

Isomers of C_{20} . Dramatic effect of gradient corrections in density functional theory

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Density functional techniques including gradient corrections are used to investigate the relative energies of the ring, bowl (corannulene-like), and cage (fullerene-like) isomers of C_{20} . In agreement with previous studies, the local density approximation yields the cage to be the most stable isomer with the bowl and ring forms being significantly higher in energy. However, the inclusion of gradient corrections completely reverses the energy ordering of the isomers. The gradient correction alters the relative energy between the cage and ring isomers by more than 7 eV and yields the ring as the most stable form.

1. Introduction

The macroscopic preparation [1] of C_{60} and other fullerenes has raised interesting questions about the mechanism of formation of spheroidal carbon clusters. Detailed understanding of the factors which determine the structures and stabilities of smaller carbon clusters is of obvious importance in this regard. In particular, the question of the smallest carbon cluster with a fullerene-like ground state has been controversial. While fullerenes are not seen experimentally for clusters smaller than C_{28} [2], theoretical studies [3–5] have suggested that even smaller carbon clusters may have such ground state structures.

C_{20} is the smallest carbon cluster which can exist as a fullerene cage. While the hydrogenated form $C_{20}H_{20}$ (dodecahedrane) [6] is well known, it is not obvious if the bare C_{20} cluster should be stable as a

cage structure. Experimentally, mobility measurements performed by von Helden et al. [7] provide the most clear-cut evidence for the nature of the observed C_{20} structures. For both C_{20}^+ and C_{20}^- the most dominant isomer corresponds to a monocyclic ring. While there is no evidence for any other isomer for the cation, the anion shows very weak features tentatively assigned to a linear isomer as well as a bicyclic isomer. There is no evidence for cage (fullerene-like) or bowl (corannulene-like) isomers in these experiments.

There have been several recent theoretical studies [3–5,8] on C_{20} isomers. Most of these have focused on four isomers: a linear form, a monocyclic form (ring), a corannulene-like form (bowl) and the fullerene form (cage). Almlöf and co-workers [3,4] obtain the ring as the most stable form at the Hartree-Fock (HF) level while second-order perturbation theory (MP2) predicts the fullerene to be most stable. Von Helden et al. [7] have obtained similar results with slightly different basis sets. Brabec et al.

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[5] have performed local density functional studies and obtain the cage to be the ground state with the bowl, ring, and linear forms being 0.75, 2.65, and 10 eV higher in energy. They have suggested that entropic factors at high temperatures may favor the bowl form relative to the cage. Slanina and Adamowicz [8] have used the semi-empirical AM1 procedure and obtain a ring ground state.

Recently, there has been considerable interest in density functional treatments including density gradient corrections [9,10]. These gradient corrected schemes appear to solve one of the principal drawbacks of traditional density functional methods: the overestimation of bond energies by local density approximation. These methods are particularly promising for larger systems because of their favorable scaling with the size of the system when compared to correlated *ab initio* techniques. In this Letter, we use gradient-corrected density functional methods and find that the previous conclusions of local density methods are reversed.

2. Theoretical methods

In this Letter, we restrict our calculations to three structures: cage, bowl, and ring isomers. These may be considered as representative examples of three-, two-, and one-dimensional structures. The linear isomer is not included because it does not appear to be a candidate for the ground state of C_{20} . For each isomer, we consider only singlet electronic states to facilitate comparisons with previous studies and to stimulate future investigations with other techniques. In order to have well-defined molecular geometries, we have performed complete geometry optimizations at the Hartree-Fock level with the polarized double-zeta 6-31G* basis set^{#1}. Vibrational analysis has been carried out on all structures and symmetry restrictions are relaxed until true local minima are obtained.

The HF/6-31G* geometries of the three isomers have been 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 [12]. The second includes density gradient corrections with the B-LYP functional (Becke functional [13] for exchange and correlations functional [14] by Lee, Yang, and Parr) applied to the HF density. This is a hybrid referred to as B-LYP/HF [15,16]. The third method obtains the fully self-consistent solutions of the Kohn-Sham equations employing the B-LYP functional. Numerical integrations for the neutral species are performed using the 50 point Euler-Maclaurin scheme for radial integrations [17] and the 194 point Lebedev formula for angular integrations using a modified version of the GAUSSIAN 92 program [18]. Numerical integrations for the positive ions are performed using 64 Gauss-Legendre radial points and Lebedev's 302 point angular grid using a program developed at Rice University. The larger 6-311G* basis set [11] is used in all density functional calculations. This basis set which has valence-triple-zeta sp functions along with a set of d functions on each carbon appears to yield converged results for smaller carbon clusters [19].

3. Results and discussion

It is well known that the cage structure of C_{20} (dodecahedron) with icosahedral symmetry has a degenerate electronic ground state and is thus subject to Jahn-Teller distortion. Parasuk and Almlöf [3] studied a D_{3d} triplet isomer obtained by distortion along one of the fivefold axis. We find that for the singlet state considered, distortion along the three fold axis to yield a D_{3d} isomer is more favorable than the D_{5d} form. However, the D_{3d} form still has a pair of degenerate e_g imaginary frequencies indicating that further symmetry lowering is required. A lower symmetry C_s structure has one a'' imaginary frequency while a C_2 form is a true local minimum at the HF/6-31G* level (fig. 1). For the ring, Parasuk and Almlöf [3] have suggested that a bond-alternating D_{10h} structure may be the most stable form at the HF level. However, at the HF/6-31G* level, this has three imaginary frequencies and symmetry lowering to C_{10h} yields a local minimum (fig. 2) though the energy lowering due to this distortion is very small. Finally, for the bowl form, the obvious C_{3v} isomer is found to be a local minimum (top and side views in fig. 3).

^{#1} For the standard basis sets used in this paper, see ref. [11].

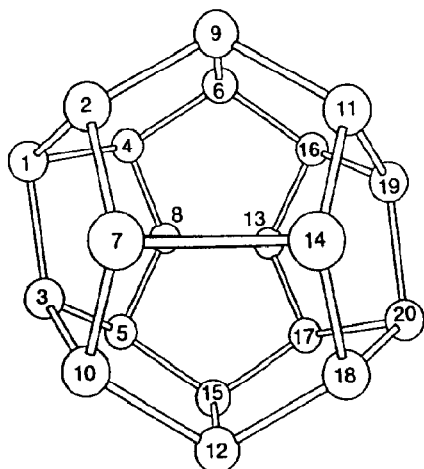


Fig. 1. The cage (fullerene-like) isomer of C_{20} (C_2 symmetry).

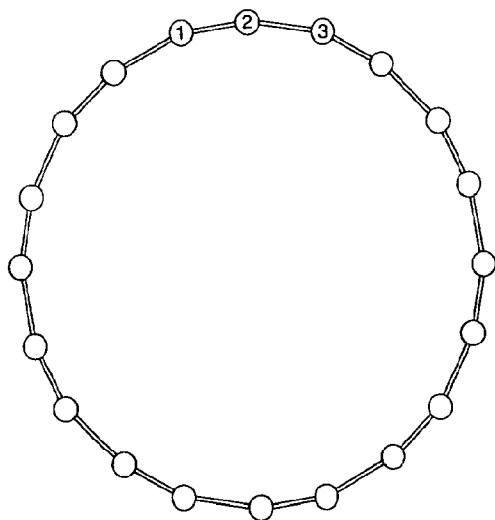


Fig. 2. The ring isomer of C_{20} (C_{10h} symmetry).

Slanina and Adamowicz [8] also obtain similar minima for all three structures with the semi-empirical AM1 method. The geometrical parameters of the three isomers are listed in table 1 and HF/6-31G* harmonic vibrational frequencies are given in table 2.

Our calculated relative energies using the three density functional methods (6-311G* basis set) are listed along with the corresponding HF values in table 3. As seen in previous papers, the ring is the

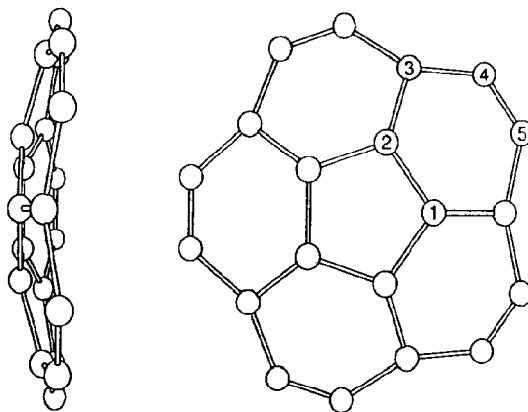


Fig. 3. Two views of the bowl (corannulene-like) isomer of C_{20} (C_{2v} symmetry).

Table 1

Bond lengths (Å) and bond angles (deg) for C_{20} isomers

Structure	Parameter ^{a)}	HF/6-31G*
ring	C ₁ -C ₂	1.196
	C ₁ -C ₂	1.381
	C ₁ -C ₂ -C ₃	164.5
bowl	C ₁ -C ₂	1.429
	C ₂ -C ₃	1.397
	C ₃ -C ₄	1.424
	C ₄ -C ₅	1.218
cage	C ₁ -C ₂	1.504
	C ₁ -C ₃	1.437
	C ₁ -C ₄	1.451
	C ₂ -C ₇	1.385
	C ₂ -C ₉	1.437
	C ₃ -C ₅	1.481
	C ₃ -C ₁₀	1.406
	C ₄ -C ₆	1.423
	C ₄ -C ₈	1.460
	C ₅ -C ₈	1.367
	C ₅ -C ₁₅	1.469
	C ₆ -C ₉	1.413
	C ₇ -C ₁₀	1.444
	C ₇ -C ₁₄	1.479
	C ₈ -C ₁₃	1.497
	C ₉ -C ₁₁	1.455

^{a)} For the numbering system see figs. 1-3.

ground state at the HF level. The energy difference between the ring and the cage (4.03 eV) is slightly smaller than the value (4.6 eV) obtained by Parasuk and Almlöf [3] for the triplet form of the cage. As

Table 2
Harmonic vibrational frequencies (cm^{-1}) for the isomers of C_{20}

Structure	HF/6-31G* frequencies
ring ^{a)}	53(e), 69(e), 143(e), 161(e), 252(e), 273(e), 340, 369, 395, 396, 425, 463(e), 514(e), 527(e), 536, 544(e), 577(e), 615(e), 618(e), 702(e), 757(e), 761, 869(e), 1173(e), 1417(e), 1519, 2346, 2393(e), 2477(e), 2495, 2506(e), 2522(e)
bowl	153(a ₁), 173(e ₂), 330(e ₂), 379(a ₂), 399(e ₂), 412(e ₁), 425(e ₁), 450(e ₂), 457(e ₁), 481(a ₂), 518(e ₂), 530(e ₁), 639(a ₁), 684(e ₁), 706(e ₂), 707(a ₁), 830(e ₂), 880(a ₂), 890(e ₁), 973(e ₂), 1064(a ₁), 1218(e ₁)m 1282(e ₂), 1448(e ₂), 1467(e ₁), 1552(a ₁), 1559(a ₂), 1596(e ₁), 1612(e ₂), 2169(e ₂), 2235(e ₁), 2252(a ₁)
cage	161(b), 221(a), 285(b), 505(a), 531(b), 547(a), 560(b), 570(a), 593(a), 601(b), 656(a), 681(b), 682(a), 713(a), 730(b), 742(a), 744(b), 795(a), 811(b), 815(a), 830(b), 849(b), 852(b), 853(a), 882(a), 964(b), 972(a), 975(b), 1060(b), 1062(a), 1142(a), 1161(a), 1166(b), 1188(a), 1198(b), 1250(a), 1281(b), 1301(a), 1307(b), 1317(a), 1321(b), 1343(a), 1360(b), 1369(a), 1393(b), 1400(a), 1413(b), 1452(a), 1464(b), 1476(a), 1514(b), 1476(a), 1609(b), 1616(a)

^{a)} Detailed symmetry assignments are not given for this C_{10h} isomer. However, the degenerate representations are denoted as (e).

Table 3
Relative energies (eV) for the isomers of C_{20}

Structure	Symmetry	HF	LDA	B-LYP/HF	B-LYP
ring	C_{10h}	0.0	3.84	0.0	0.0
bowl	C_{2v}	1.35	1.01	0.61	1.07
cage	C_2	4.03	0.0	3.81	3.44

^{a)} The 6-31G* basis set used with optimized HF/6-31G* geometries.

shown previously [3], electron correlation effects evaluated with the MP2 method favor the cage relative to the ring by about 8 eV making the cage the ground state at the MP2 level. Overall, the LDA method appears to behave somewhat similar to MP2. Thus, as shown by Brabec et al. [5], the cage is also the most stable form at the LDA level. Our calculated LDA energy differences between the isomers (1.01 and 3.84 eV) are somewhat larger than the values obtained by Brabec et al. [5] (0.75 and 2.65 eV) and may be partly due to the use of different geometries.

Dramatically different results are obtained when the gradient corrections are included. Gradient corrections stabilize the ring by 7.28 eV (168 kcal/mol) relative to the cage at the B-LYP level and by a slightly larger amount (7.65 eV) at the hybrid B-LYP/HF level. The ring is now more stable than the cage by 3.44 eV at the B-LYP level. The bowl is intermediate in stability between the ring and the cage at all levels of theory. At the B-LYP and B-LYP/HF

levels, the energy difference between the ring and the bowl is comparatively smaller. Overall, B-LYP reverses the findings of the LDA method and the final B-LYP energy differences are quite close to those seen at the HF level of theory.

We have evaluated the effect of higher temperatures on the energy difference between the isomers. As suggested by Brabec et al. [5], the lowering of the free energy of the isomers at higher temperatures is in the sequence ring > bowl > cage. Entropic factors favor the ring due to the presence of many low-frequency vibrational modes in the ring relative to the other isomers. Using the HF/6-31G* vibrational frequencies scaled by a factor of 0.89 to take into account the systematic overestimation of the frequencies, we calculate that temperature effects stabilize the ring relative to the cage by 0.5 eV at 298 K and by 2.0 eV at 1000 K. As expected, the effect on the bowl lies in between the ring and the cage.

In order to compare our results with experimental measurements, which are usually carried out on

Table 4
Relative energies (eV) for the positive ions of C₂₀^{a)}

Structure	HF	LDA	B-LYP/HF
ring	0.0	2.87	0.0
bowl	3.69	2.20	2.77
cage	2.33	0.0	3.49

^{a)} The 6-31G* basis set used with optimized HF/6-31G* geometries.

charged clusters, we have also carried out LDA and B-LYP/HF calculations on the positive ions of C₂₀ and the results are summarized in table 4. Comparison of tables 3 and 4 clearly shows that there are major quantitative changes between the neutrals and positive ions. However, the qualitative picture remains the same, viz. the ring is most stable at the HF and B-LYP levels of theory while the cage is most stable with the LDA method.

These results have profound implications for the applications of density functional methods in general and for the study of carbon clusters in particular. The dramatic difference between the LDA and B-LYP methods shows clearly that one of the two is completely in error. Since the ring isomer is seen predominantly in experimental studies [7], it appears likely that it is the ground state of C₂₀ suggesting that the gradient corrected results are qualitatively correct. Though LDA appears to agree with the MP2 results, the reliability of MP2 theory in this case is uncertain since it is well known that perturbation theory tends to exhibit oscillatory behaviour in many cases. It should also be noted that the number of carbon-carbon bonds in the ring, bowl, and cage isomers is 20, 25, and 30, respectively. Thus, given that LDA overestimates bond energies, it is not surprising to find that LDA favors the cage isomer. It would be interesting to perform geometry optimizations with the B-LYP method, although we deem it unlikely that our qualitative conclusions would be changed. High quality quantum-chemical calculations (such as the infinite-order CCSD(T) results) [20,21] on the three isomers are not yet available to calibrate these calculations. It is clear that if LDA and B-LYP give qualitatively different results, one should be very careful in drawing final conclusions. The performance of these methods has to be assessed in other situations where such completely different structural energy differences are important.

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References

- [1] W. Krätschmer, L.D. Lamb, K. Fostiropoulos and D.R. Huffman, *Nature* 347 (1990) 354.
- [2] T. Guo, M.D. Diener, Y. Chai, M.J. Alford, R.E. Haufler, S.M. McClure, T. Ohno, J.H. Weaver, G.E. Scuseria and R.E. Smalley, *Science* 257 (1992) 1661.
- [3] V. Parasuk and J. Almlöf, *Chem. Phys. Letters* 184 (1991) 187.
- [4] M. Feyereisen, M. Gutowski, J. Simons and J. Almlöf, *J. Chem. Phys.* 96 (1992) 2926.
- [5] C.J. Brabec, E.B. Anderson, B.N. Davidson, S.A. Kajihara, Q.-M. Zhang, J. Bernholc, and D. Tomanek, *Phys. Rev. B* 46 (1992) 7326.
- [6] L.A. Paquette, R.J. Ternansky, D.W. Balogh and G.J. Kentgen, *J. Am. Chem. Soc.* 105 (1983) 5446.
- [7] G. von Helden, M.T. Hsu, N.G. Gotts, P.R. Kemper and M.T. Bowers, *Chem. Phys. Letters* 204 (1993) 15.
- [8] Z. Slanina and L. Adamowicz, *Fullerene Sci. Tech.* 1 (1993) 1.
- [9] A.D. Becke, *J. Chem. Phys.* 96 (1992) 2155; 97 (1992) 9173; 98 (1993) 1372.
- [10] B.G. Johnson, P.M.W. Gill and J.A. Pople, *J. Chem. Phys.* 97 (1992) 7846; 98 (1993) 5612.
- [11] W.J. Hehre, L. Radom, P. von R. Schleyer and J.A. Pople, *Ab initio molecular orbital theory* (Wiley, New York, 1986).
- [12] W. Kohn and L. Sham, *Phys. Rev. A* 140 (1965) 1133.
- [13] A.D. Becke, *Phys. Rev. A* 38 (1988) 3098.
- [14] C. Lee, W. Yang and R.G. Parr, *Phys. Rev. B* 37 (1988) 785.
- [15] P.M.W. Gill, B.G. Johnson, J.A. Pople and M.J. Frisch, *Intern. J. Quant. Chem. Symp.* 26 (1992) 319; *Chem. Phys. Letters* 197 (1992) 499.
- [16] G.E. Scuseria, *J. Chem. Phys.* 97 (1992) 7528.
- [17] C.W. Murray, N.C. Handy and G.J. Lamming, *Mol. Phys.* 78 (1993) 997.
- [18] M.J. Frisch, G.W. Trucks, M. Head-Gordon, P.M.W. Gill, M.W. Wong, J.B. Foresman, B.G. Johnson, H.B. Schlegel, M.A. Robb, E.S. Replogle, R. Gomperts, J.L. Andres, K. Raghavachari, J.S. Binkley, C. Gonzalez, R.L. Martin, J.D. Fox, D.J. Defrees, J. Baker, J.J.P. Stewart and J.A. Pople, *GAUSSIAN 92 Computer Program* (Gaussian, Inc., Pittsburgh, PA, 1992).
- [19] K. Raghavachari, J.A. Pople, B.G. Johnson and P.M.W. Gill, to be published.
- [20] K. Raghavachari, *Ann. Rev. Phys. Chem.* 42 (1991) 615.
- [21] K. Raghavachari, G.W. Trucks, J.A. Pople and M. Head-Gordon, 157 (1989) 479.