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Exploring new structural motifs using computational methods*

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Abstract

The potential of using computational methods to examine new molecular structural motifs is illustrated. Geometrical parameters, energetics, strain, electronic structures, frontier orbital separations, and estimates of band gaps of polycyclic molecules with parallel stacks of C=C bonds have been obtained using AM1 calculations. Similar details have been derived for the cyclic pentaphenylene molecule, a fragment of C_{70}. The molecule is predicted to adopt a quinonoid form.

Keywords: Electronic effects, conformations, AM1 calculations.

1. Introduction

Chemists have the privilege of creating, themselves, the objects of their interest. Usually, nature provides inspiration for the systems they choose to synthesise. Naturally occurring molecules and substances have enough variation and complexity to test the skills of chemists and often have the added advantage of having useful properties. Synthetic targets are also chosen on the basis of aesthetic appeal (*e.g.*, dodecahedrane). The pleasure of being the first to make a molecule is undeniable. A chemist who is asked the reason for the monumental efforts expended in trying to make a highly strained molecule may well answer: "Because it is *not* there!" Everyday objects of the macroscopic world can also serve as goals (*e.g.*, tinker toys provided the motivation for the synthesis of the series of molecules called *n*-staffanes).

There is increasing realisation that the scope of synthetic goals must be expanded. Instead of trying to make specific molecules, the focus should be on properties. The decision of what to make should be as important as how to make. But how does one know the properties of a molecule before creating it first?

Computational chemistry of small molecules has reached sufficient levels of reliability to predict at least some molecular properties of general interest. The possible existence of a molecular entity in isolation as a long-lived species on the potential energy

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surface can be determined. The magnitude of strain energy with respect to related known molecules can be derived. Geometries can be obtained to great precision. Key features of electronic structures can be elucidated. Many other molecular properties can also be calculated fairly accurately. The challenging problem of extending our knowledge of individual molecules to a collection of them in solution or in different periodic arrangements can also be approached using appropriate models. In effect, computational work can be used to design new synthetic targets. The methods can also be utilised to evaluate the thermodynamic likelihood of successful synthesis and perhaps even the worthiness of the effort.

The claims made above are not far-fetched. Many instances can be quoted in which chemically interesting predictions have been made using theory. The electronic structure of a complex system such as polyacetylene was debated and fairly accurately resolved by theoreticians[1] long before the material was made. The theoretical prediction of the existence and stability of C_{60} remained buried in a Japanese journal unsung, unhonoured and uncited for several years[2]. Occasionally, there is the happy instance of an experimental chemist who trusts an unusual theoretical prediction sufficiently enough to try and prove it in the laboratory. Two spectacular cases come to my mind; a dication derived from adamantane with no hydrogen atoms at the bridgehead positions[3] and [1.1.1]propellane[4]. These remarkable structures were correctly predicted to be synthesisable. (It so happens that the experimental work was done by the same groups which did the calculations.)

In this talk, I shall try to demonstrate the usefulness of computational methods for analysing new structural motifs which are likely to have interesting chemical features. I shall discuss two classes of molecules. The first has a series of parallel C=C bonds. The second is a molecular fragment of C_{70}, whose possible independent existence as well as properties are evaluated.

2. Computational details

All calculations were done using the AM1 hamiltonian[5] with full geometry optimisation. Symmetry constraints were imposed in a few cases to examine specific geometries of interest. A modified MOPAC package was used.

3. Polycyclic derivatives with stacked double bonds

The possible existence of allotropes of carbon was considered by Hoffmann and coworkers[6] before the first report of C_{60}. While modelling various networks, the authors noted that parallel stacks of C=C double bonds (Fig. 1) have an interesting band structure, resulting from through-space interactions. Although the band gaps and bandwidths strongly depend on the inter-alkene distance, metallic behaviour was predicted for distances shorter than 2.4 Å. The conclusion was based on tight-binding calculations on stacks constructed from units such as A and B[7].

It is indeed remarkable that through-space interactions can be as effective as direct conjugation in creating small band gaps. Experimental realisation of this idea is not straightforward since alkenes do not prefer to stack in a parallel manner. AM1 calcula-

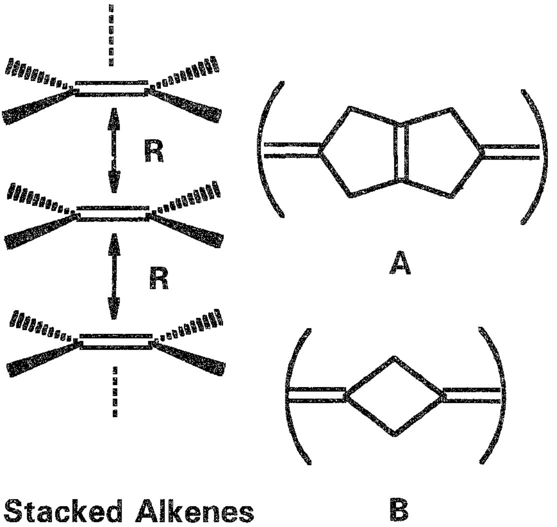

FIG. 1. Model of stacked olefines and structures A and B considered in this arrangement.

tions on units of 5 or 10 ethylene molecules reveal strong repulsions between the closed shell molecules, especially at the more interesting shorter distances. In principle, the ideas of crystal engineering can be used to align molecules in the desired fashion with appropriate substitution. Unfortunately, our control over noncovalent interactions in a large molecular assembly is far from complete. Further, large perturbations which lead to the preferred mode of packing may destroy the desired band structure.

An alternative is to hold the C=C units in place by covalent linkages in a polycyclic framework. Two possible series of molecules, **1** and **2**, appear attractive in this regard. The first series has cyclobutene rings fused to a ladderane skeleton (Fig. 2). The second set of molecules represent larger homologues, with endo-fused cyclobutenes on a norbornyl framework (Fig. 3).

As may be expected, the ladderane-fused system is highly strained. The computed heat of formation of **1a** is 170.8 kcal/mol. Each subsequent expansion of the skeleton leads to a large increase of energy. Interestingly, the increase is roughly constant at 141 kcal/mol, on going from **1a** to **1b** to **1c** and on to **1d**. On thermodynamic grounds, it will be a challenging task to make this series of molecules. But the goal is not altogether impossible, since ladderanes functionalised on the same side are already known[8].

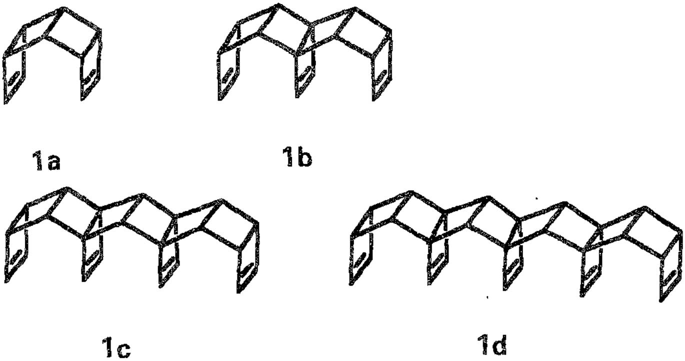
1a **1b** **1c** **1d**

FIG. 2. Structures of stacked olefines covalently linked to a ladderane framework.

The important structural feature of **1** is the inter-double bond distance. In **1a**, the calculated value is 2.83 Å. The value increases marginally in the larger derivatives. In both **1c** and **1d**, the outer double bonds are 2.84 Å apart, while the inner double bonds have a separation of 2.87 Å. *These distances are in the region in which the band gaps are fairly* large. The computed π MOs in the largest model **1d** are spread over a range of 1.5 eV,

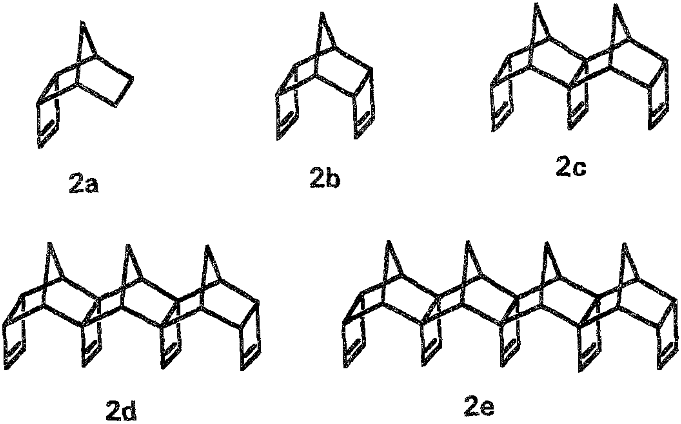
2a **2b** **2c** **2d** **2e**

FIG. 3. Structures of stacked olefines covalently linked to a norbornyl framework.

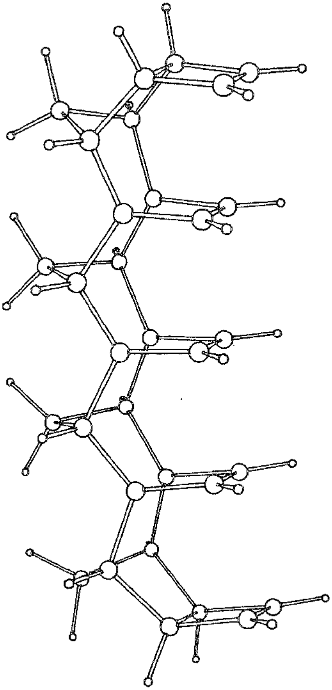

FIG. 4. AM1 optimised geometry of **2e**.

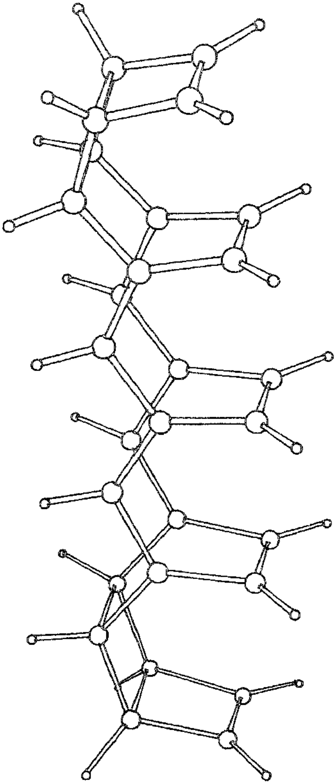

FIG. 5 AM1 optimised geometry of **1d**.

while the π* MOs are in a range of 0.8 eV. The HOMO–LUMO gap is 9.5 eV, while the estimated S_0–S_1 transition energy using limited CI is around 5 eV.

The strain in the ladderane series is evident in large bond lengths in the fused cyclobutane rings. In the larger derivatives, these distances are as large as 1.68 Å. As a result, many σ MOs interact very strongly with the π MOs, both in the filled and unfilled manifolds.

The fused norbornyl derivatives are more interesting from several points of view. They are far less strained and hence must be amenable to synthesis on thermodynamic grounds. Elaboration of the skeleton in **2** increases the heat of formation in the range of 115 kcal/mol. More importantly, the C=C bonds are much closer to each other. While the distance is 2.72 Å in **2b** (due to strong filled orbital repulsions), it becomes successively shorter in the larger derivatives. The inner double bonds in **2e** are within 2.48 Å of each other. This reduction in distance is not a consequence of any attractive interaction between the alkenes. It is more a result of the angular preferences in the fused norbornyl skeleton. The double bonds lie on a curved surface (Fig. 4). From the computed curvature, the cycle is expected to come full circle in about 44 units! Interestingly, the double bonds of the ladderane series, **1**, are curved in the reverse fashion (Fig. 5). A strategy to construct a very long polymeric chain of roughly parallel C=C double bonds is to intersperse the two structural motifs **1** and **2**!

The shorter inter-olefin distance in **2e** leads to a large spread of the π and π^* 'bands'. They vary over 3 and 1.5 eV, respectively. The widths are comparable in magnitude to those computed for long conjugated chains of C=C bonds[9]. The frontier orbital separation is 8.3 eV in **2e**. An estimate of the 'optical band gap' obtained *via* limited CI calculations is around 3 eV, again comparable to that calculated for linearly conjugated polyenes. Based on computed and experimental results on models of polyenes and polyacetylene, the band structure of a large oligomer of **2** is likely to be similar to that of polyacetylene. Hence, such systems would be attractive synthetic targets as a model organic semiconductor, although perhaps not as a metal.

4. Cyclic pentaphenylene

The molecular and electronic structure as well as many aspects of chemical reactivity of C_{70} can be understood in terms of a simple bonding picture. The molecule can be visualised as being built of two corannulene rings held together by a central pentaphenyl belt[10]. Corannulene is a well-studied aromatic molecule. But the properties and even the possible existence of the central unit as an independent molecular entity has not been explored. The closest systems considered are beltenes, with edge-fused hexagons[11], and polyphenylenes, both as oligomers and as an infinite chain.

The optimised structure of cyclic pentaphenylene, $(C_6H_4)_5$, **3**, is remarkable in many ways. The D_{5h} symmetric structure is a true minimum on the potential energy surface. The benzene rings are highly distorted to boat forms (Fig. 6). The estimated extra strain relative to linearly fused pentaphenyl[9] is about 100 kcal/mol. The approximate diameter of the ring (6.7 Å) is quite similar to the equatorial diameter of C_{70} (6.9 Å). However, **3** is unique in one respect. The computed bond lengths reveal that the benzene rings are in the quinonoid form. While the two central C–C distances in the ring are 1.35 Å, four other ring distances are 1.46 Å. Further, the inter-ring distance is 1.36 Å. In contrast, the rings have more uniform bond lengths in the pentaphenyl belt of C_{70} as well as in polyphenylene at the same level of theory.

The preferred quinonoid form leads to a small gap between the frontier orbitals in **3**. Previous calculations have shown that polyphenylene has indeed a small band gap if it

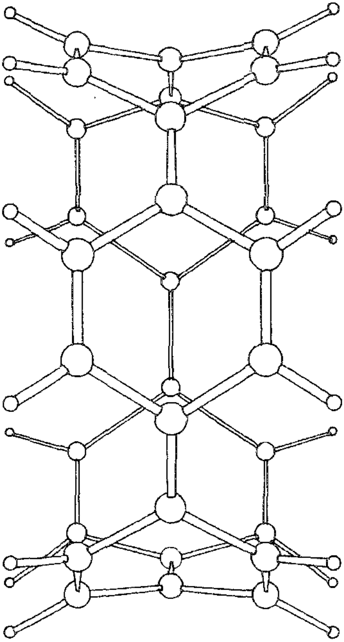

FIG. 6. AM1 optimised geometry of **3**.

adopts the quinonoid form[12]. Geometry optimisations have also revealed that the corresponding form does not exist as an independent minimum for polyphenylene[9]. The large angular distortion in the cyclic structure reverses the geometric preference.

Cyclic pentaphenylene is expected to have interesting molecular properties. Intermolecular interactions are also likely to be significant in this system. It would be an excellent, though somewhat difficult, synthetic target. It may be visualised as perhaps the smallest possible molecular tubule. Planned synthesis of larger cyclic polyphenylenes would also be of interest.

Acknowledgements

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