MINDO study of vicinal dihydrides of C_{70}: Interpretation of relative stability on the basis of electronic and molecular structures

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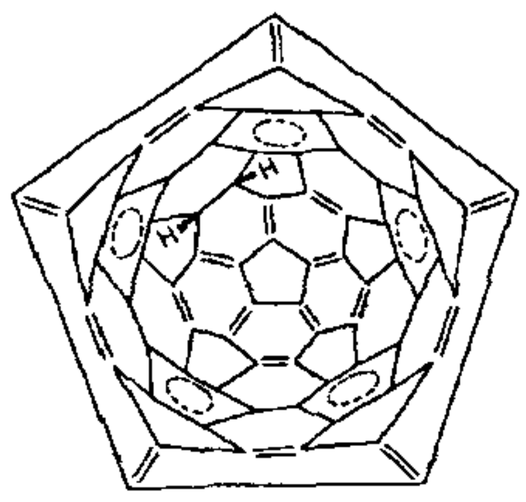
The structures and stability of isomeric vicinal dihyrides of C_{70} are computed at the MNDO level. Their predicted stability is interpreted by comparing their electronic and molecular structures with those of C_{70}. While the two most stable isomers correspond to those obtained by hydrogenating the two most electron-rich bonds in C_{70}, the variations in the relative stability of the other isomers do not strictly parallel the bond orders of the bonds being hydrogenated. Changes in angle strain and the extent of π reorganization accompanying hydrogen addition are suggested to control the relative stability of the $C_{70}H_2$ isomers.

EVEN though C_{70} and its illustrious counterpart, buckminsterfullerene (C_{60}), were identified through mass spectrometry at the same time[1], the chemical behaviour of the two fullerenes is not equally understood. While numerous derivatives of C_{60} have been spectrally and structurally characterized[2–13], reports on the chemical reactivity of C_{70} have been restricted to the iridium complex, (η^2-C_{70}) Ir (CO) Cl (PPh_3)$_2$ – whose crystal structure has been determined[14] – and the partially characterized $C_{70}O$. Experimental studies on C_{70} are hampered by the difficulty associated with its synthesis in pure form in significant quantities. Although improved experimental procedures would alleviate this problem, the complexity associated with C_{70} poses special difficulties. Unlike C_{60}, C_{70} has five different kinds of carbon atoms and eight distinct C–C bonds. While the chemistry is likely to be correspondingly rich, the absence of any symmetry in most derivatives and the staggeringly large number of possible isomers for a given composition make the problem rather intractable.

Theoretical studies are valuable for predicting some general guidelines concerning the structures and energetics of fullerene derivatives. The usefulness of computational studies has been well established[16–22] in the case of the derivatives of C_{60}. While the structure and bonding in C_{70} also have received considerable theoretical attention[23–25], only two quantitative calculations have been reported on the derivatives of C_{70}. The first study[26] considered the energetics of isomeric structures of $C_{70}O$. Although the results are of interest in view of the experimental isolation of $C_{70}O$, general conclusions regarding the reactivity of C_{70} cannot be derived from this study. For example, the isomer formed by oxidation of a formal C–C single bond is predicted to be the most stable one. In most reactions which are kinetically controlled or which require chemical activation, additions to bonds with double-bond character are likely to be preferred. Further, oxidation of such C=C bonds may lead to epoxide formation or an open-ring structure to reduce ring strain. These complications may not be relevant in other simple addition reactions. A thorough semi-empirical study has indeed been carried out[27] for the addition of hydrogen and alkyl groups to C_{70}, and the seven most stable isomers out of the 143 possible $C_{70}X_2$ structures have been identified. Although the computed energetics are useful, the study does not provide a detailed insight into the factors contributing to the relative stabilities of C_{70} derivatives.

In the present communication, we report the structures and energies of the eight possible vicinal dihydrides of C_{70} (**1–8**) computed at the MNDO level[28]. Using the available knowledge on the electronic and molecular structures of C_{70} as the basis[23–25], the variations in the computed energetics of the isomers are analysed. The interpretations are extended to account for the computed results for other types of dihydrides as well.

The eight vicinal isomers of $C_{70}H_2$ (**1–8**) can be classified using the atom-labelling scheme proposed recently[2]. By viewing the molecule down the C_5 axis, the distinct atom types a, b, c, d (along with their



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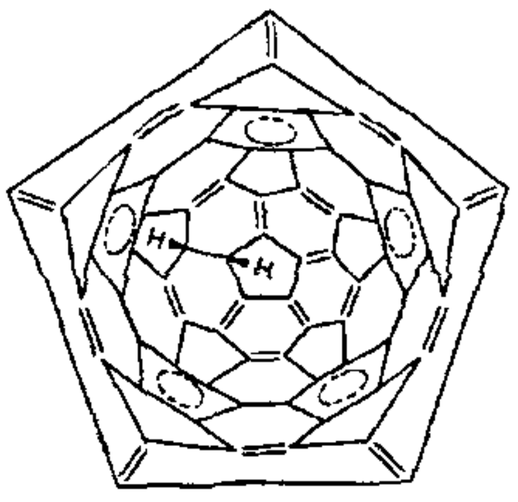

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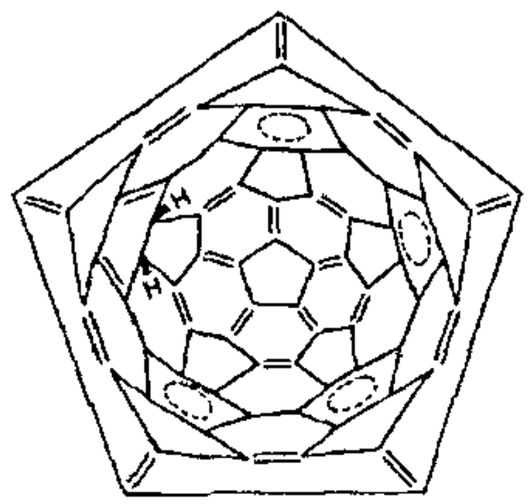

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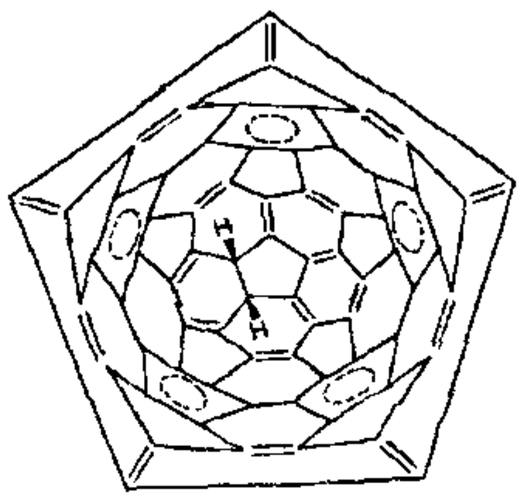

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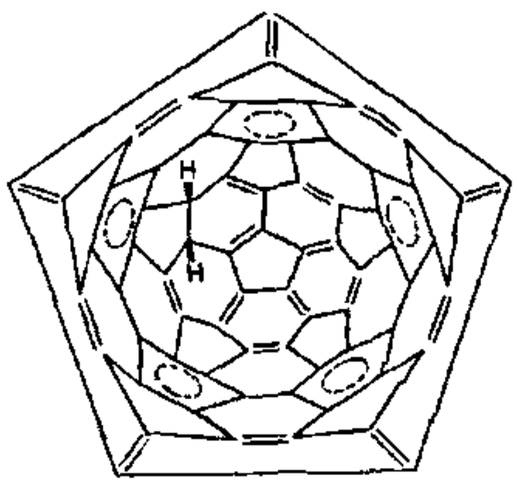

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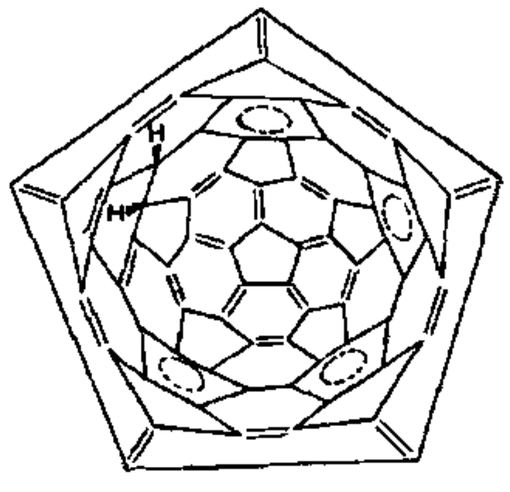

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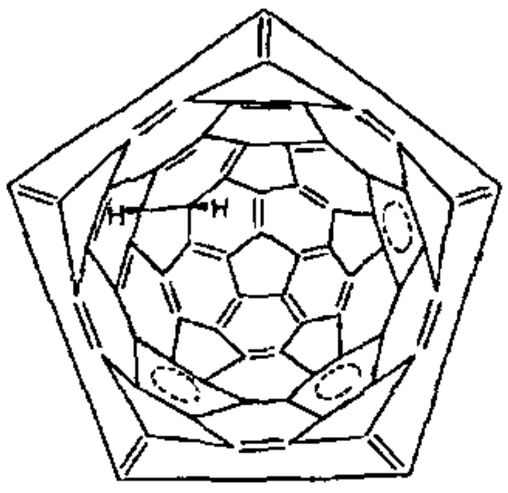

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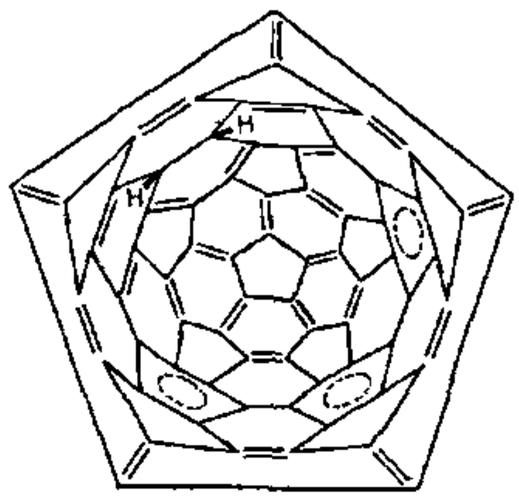

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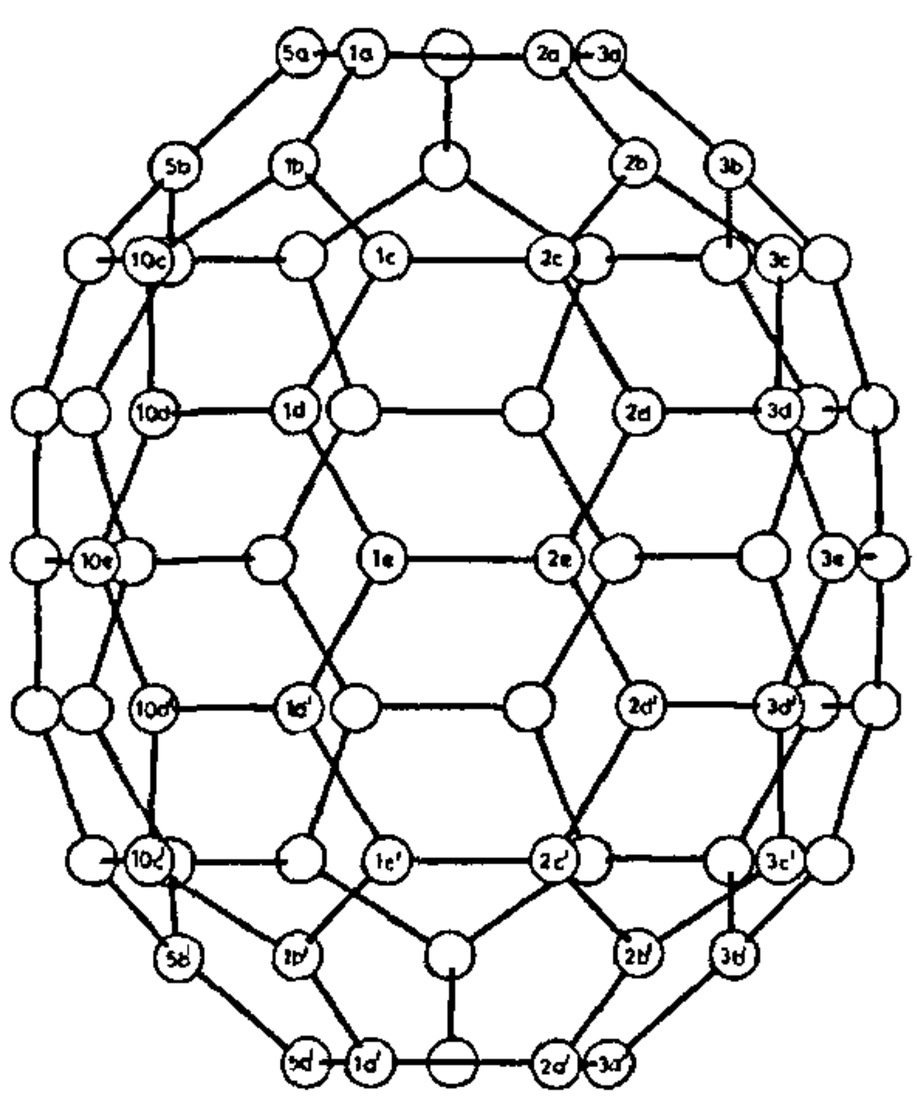

Figure 1. Atom-labelling scheme in C_{70}. Labels are omitted for symmetry-related atoms for the sake of clarity.

mirror images a', b', c', d') and e can be readily recognized in each successive layer (Figure 1). By adding two hydrogen atoms to neighbouring carbon atoms, the structures 1a–2a, 1a–1b, 1b–1c, 1c–2c, 1c–1d, 1d–10d, 1d–1e and 1e–2e are obtained. The calculated heats of formation of the eight isomeric dihydrides in decreasing order of stability are given in Table 1.

Before considering the computed energetics in detail, it is instructive to recapitulate the key molecular and electronic structural features of C_{70}. The calculated bond lengths and bond orders show significant variations and, as expected, are inversely related. The a–b and c–c bonds have the highest bond order (1.489 and 1.544, respectively). The d–d and d–e bonds also have significantly large bond orders (1.313 and 1.312). All the remaining C–C bonds have bond orders of around 1.1 and lengths of about 1.48 Å, characteristic of a single bond between two sp^2 carbon atoms. These variations are compatible with the following simplified electronic structure. Viewed down the fivefold axis, the molecule consists of two corannulene units, one at the top and the other at the bottom, held together by an equatorial belt of a pentaphenyl moiety (Figure 2). The two corannulene rings are characterized by bond alternation, which ensures a benzenoid Kekule form for each hexagon and no double bonds in the central pentagon. In contrast, the equatorial pentaphenyl belt consists of five 'aromatic' benzene rings with little bond alternation in each ring connected by formal single bonds .These features have no analogues in C_{60}. Although this description of the electronic structure of C_{70} emphasizes a unique canonical form of a potentially highly delocalized molecule[23], the simplification proves to be valuable for interpreting the computed results.

As expected from the above analysis, the most stable isomers of $C_{70}H_2$ (**1** and **2**) are obtained by hydrogenating the C=C bonds with maximum double bond character. Thus, the 1a–1b and the 1c–2c isomers correspond to reduction of the inner and the outer double bonds of a corannulene unit, respectively. While

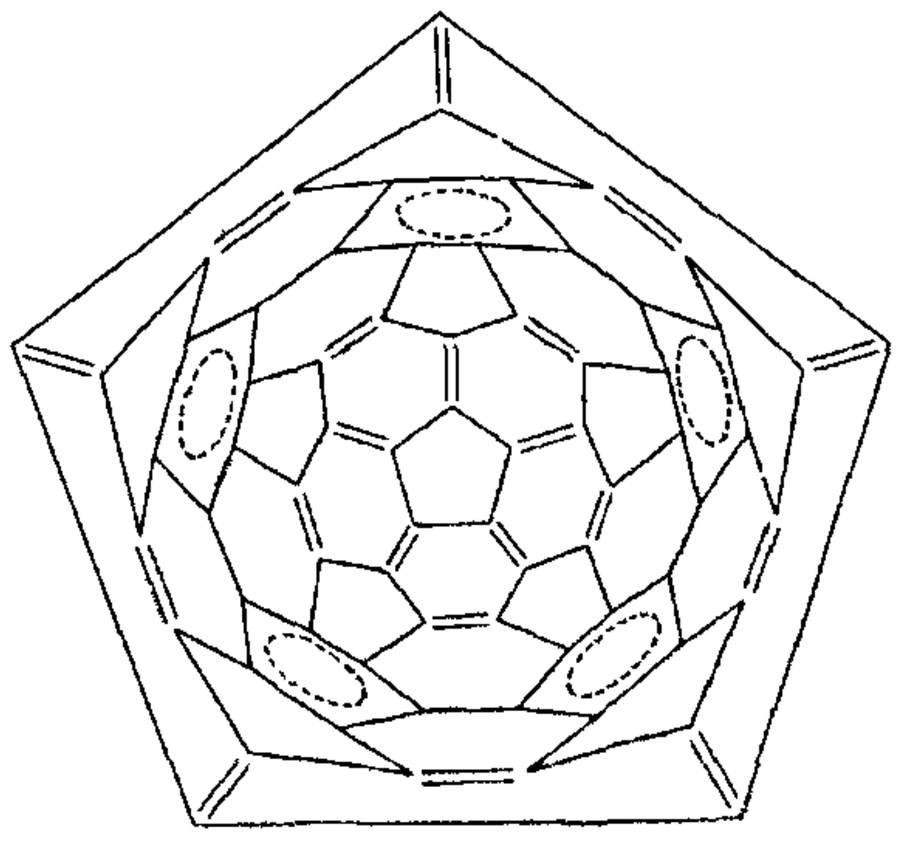

Figure 2. Two-dimensional projection of C_{70}, emphasizing the presence of corannulene units at the top and the bottom as well as the central pentaphenyl moiety.

Table 1. Calculated MNDO heats of formation and relative energies (kcal/mol) of $C_{70}H_2$ isomers

Isomer	Bond reduced	Bond order in C_{70}	Heat of formation	Relative energy
1	1c–2c	1.544	897 6	0.0
2	1a–1b	1 489	897.7	0 1
3	1d–10d	1 313	904.5	6 9
4	1a -2a	1 105	911 0	13 4
5	1b–1c	1 109	912 8	15.2
6	1d–1e	1 312	914 4	16 8
7	1c–1d	1 060	927.3	29 7
8	1e–2e	1.085	941.8	44.2

the previous AM1 calculations[27] predicted a small energy difference of 1 kcal/mol in favour of the latter, the heats of formation of the two isomers are virtually identical at the MNDO level (Table 1). Two opposing factors contribute to the relative energy of these isomers. Assuming that C_{70} consists of electronically isolated corannulenes and pentaphenyl fragments, disruption in conjugation in each of these units due to hydrogenation would be a significant factor. Whereas two benzenoid rings are affected in the 1a–1b isomer, only a single benzene ring loses conjugation in the 1c–2c isomer. Hence, the latter is expected to be more stable. However, this preference is reduced due to a structural factor. The C_{70} cage has the greatest curvature near the a-type atoms. Pyramidalization at these centres to accommodate sp^3-hybridized atoms is more easily achieved. Therefore, additions to a-type atoms would be preferable. Interestingly, this second argument has been emphasized[14] while interpreting the crystal structure of the iridium complex, in which metal coordination takes place at the a–b bond and not at the c–c-type bond. However, in view of the calculated relative stability of the isomeric dihydrides **1** and **2**, steric interactions with the ligands probably contribute to the observed preference for the a–b coordination in the iridium–C_{70} complex.

On the basis of the bond orders in C_{70}, the isomers next in the stability order are expected to be those obtained by hydrogenating the equatorial benzenoid rings. While the 1d–10d isomer (**3**) follows the expected pattern (Table 1), the 1d–1e isomer is much higher in energy. In spite of the nearly identical bond orders of the 1d–2d and 1d–1e bonds of C_{70}, the corresponding dihydrides differ by 10 kcal/mol in energy. Strain effects associated with the molecular structures of **3** and **6** have to be invoked to account for the computed energy difference. As confirmed by the calculated bond lengths, a double bond is localized in a pentagon in **6**. On the other hand, hydrogenation of the 1d–10d bond forces a Kekule form for an equatorial benzene ring in such a way that double bonds remain exocyclic to pentagons. In view of previous suggestions that greater strain is involved in structures with cyclopentene units[29], the stability of **3** relative to **6** can be understood. It is likely that another structural factor contributes to the reduced stability of **6**. In **6**, an e-type atom has sp^3 hybridization. Since this atom is common to three hexagons, the angle strain would be less if sp^2 hybridization is present. Hence, addition to this centre leads to considerable destabilization. Thus, the energy difference between **3** and **6** emphasizes the important role of molecular structural effects in determining the stabilities of C_{70} derivatives.

The calculated energy differences of the isomers obtained by hydrogenating the formal single bonds of C_{70} are also revealing. While the bond orders of the a–a, b–c, c–d and e–e bonds in C_{70} are very similar, the corresponding hydrogenated isomers differ in energy by over 30 kcal/mol. These variations can be understood on the basis of a combination of electronic and structural factors. Addition of hydrogen atoms to formal single bonds necessarily involves considerable reorganization of the cage π bonds. The computed structures reveal that the redistribution of single and double bonds is concentrated in a single corannulene unit in isomer **4** and **5**. In both structures, conjugation in three benzene rings is disrupted. Further, two C=C double bonds are localized in pentagons, leading to increased strain In **7** and **8**, hydrogenation leads to even larger reorganization of bonds. In addition to two of the benzene rings in the central pentaphenyl unit, a benzene ring in one of the corannulene fragments loses conjugation in these dihydrides. Hence, the isomers **7** and **8** are computed to be the least stable of the vicinal dihydrides.

In addition to extensive π bond reorganization, one more structural factor seems to contribute to variations in the relative stability of the dihydrides. As noted above, it is easier to accommodate a pyramidal carbon near the polar regions of C_{70} than to the flatter equatorial belt. Hence, it becomes increasingly difficult to convert carbon atoms into sp^3 centres along the series a–e. This interpretation would account for the slightly greater stability of **5** relative to **4** (the type and extent of bond reorganization is identical in the two isomers). Further, the dramatic destabilization of the 1e–2e isomer, **8**, can also be readily understood.

The interpretation of the relative energy of the vicinal dihydrides **1**–**8** can be extended to other types of isomers considered before[27]. Interestingly, **1** and **2** correspond to the lowest-energy structures of the 143 possible isomers of $C_{70}H_2$. Further, **3** is the fifth most stable isomer. The four other structures in the group of the seven most stable isomers of $C_{70}H_2$ are all derived by 1,4-addition of hydrogen atoms to C_{70}. These isomers do not suffer eclipsing interactions found in the vicinal dihydrides. However, reorganization of single and double bonds is unavoidable, leading to destabilization. The lowest-energy 1,4-adduct corresponds to the 1d–10d' isomer, in which a central benzene ring is

reduced. Since there is disruption of conjugation in a single benzene ring, the structure is predicted to be just 1.7 cal/mol higher than **1** at the AM1 level. The heat of formation of the alternative 1e–10e 1,4-isomer has not been reported. But the isomer is expected to be quite destabilized. There would be increased strain not only from two C=C bonds localized in pentagons but more importantly from sp^3 carbon atoms at two of the e-type centres. Two other stable isomers (1a–2c and 1b–2b) pointed out in the previous study[27] correspond to the two possible 1,4-adducts to a benzene ring of a corannulene unit. These structures involve fairly significant reorganization of bonds in a corannulene fragment and hence are 3–7 kcal/mol less stable than **1**. The seventh isomer of $C_{70}H_2$ in the overall order of stability is the 1c–3d structure, in which disruption of conjugation occurs in one benzene ring each of a corannulene unit and the pentaphenyl belt. The fact that all the 1,3- and 1,*n*-isomers ($n > 4$) are more than 10 kcal/mol higher in energy than **1** confirms that thermodynamic stability of the adducts is reduced to a significant extent whenever π bond reorganization is involved.

It is instructive to compare the computed energetics of the dihydrides of C_{60} and C_{70}. In both fullerenes, the most stable dihydrides are obtained by hydrogenation of the C–C bond with the highest bond order. The bond shared by two hexagons of C_{60} is calculated to have a bond order of 1.51, a value close to that computed for the 1c–2c and 1a–1b bonds of C_{70} (Table 1). The heat of hydrogenation is also computed to be remarkably similar for C_{60} (41.0 kcal/mol) and C_{70} (41.7 kcal/mol). In view of the experimental characterization of $C_{60}H_2$ (with the same structure as predicted by semiempirical MO calculations)[2], prospects for similar success with $C_{70}H_2$ must be termed good on energetic grounds. Possible formation of at least two isomers and the likelihood of multiple additions represent difficulties to be overcome by the experimentalists.

In summary, the chemical behaviour of C_{70} can be understood by visualizing the molecule as a combination of two corannulene units held by a central pentaphenyl belt. Additions to electron-rich corannulene double bonds should be kinetically and thermodynamically favoured. The stability of adducts is reduced whenever extensive π bond reorganization is involved. Further, the varying curvature of the fullerene cage leads to an important strain effect. It should be more difficult to pyramidalize the carbon atom in the flatter equatorial region; hence, the corresponding adducts should be destabilized. In particular, additions to the e-type carbon atom, which are common to three hexagons each, are the least preferred. As an interesting consequence, the 1,4-reduction of a central benzene ring should occur unsymmetrically (i e. in a way which destroys the σ_h plane of symmetry). These generalizations have obvious implications for determining the structures of higher derivatives of C_{70} (ref. 30).

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