

Isomers of C_{24} . Density functional studies including gradient corrections

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Received 31 January 1994

Abstract

Density functional techniques are used to investigate the relative energies of seven different structural isomers of C_{24} . The traditional local density approximation yields the fullerene-like isomer to be the most stable. As in the case of C_{20} , the inclusion of gradient corrections has a dramatic effect on the relative energies. The gradient-corrected B-LYP method yields the monocyclic ring and graphite-like isomers to be almost isoenergetic (and most stable) while the bicyclic ring, fullerene-like, and bowl-like isomers are progressively higher in energy. The Hartree–Fock results are quite similar to the B-LYP results. Implications to fullerene growth mechanisms are pointed out.

1. Introduction

The mechanism of formation of fullerenes has been a challenging and controversial area of active research [1–8]. An important relevant question is the identification of the smallest carbon cluster which has a fullerene-like ground state. While fullerenes are not seen experimentally for clusters smaller than C_{28} [9], theoretical studies [10,11] have suggested that even smaller carbon clusters may have such ground-state structures.

We recently carried out a detailed theoretical study using density functional methods on C_{20} , the smallest carbon cluster which can exist as a fullerene cage [12]. While the local density approximation yielded a fullerene-like ground state, the inclusion of the gradient corrections completely reversed the energy ordering of the isomers and yielded a monocyclic ring as the most stable form. This is consistent with the experimental mobility measurements performed by von

Helden et al. [13] which showed that the dominant isomer of C_{20} is a monocyclic ring.

Another carbon cluster which is important in understanding the relative stabilities of different fundamental structural units is C_{24} . C_{24} is the first cluster (apart from the trivial case of C_6) which contains a stable planar graphite-like fragment. It is thus clearly important in comparing fullerene-like cluster growth with graphite-like growth. However, neither fullerene-like nor graphite-like isomers have been observed experimentally for C_{24} [13,14]. Studies by von Helden et al. [13] have shown clearly that the dominant isomer of C_{24} is also a monocyclic ring though a ‘bicyclic ring’ is also seen for the negative ion. There have been several previous studies on C_{24} at levels of theory ranging from empirical to ab initio quantum chemistry [15–22]. The most detailed study has been by Jensen and Toftlund [22] who investigated four isomers using Hartree–Fock and second order Møller–Plesset perturbation theory. In this study, we

have carried out a detailed theoretical investigation on seven different structural isomers of C_{24} using Hartree–Fock and density functional methods.

2. Theoretical methods

In our previous study on C_{20} [12], complete characterization of three structural isomers was carried out with ab initio Hartree–Fock level of theory using the 6-31G* basis set (HF/6-31G*)^{#1}. In this study, since there are many more isomers with unknown symmetries, we used the semi-empirical MNDO procedure [24] in the initial phase of the work. We performed geometry optimizations as well as complete vibrational analysis on each of the isomers at the MNDO level. Symmetry restrictions were relaxed until local minima were obtained in each case as confirmed by the force constant analysis. Complete optimizations were then performed at the HF/6-31G* level of theory as in our previous study. However, the vibrational analyses were not repeated at this level. While it is possible that some of our calculated ab initio structures may go to lower symmetries, we believe that the principal conclusions are not likely to change.

The HF/6-31G* geometries of the isomers were then used to perform single-point calculations using three density functional methods. The first is the traditional local density approximation (LDA) determined self-consistently by the solution of the Kohn–Sham equations [25]^{#2}. The second includes density gradient corrections with the B-LYP functional (Becke functional [27] for exchange and correlation functional [28] by Lee, Yang, and Parr) applied to the HF density. This is a hybrid method referred to as B-LYP/HF [29]. The third method obtains the fully self-consistent solutions of the Kohn–Sham equations employing the B-LYP functional. All calculations were carried out with a modified version of the GAUSSIAN 92 program [30]. The larger 6-311G* basis set (see footnote 1) was used in all density functional calculations. This basis set which has valence-triple-zeta sp functions along with a set of d

^{#1} For the standard basis sets used in this Letter, see ref. [23].

^{#2} For the correlation part of the LDA calculations, we have used Functional V from ref. [26].

functions on each carbon appears to yield converged results for smaller carbon clusters [31].

3. Isomers considered

In our previous study on C_{20} [12], we studied three isomers: a monocyclic form (ring), a corannulene-like form (bowl) and the fullerene form (cage). In the case of C_{24} , we have considered seven isomers in detail. In roughly increasing order of dimensionality, the isomers (and their symmetries) are: a monocyclic ring (1, Fig. 1, D_{12h}), a bicyclic ring (2, Fig. 2, D_{2h}), a graphite-like form (3, Fig. 3, D_{6h}), two different bowl-like forms (Fig. 4), one of them with only one pentagon (4a, C_s) and the other with three pentagons (4b, C_s), and two different cage forms (Fig. 5), a fullerene-like cage containing six- and five-membered rings (5a, D_6) and another cage structure which has six- and four-membered rings (5b, O_h).

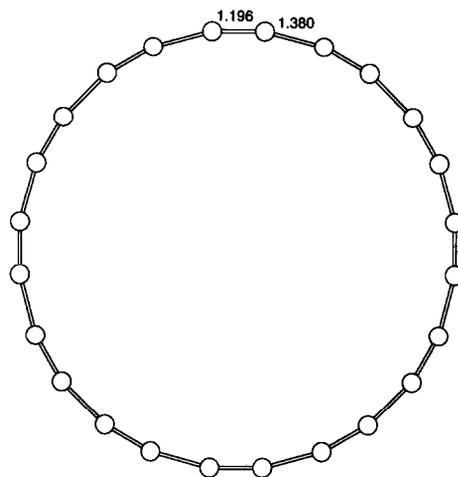


Fig. 1. The monocyclic isomer of C_{24} (1, D_{12h} symmetry).

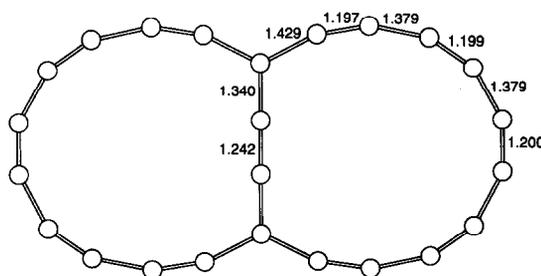


Fig. 2. The bicyclic isomer of C_{24} (2, D_{2h} symmetry).

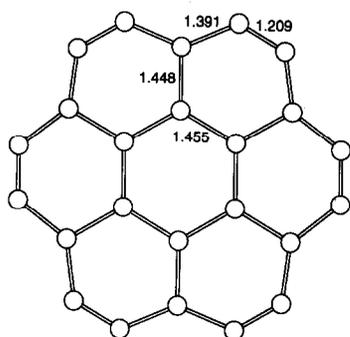
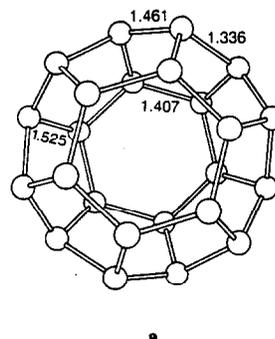
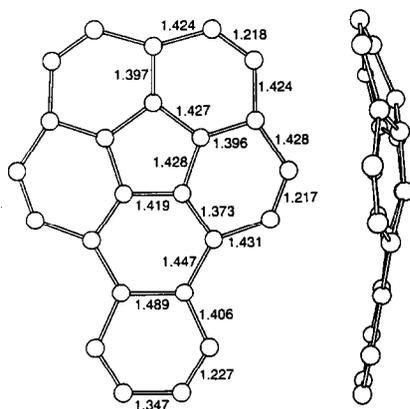


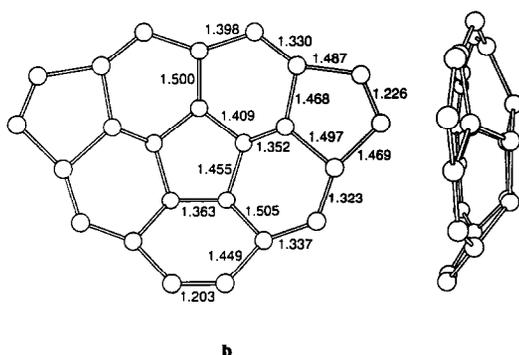
Fig. 3. The graphite-like isomer of C_{24} ($3, D_{6h}$ symmetry).



a

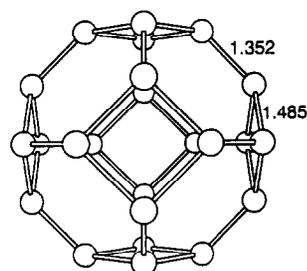


a



b

Fig. 4. Two different bowl-like isomers of C_{24} . The top pictures (4a) show two views of the bowl isomer containing only one pentagon (C_4 symmetry) and the bottom pictures (4b) show two views of the bowl isomer containing three pentagons (C_4 symmetry).



b

Fig. 5. Two different cage isomers of C_{24} . The top picture (5a) shows the fullerene-like isomer containing six- and five-membered rings (D_6 symmetry) and the bottom picture (5b) shows another cage isomer containing six- and four-membered rings (O_h symmetry).

While some of the isomers are obvious candidates, the selection of the others requires additional comments. In particular, many different possibilities exist for the 'bicyclic' form as pointed out previously by von Helden et al. [13]. We considered a variety of possibilities using a simple tight-binding Hamiltonian [32] and then selected the most stable isomer for the higher level study in this work. This D_{2h} structure (2) is obtained by a fusion of two 14-membered rings with four atoms being shared at the junction. While this may not be the most stable bicyclic isomer at ab initio levels, it appears to be relatively stable and should provide useful information for that family of structures. Two different bowl isomers (4a and 4b) were considered because unlike C_{20} which has a unique bowl form (a central pentagon surrounded by hexagons), several such isomers are possible for C_{24} . We have considered one isomer where the added four atoms complete one more hexagon (4a) and another isomer where the added four atoms complete two

more pentagons (**4b**). Interestingly, both **4a** and **4b** are fragments of C_{60} and thus understanding their stabilities has consequences for the growth mechanisms of fullerenes.

4. Results and discussion

The principal geometrical features (bond lengths in Å) of the different isomers are shown in Figs. 1–5. Among the isomers considered, **1**, **3**, **5a**, and **5b** have been considered previously by Jensen and Toftlund [22]. They have performed Hartree–Fock optimizations with a polarized double-zeta basis set (HF/DZP) and single-point calculations at these geometries using second order Møller–Plesset perturbation theory (MP2). As expected, our HF/6-31G* geometries are virtually identical to the HF/DZP geometries of Jensen and Toftlund and we do not discuss them in detail. The bicyclic isomer (**2**) shows bond alternation (polyacetylenic character) away from the central ring fusion in a manner very similar to that of the monocyclic ring (**1**). Both of the bowl forms **4a** and **4b** show characteristic short peripheral bonds similar to that in the graphite form indicating significant triple bond character. The structure **4b** containing three pentagons is significantly more curved than **4a** containing only one pentagon. This is consistent with the expectation that each pentagon introduces local curvature in the structures of fullerenes.

Our calculated relative energies using the three density functional methods (6-311G* basis set) are listed along with the corresponding HF values in Table 1. The ring is the ground state at the HF/6-311G* level of theory with the graphite form being very close

in energy (0.40 eV). This is the reverse of the ordering obtained by Jensen and Toftlund [22] and is due to the use of the larger triple-zeta basis set in our work. The other isomers are considerably higher in energy at the HF level. However, as in the case of C_{20} [12], the local density approximation behaves completely differently. The LDA method favors the cage structures substantially so that **5a** is 6.5 eV more stable than the monocyclic ring. As shown previously [22], electron correlation effects evaluated with the MP2 method also favor the cage relative to the ring by more than 5 eV. This is clearly at odds with the experimental works [13,14], which suggest strongly that a monocyclic ring is the ground state. It appears likely that both the LDA and the MP2 methods have substantial deficiencies and do not predict the ground state isomer of C_{24} correctly.

As in the case of C_{20} [12], dramatically different results are obtained when the gradient corrections are included. Gradient corrections stabilize the ring by more than 8 eV relative to the fullerene cage so that the ring is now more stable than the cage by 2.01 eV at the B-LYP level. This is very similar to our previous observation on C_{20} [12]. It is interesting to note that the energy difference between the monocyclic ring **1** and the fullerene form **5a** is very similar at the HF, B-LYP, and B-LYP/HF levels. The graphite form **3** is essentially isoenergetic with the monocyclic ring **1** at the B-LYP level. The bicyclic isomer is intermediate in stability between the monocyclic ring and the fullerene cage. At all levels of theory, the cage structure containing six- and four-membered rings (**5b**) is at least 1 eV less stable than the fullerene form **5a** containing six- and five-membered rings. This is obviously an effect of the angle strain introduced by the

Table 1
Relative energies (eV) for the isomers of C_{24} *

Structure	Symmetry	HF	LDA	B-LYP/HF	B-LYP
1	D_{12h}	0.0	0.0	0.0	0.0
2	D_{2h}	2.15	0.61	1.48	1.53
3	D_{6h}	0.39	-4.57	-0.79	0.00
4a	C_s	2.96	-2.39	1.69	2.31
4b	C_s	10.57	2.47	8.16	7.41
5a	D_6	1.89	-6.53	1.81	2.01
5b	O_h	2.99	-5.03	2.82	3.02

* The 6-311G* basis set used with optimized HF/6-31G* geometries.

four-membered rings in **5b**. Among the two different bowl structures, **4a** with only one pentagon is substantially (≈ 5 eV) more stable than **4b** with three pentagons. Overall, the final B-LYP energy differences are quite close to those seen at the HF level of theory. It will be interesting in the future to perform high quality quantum chemical calculations (such as infinite order CCSD(T) [33,34]) to calibrate these results.

Thus, at the B-LYP level of theory which is likely to be the most reliable, the most stable isomers of C_{24} are the monocyclic ring **1** and the graphite-like form **3** with the bicyclic form being 1.5 eV higher in energy. Experimentally, however, while the monocyclic ring is clearly the dominant isomer, the graphite form has never been seen [13,14]. There may be two reasons for this discrepancy. Firstly, the experiments have been performed on ionic forms whereas the calculations refer to neutral systems. We have looked at the orbital energies of the highest occupied (HOMO) and lowest unoccupied (LUMO) molecular orbitals at the B-LYP level to consider this approximately. At the one-electron level, the graphite-form has an ionization potential which is larger than that of the ring by 0.4 eV and an electron affinity which is smaller than that of the ring by 0.2 eV. Thus, the graphite form is comparatively less stable both as a positive and as a negative ion. The effect on the bicyclic ring lies in between as expected. Effects of geometry relaxation on the ions may also be larger for the monocyclic ring with its more flexible structure. An additional factor which contributes considerably to the stability of the rings at higher temperatures is due to entropic factors. We have evaluated the effect of higher temperatures on the energy difference between the isomers **1–3**. As expected from our previous study on C_{20} [12], the lowering of the free energy of the isomers at higher temperatures is in the sequence monocyclic ring **1** > bicyclic ring **2** > graphite form **3**. Entropic factors favor the rings due to the presence of many low-frequency vibrational modes relative to the other isomers. Using the MNDO vibrational frequencies, we calculate that temperature effects stabilize the monocyclic ring relative to the graphite form by 1.5 eV at 1000 K. As expected, the effect on the bicyclic ring is intermediate, being stabilized by 1.0 eV at 1000 K relative to the graphite form. Finally, kinetic factors such as large activation

barriers may also be partially responsible for the lack of the graphitic form [14].

One of the earliest proposed mechanisms of fullerene formation is by means of curling of graphitic sheets by incorporation of pentagons [1–3]. For example, in the ‘pentagon road’ mechanism [3], Smalley and co-workers have proposed that the ground state of intermediate-sized clusters (such as C_{24}) minimize the number of dangling bonds by having as many pentagons as possible while avoiding adjacent pentagons. Such a mechanism would suggest that the ground state of C_{24} should be the bowl structure **4b** containing three pentagons. However, our study clearly shows that such a structure is very unstable and rules it out as a possible ground-state candidate. Though such a structure is appealing because it naturally leads to C_{60} , it is clear that ideas based on the pentagon rule are unlikely to govern the growth of fullerenes. More recent experimental work [6–8] has suggested that fullerenes form by annealing and coalescence of large rings. The stability of the ring forms in our study lends support to such a mechanism.

Acknowledgement

This work was partly supported by the National Science Foundation under grants CHE-8918623 (Carnegie-Mellon). BGJ thanks the Mellon College of Science for a Graduate Fellowship.

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