons of various dihydride energies, a quantitation of the aromatic character imbedded in the fullerene structure. Additionally, cage-opened dihydrides are found to be energetically reasonable species, and may provide an avenue for improved production of endohedrally encapsulated fullerenes.

The growth in the chemistry of C_{60}[1] and its derivatives[2] has been partially paralleled by theoretical investigations.[2i,3] The importance of the curvature of the bent aromatic surface of C_{60} has received attention,[3a] but the connection with other aromatic compounds has not been fully emphasized. Reduction of C_{60} to $C_{60}H_2$ is a prototypical addition reaction;[4] two recent reports detail alternative routes to the 6,6-ring junction vicinal dihydride. The first of these, hydroboration/oxidation,[5] was destined to give a vicinal adduct (although it could have been of the 5,6-ring junction variety), but the second, Rh-catalyzed reduction,[6] could have given any of the possible $C_{60}H_2$'s. The observation of only one major dihydride, which is the one calculated[3f,8] to be the most stable of the 23 considered, was taken as a validation of the *a priori* theoretical work. Another concern is the role of aromaticity in stabilizing C_{60}.[3a] The dissection of the contributions of strain and aromatic character to the overall energy of C_{60} is difficult. In this paper, we use AM1 calculations[7,8] on model compounds to shed light on these aspects of fullerene chemistry.

Dixon, et al.,[3b] previously compared the internuclear H-H distances and related bond angles of 1,2-dihydro- and dihaloethenes with similar values for the 6,6-ring junction vicinally disubstituted C_{60}'s (the 1,9-adducts). They attributed the shorter internuclear distances in the fullerenes (2.23Å vs. 2.31Å for the dihydrides) to effects of the C_{60} cage. As shown in Table 1, the fullerene internuclear H-H distance is not short, but rather a bit longer (due to molecular curvature) than model flat compounds, and the same as found for other curved models. The negative Heats of Hydrogenation (ΔH_H) (Table 1) for the simple model compounds reflect the destruction of 2 aromatic rings. For **9**, the almost zero ΔH_H indicates that the central 2 rings of **dehydro-9** possess diminished aromatic character. For the remainder of the cases, including the fullerene, the positive ΔH_H's are caused by the increasing strain of the increasingly curved surfaces of these compounds. A perhaps more effective way to address the issue of aromaticity in fullerenes is to examine the energy differences between the "1,2-" (vicinal) and "1,4-" dihydrides (Table 1--the "1,4-" isomers are **2**, **4**, **6**, **8**, **10**, **12**, **14**, **16**, **18**, and 1,7-$C_{60}H_2$). For the first 3 cases, there is no difference in the number of aromatic rings for the 2 isomeric types. The best model is the **5**, **6** pair, since the double bond substitution patterns do not change on going from one isomer to the other; the 7.0 kcal/mol energy difference means that the 1,4-isomer, **6**, is more stable. For flat models **7** and **9**, and their corresponding isomers, the energy difference is negative, the 1,2-isomer is more stable, and there is one more aromatic ring in the 1,2-isomer. This yields values of 18.9 and 17.7 kcal/mol, respectively, for the "aromaticity" of a benzene ring in these model systems. Models **11**, **13**, **15**, and **17** are more complex, since there is not uniform curvature in these compounds. POAV analysis,[3e] however, may be utilized in these cases to determine the approximate strain energy contribution to the $\Delta E_{(1,2-1,4)}$'s. To calibrate the method, we calculated the strain in **dehydro-11** by multiplying the sum of the squares of the pyramidalization angles by 200 kcal/mol; this gave a total strain energy of 51.8 kcal/mol. The AM1-calculated energy difference between **dehydro-11**, which is curved, and its isomer, **dehydro-9**, which is flat, is 50.6 kcal/mol, which can be attributed to the strain energy of **11**. With this confirmation of the methodology, we calculated that the strain energy contribution to the $\Delta E_{(1,2-1,4)}$ for **11** is 5.6 kcal/mol (more strain relieved for **11** than **12**, which means that the "$\Delta E_{(electronic)}$" should be -15.1 kcal/mol), for **13** is 3.1 kcal/mol ($\Delta E_{(electronic)}$ = -12.0 kcal/mol), for **15** is -8.6 kcal/mol ($\Delta E_{(electronic)}$ = -3.8 kcal/mol), and for **17** is -8.6 kcal/mol ($\Delta E_{(electronic)}$ = -7.1 kcal/mol). This analysis gives a value of 22.1 kcal/mol for the lost aromatic ring in the **11** to **12** isomerization (using the 5-6 energy difference without modification for the slightly increased H-H distance), and 19.0 kcal/mol for the **13** to **14** isomerization, both of which are close to the values for the flat model systems; **11** and **13** are less curved than C_{60}. The last two systems, as well as C_{60} itself, show diminished aromaticity. For C_{60}, the value becomes 11.4 kcal/mol, which is around 60% of the value for flat compounds. If one uses the energy of the 5,6-ring junction vicinal $C_{60}H_2$ (Table 2), in which there are 2 fewer aromatic rings than in the global minimum dihydride, the resonance energy of each ring becomes 9.2 kcal/mol. Either of these values are in accord with the assertion that the fullerene aromaticity lies within 2 kcal/mol per carbon of a hypothetical ball of rolled-up graphite (10 kcal/mol/ring would give a value for the resonance energy of 3.33 kcal/mol/C, while graphite has a resonance energy of 3-5 kcal/mol/C).

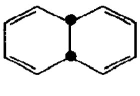
Table 1. AM1-Calculated Parameters and Energies for Model Fullerene 1,2-Dihydro Compounds. Comparisons with Model 1,4-Dihydro Isomers.



Cpd.	ΔH_f kcal/mol	$r_{H,H}$, Å	∢HCC, °	∢HCCH,°	$E_{1,2}$-$E_{1,4}$[a] kcal/mol	ΔH_H[1,2 b] kcal/mol	Δ arom. rings, shape[c]
1	57.87	2.24	106.3	28.6	5.3	-30.9	0, flat
3	82.43	2.18	107.4	4.9	7.8	-19.6	0, flat
5	90.30	2.18	106.4	1.5	7.0	-12.1	0, flat
7	99.24	2.13	104.3	5.0	-11.9	-22.8	1, flat
9	139.49	2.12	103.9	0.1	-10.7	0.4	1, flat
11	165.23	2.24	109.0	0.7	-20.7	25.2	1, curved
13	239.52	2.23	107.8	0.0	-15.1	32.3	1, curved
15	343.57	2.23	107.2	0.2	4.8	36.9	1, curved
17	444.73	2.23	106.5	0.0	1.5	41.8	1, curved
1,9-$C_{60}H_2$[d]	776.1	2.23	107.4	0.0	-4.4	22.2	1, curved

[a] ΔE between the 1,2-H_2 and 1,4-H_2 isomers--a negative value means the 1,2-H_2 isomer is more stable; [b] Heat of Hydrogenation for the 1,2-H_2 isomer calculated from ΔH_f(aromatic precursor) - 13.4 - ΔH_f(1,2-H_2);[3f] [c] change in number of formal benzene rings on going from 1,2-H_2 to 1,4-H_2, and architecture of aromatic precursor; [d] data from reference 3h.

Previous work has enumerated the 23 possible dihydrides around the surface of the C_{60} cage. Omitted, however, were the 2 dihydrides with ring-opened structures (fulleroids). Our calculations indicate that the fulleroid structure based on addition to the 6,6-ring fusion is never a singlet energy minimum. The other one, however, is (see **20**, **22**, **25**, and **27**). For **25**, whose curvature is close to C_{60}, the fulleroid structure lies only 38.4 kcal/mol above the global minimum, and but 11.1 kcal/mol above the corresponding fullerene (**24**). This implies that the corresponding $C_{60}H_2$ fulleroid would be energetically below several of the 23 fullerene dihydrides already considered. The recent proposal[9] that ring-opening of the C_{60} cage gives rise to a "window" mechanism for the incorporation of foreign atoms into the fullerene center, provides added interest to the possibility of ring-opening in the dihydrides. For C_{60}, the ring-opened structure was calculated to lie at least 120 kcal/mol above the ground state (and on the triplet surface), while experimental evidence suggests an 81 kcal/mol barrier. Our calculations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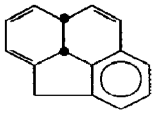
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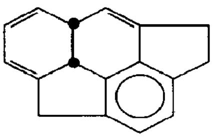
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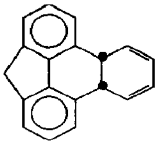
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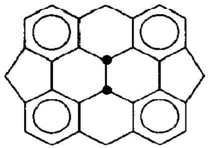
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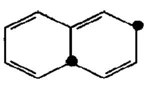
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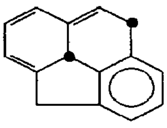
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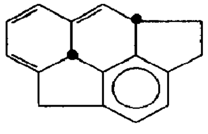
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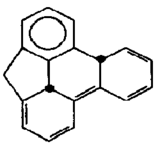
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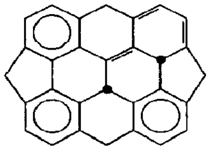
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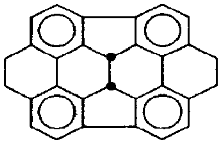
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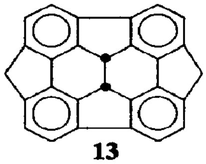
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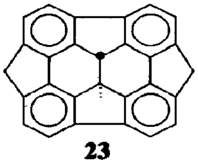
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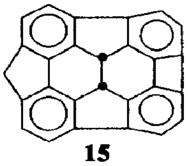
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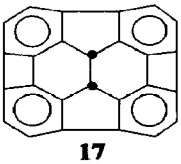
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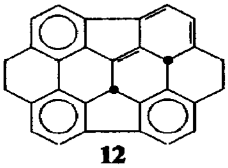
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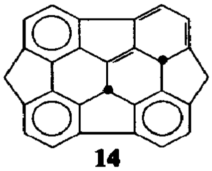
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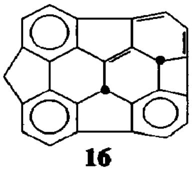
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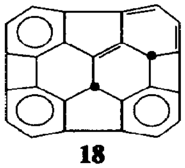
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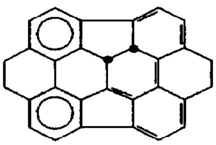
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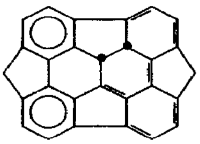
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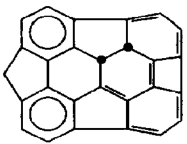
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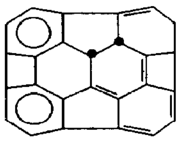
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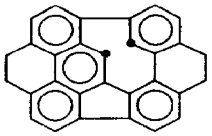
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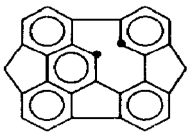
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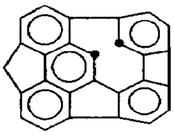
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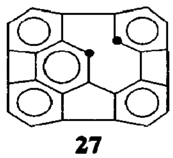
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Table 2. AM1-Calculated Energies of Some Model Fullerene Dihydrides.[a]

Cpd.	E_{rel}[b]	Cpd.	E_{rel}[b]	Cpd.	E_{rel}[b]	Cpd.	E_{rel}[b]
11[c]	(0)	13[c]	(0)	15[c]	(0)	17[c]	(0)
19[c]	30.3	21[c]	31.8	24[c]	27.3	26[c]	30.9
20[d]	62.3	22[d]	59.8	25[d]	38.4	27[d]	45.3
		23	56.5				

[a] 1,7-$C_{60}H_2$, the 5,6-ring junction vicinal dihydride, lies 18.4 kcal/mol (PM3)[3f,g] above the 6,6-ring junction vicinal one, which is the global minimum; [b] in kcal/mol; [c] these compounds have $r_{C-C}(sp^3\text{-}sp^3)$ = 1.51-1.60Å and r_{H-H} = 2.23-2.30Å; [d] these have $r_{C-C}(sp^3\text{-}sp^3)$ = 2.34-2.41Å and r_{H-H} = 1.80-1.85Å.

suggest a much lower barrier for the 5,6-vicinal dihydride. Perhaps photolysis or pyrolysis of this compound would lead to various endohedrally encapsulated products, after which hydrogen ejection would yield the parent endohedral fullerene complexes.

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