MNDO study of vicinal dihydrides of C\textsubscript{70}: Interpretation of relative stability on the basis of electronic and molecular structures

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The structures and stability of isomeric vicinal dihydrides of C\textsubscript{70} are computed at the MNDO level. Their predicted stability is interpreted by comparing their electronic and molecular structures with those of C\textsubscript{60}. While the two most stable isomers correspond to those obtained by hydrogenating the two most electron-rich bonds in C\textsubscript{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 \(\pi\) reorganization accompanying hydrogen addition are suggested to control the relative stability of the C\textsubscript{70}H\textsubscript{2} isomers.

Even though C\textsubscript{70} and its illustrious counterpart, buckminsterfullerene (C\textsubscript{60}), were identified through mass spectrometry at the same time\textsuperscript{1}, the chemical behaviour of the two fullerenes is not equally understood. While numerous derivatives of C\textsubscript{60} have been spectroscopically and structurally characterized\textsuperscript{2-13}, reports on the chemical reactivity of C\textsubscript{70} have been restricted to the iridium complex, (\(\eta^2\)-C\textsubscript{70}) Ir(CO) Cl (PPh\textsubscript{3})\textsubscript{2} - whose crystal structure has been determined\textsuperscript{14} - and the partially characterized C\textsubscript{70}O. Experimental studies on C\textsubscript{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\textsubscript{70} poses special difficulties. Unlike C\textsubscript{60}, C\textsubscript{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\textsuperscript{16-22} in the case of the derivatives of C\textsubscript{60}. While the structure and bonding in C\textsubscript{70} also have received considerable theoretical attention\textsuperscript{23-25}, only two quantitative calculations have been reported on the derivatives of C\textsubscript{70}. The first study\textsuperscript{26} considered the energetics of isomeric structures of C\textsubscript{70}O. Although the results are of interest in view of the experimental isolation of C\textsubscript{70}O, general conclusions regarding the reactivity of C\textsubscript{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\textsuperscript{27} for the addition of hydrogen and alkyl groups to C\textsubscript{70}, and the seven most stable isomers out of the 143 possible C\textsubscript{70}X\textsubscript{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\textsubscript{70} derivatives.

In the present communication, we report the structures and energies of the eight possible vicinal dihydrides of C\textsubscript{70} (1-8) computed at the MNDO level\textsuperscript{28}. Using the available knowledge on the electronic and molecular structures of C\textsubscript{70} as the basis\textsuperscript{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\textsubscript{70}H\textsubscript{2} (1-8) can be classified using the atom-labelling scheme proposed recently\textsuperscript{2}. By viewing the molecule down the C\textsubscript{4} axis, the distinct atom types a, b, c, d (along with their
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 sp² 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 Kekulé 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, 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 1. Atom-labelling scheme in C_{70}. Labels are omitted for symmetry-related atoms for the sake of clarity.](image1)

![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.](image2)
the previous AM1 calculations predicted a small energy difference of 1 kcal/mol in favor 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 C70 consists of electronically isolated coronulenes and pentaphenyl fragments, disruption in conjugation of 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-2e isomer. Hence, the latter is expected to be more stable. However, this preference is reduced due to a structural factor. The C70 cage has the greatest curvature near the a-type atoms. Pyramidalization at these centers to accommodate sp3-hybridized atoms is more easily achieved. Therefore, additions to a-type atoms would be preferable. Interestingly, this second argument has been emphasized 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-C70 complex.

On the basis of the bond orders in C70, 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 C70, 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, 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 sp3 hybridization. Since this atom is common to three hexagons, the angle strain would be less if sp2 hybridization is present. Hence, addition to this center 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 C70 derivatives.

The calculated energy differences of the isomers obtained by hydrogenating the formal single bonds of C70 are also revealing. While the bond orders of the a-a, b-c, c-d and e-e bonds in C70 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 coronulene 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 coronulene 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 C70 than to the flatter equatorial belt. Hence, it becomes increasingly difficult to convert carbon atoms into sp3 centers along the series a-c. 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 1c-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. Interestingly, 1 and 2 correspond to the lowest-energy structures of the 143 possible isomers of C70H2. Further, 3 is the fifth most stable isomer. The four other structures in the group of the seven most stable isomers of C70H2 are all derived by 1,4-addition of hydrogen atoms to C70. 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
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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 I 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 sp3 carbon atoms at two of the o-type centres. Two other stable isomers (1a-2c and 1b-2b) pointed out in the previous study27 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 I.

The seventh isomer of C70H2 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 1,4-isomers (n > 4) are more than 10 kcal/mol higher in energy than I confirms that thermodynamic stability of the adducts is reduced to a significant extent whenever p bond reorganization is involved.

It is instructive to compare the computed energetics of the dihydrogen of C60 and C70. In both fullerences, the most stable dihydrogen are obtained by hydrogenation of the C–C bond with the highest bond order. The bond shared by two hexagons of C60 is calculated to have a bond order of 1.51, a value close to that computed for the 1e–2c and 1a–1b bonds of C70 (Table 1). The heat of hydrogenation is also computed to be remarkably similar for C60 (41.0 kcal/mol) and C70 (41.7 kcal/mol). In view of the experimental characterization of C60H2 (with the same structure as predicted by semiempirical MO calculations), prospects for similar success with C70H2 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 C70 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 p 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 fullerene equatorial region; hence, the corresponding adducts should be destabilized. In particular, additions to the o-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 σd plane of symmetry). These generalizations have obvious implications for determining the structures of higher derivatives of C70 (ref. 30).


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