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Conformational Study of the Structure of Free 12-Crown-4

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A conformational search at the MM3 level was performed for 12-crown-4 (12c4) whereby 180 conformations were predicted. To determine the lowest energy conformations and to get a more accurate energy order of the predicted conformations, geometry optimization was performed for the 180 conformations at the HF/STO-3G level and for the 100 lowest energy conformations, according to HF/STO-3G energy order, at the HF/4-31G and HF/6-31+G* levels. Some of the 100 conformations had equal energies at the three above-mentioned levels and consequently 37 conformations were excluded. Further computations were performed for the 20 lowest energy unique conformations, according to the MP2/6-31+G*//HF/6-31+G* energy order, at the B3LYP/6-31+G*, MP2/6-31+G*//B3LYP/6-31+G*, and MP2/6-31+G* levels. Good agreement was found between the energy order of the conformations at the MP2/6-31+G*//HF/6-31+G* and MP2/6-31+G*//B3LYP/6-31+G* levels and that at the MP2/6-31+G* level, the most accurate level considered in this work. The relative energies of the predicted conformations at the MP2/6-31+G*//B3LYP/6-31+G* level are close to those at the MP2/6-31+G* level, to within 0.1 kcal/mol at most. This is with the exception of only two conformations. This suggests that the cheaper MP2/6-31+G*//B3LYP/6-31+G* level may be used to determine the relative energy order of conformations of larger molecules where the MP2/6-31+G* computations are prohibitively expensive. The closeness of the MP2/6-31+G*//B3LYP/6-31+G* and MP2/6-31+G* relative energies is shown to be a reflection of the closeness of the B3LYP6-31+G* and MP26-31+G* optimized geometries. For the two conformations where the difference of the relative energies was larger than 0.1 kcal/mol, large differences between some of the B3LYP/6-31+G* and MP2/6-31+G* ring dihedral angles were found. The calculated results show that the correlation energy is necessary to obtain an accurate energy order of the predicted conformations. A rationalization of the energy order of some of the predicted conformations in terms of the CH···O interactions is given.

Introduction

Crown ethers are a very important class of molecules. They are cyclic molecules formed from $(CH_2CH_2O)_n$ groups. Crown ethers were first discovered, or rather became known, by Pedersen in 1967.[1,2] Their discovery led to the appearance of new fields in chemistry, such as molecular design[3] and supramolecular chemistry,[4] and new classes of molecules known as macrocyclic and macropolycyclic molecules.[5] Crown ethers have a quite broad range of applications. Biomedical diagnosis,[6] photochemistry,[7] chromatography,[8] treatment of nuclear waste[9] and liquid crystals[10] are only a few of the numerous applications of crown ethers. Many of the applications of crown ethers depend on their ability to bind to metal cations, especially alkali metal and alkaline earth metal cations.

Although crown ethers are such an important class of molecules, it is surprising that the number of studies of the structure and conformations of 12c4 at the ab initio level is quite limited and for only a small number of conformations.[13−22] Most of the previous studies were dependent on the conformational search by the molecular mechanics (MM) method with energies predicted at this level.[22−28] In 1991, Schaefer et al.[14] proposed a new S_4 conformation of 12c4. Computations at the HF level showed that this conformer is energetically more stable than the previously experimentally and theoretically known conformations of 12c4. Since the S_4 conformer is not as planar as the experimentally known C_i or C_4 conformations, it was rationalized that this conformer is not observed experimentally due to the crystal packing forces. Later, Hay et al.[26] performed an exhaustive conformational search of 12c4 using the MM3 method. The results of the 30 conformations within 7 kcal/mol above the lowest energy S_4 conformation were discussed. Bultinck et al.[22] conducted a similar MM3 conformational search and presented results of the 23 conformations within 6 kcal/mol above the lowest energy S_4 conformation. Optimized geometries and energies at the HF level of these 23 MM3 predicted conformations were also calculated. It was clear that some of the high-energy C_1 conformations predicted at the MM3 level could not be located at the HF level. Possible structures of 12c4 have also been proposed on a geometry basis.[29] Experimentally, C_4,[30−33] C_i,[34,35] and C_s[36] conformations were reported for free 12c4 or its cation metal complexes. An X-ray crystal study at −150 °C of free 12c4 showed that the molecule has a C_i structure.[35] A later NMR study at low temperature[37] showed evidence of rapid interconversion between different conformations but could not determine which conformation or conformations exist.

Proton affinity[38] and thermodynamic[39] calculations have been also reported for 12c4. Affinities toward cationic alkali metals have been determined both theoretically and experimentally.[40] Bond energies and the equilibrium structure of some of the 12c4 conformations with alkali metals have been determined both

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theoretically and experimentally.[15−21] The IR and Raman spectra of 12c4 have also been reported.[41]

12c4, or $(CH_2CH_2O)_4$ or 1,4,7,10-tetraoxacyclododecane, is one of the smallest and important crown ethers. The most important crown ether is $(CH_2CH_2O)_6$ or 1,4,7,10,13,16-hexaoxacyclooctadecane, known also as 18-crown-6 (18c6). Our main aim is the study of the vibrational spectra and binding properties of 18c6 with different metal cations. Since 18c6 is of large size and accurate ab initio calculations might require a significant amount of computations,[11,12] our attention was directed first to 12c4 since it is smaller and easier to study. Understanding the nature of complexes formed between 12c4 and different metal cations will facilitate the study of the larger 18c6 cation metal complexes. The first step to achieve this goal is the study of the possible conformations of free 12c4, which is the subject of the current report, and its cation metal complexes[42] at a suitable level of computations. Previous MM search of the possible conformations of free 12c4, due to the limitations of the conformational search method used, presented results for only a limited number of conformations and only at the HF level at the highest. Consequently, the subject of the current report is to perform a more detailed conformational search of free 12c4 and to calculate the energy of the predicted conformations at a more suitable level of theory through the inclusion of the correlation at the MP2 level and the use of the B3LYP functional of the DFT method.

Computations

Conformational search was performed at the MM3 level using the CONFLEX[43] method implemented in the CAChe program.[44] In this method, starting from a given initial structure, the program generates perturbed conformations. For this purpose, corner flap, edge flip, and stepwise rotation perturbation methods were used. In the corner flap, all corner ring atoms are flapped to the other side of the ring plane. In the edge flip, bonds connecting two ring atoms forming an edge are flipped. The perturbation step was followed by geometry optimization and storage of the generated conformations. Geometry optimization was done with the conjugate gradient optimization method. Before storage, the new conformations were compared with the conformations in the conformation storage and redundant conformations were excluded. In the comparison step, permute, reverse, and reflection options were used. The permutation option allows comparison for each shift of the order of the dihedral angles, whereas reflection removes mirror image conformations. These three options proved to be very useful in reducing the number of the predicted conformations of 12c4 from 1630 to 180. Each conformation in the conformation storage is considered as an initial structure and subjected to the perturbation step until all conformations in the conformation storage are exhausted. The conformational search step is followed by frequency calculation where conformations with imaginary vibrational frequencies are excluded.

In the conformational search steps just described, the total number of predicted conformations was 180 conformations after the exclusion of 542 conformations with imaginary vibrational frequencies. The number of conformations stored in the conformation storage and subjected to perturbation to generate other conformations was 171 conformations. The augmented CAChe MM3 force field was used in the calculations.

To determine the lowest energy conformations and to get a more accurate energy order of the predicted conformations, these 180 conformations were first geometry optimized at the HF/STO-3G level. The 100 lowest energy conformations of relative energies of less than 6.1 kcal/mol from the lowest energy S_4 conformation, Table 1, were geometry optimized at the HF/4-31G and HF/6-31+G* levels. It was found that some of these 100 conformations had equal energies at the three HF/STO-3G, HF/4-31G, and HF/6-31+G* levels. In addition, some had close MM3 steric energies. Consequently, 37 conformations were excluded. Energies were computed for the other 63 conformations at the MP2/6-31+G*//HF/6-31+G* level, and the 20 lowest energy unique conformations of relative energies of less than 10.5 kcal/mol, Table 1, were considered for computations at higher levels. These are the B3LYP/6-31+G*, MP2/6-31+G*//B3LYP/6-31+G*, and MP2/6-31+G* levels. Computations at these levels were also performed for the experimentally known C_4 conformation, although it had a higher relative energy, 7.85 kcal/mol at the MP2/6-31+G*//HF/6-31+G* level, than the other 20 lowest energy conformations. Geometry optimization at any given level was started from the MM3 geometry.

The additional diffuse function in the 6-31+G* basis set was used for possible future comparison with energies of the alkali and alkaline earth metal cation complexes where the diffuse function is necessary. The MP2 calculations were performed with the frozen core of the inner-shell electrons option and the full direct algorithm. The use of the frozen core option had a substantial CPU time saving for the CPU time demanding MP2 method at the expense of a small difference in the optimized geometries and energies.[45] It was reported that the neglect of the electron correlation of the core electrons produces a significant overestimation of the M−O bond lengths, where M is a metal cation, and underestimation of the bond energies.[12,46,47] Metal complexes are not the subject of the current publication and they will be dealt with in a separate report.[42] Also, the MP2 structures with and without the frozen core of the inner electrons are quite close[45] and, if necessary and if the computational time is reasonable, MP2 optimized geometries without the frozen core option can be calculated starting from the frozen core MP2 optimized geometries. The ab initio calculations were performed using the GAUSSIAN98[48] and GAUSSIAN03[49] programs. The default geometry optimization convergence parameters of the GAUSSIAN program were used in all of the ab initio computations.

Results and Discussion

The calculated energy differences between the 63 MM3 predicted conformations and the lowest energy S_4 conformation at the HF/STO-3G, HF/4-31G, HF/6-31+G*, and MP2/6-31+G*//HF/6-31+G* levels are presented in Table 1. For those conformations that converged to other conformations, the conformation number to which they converged to is given instead. The relative energies of the 20 lowest energy conformations, according to MP2/6-31+G*//HF/6-31+G* energy order, at the B3LYP/6-31+G*, MP2/6-31+G*//B3LYP/6-31+G*, and MP2/6-31+G* levels, are also given in Table 1. A conformational number, according to the HF/STO-3G energy order, and the point group are given to each conformation. A conformation description is also included in Table 1 for each of the 63 conformations according to the HF/STO-3G optimized geometry. For comparison, the conformation numbers of the 23 conformations predicted by Bultinck et al.[22] are also included in Table 1, except for conformations 18 and 22, where no HF/STO-3G energies were reported. In the following discussion, to differentiate between the conformations predicted in this work and those predicted in Bultinck et al.,[22] conformation numbers

TABLE 1: Energy Difference between the Calculated Energies and the Energy of the Lowest Energy S_4 Conformation, Conformation 1, in kcal/mol[a]

no.	sym.	HF		MP2/HF[b]		B3LYP	MP2/B3LYP[c]	MP2	(Bultinck et al.[22])[d]	Conformation description of the torsion angle[e]
		STO-3G	4-31G	6-31+ G*	6-31+G *	6-31+G*	6-31+G*	6-31+G*		
1	S_4	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1	0 + − 0 + − 0 + − 0 − +
2	C_i	1.77	4.73	1.71	2.48	1.43	2.66	2.61		0 − + 0 + + − + 0 0 − −
3	C_1	2	7.82	11.6	10.4					0 − + 0 + + − + 0 0 − −
4	C_1	2.30	1.78	1.04	2.28	1.20	2.43	2.48	7	+ − 0 0 + 0 0 − + − 0 0
5	C_1	2.46	5.76	2.50	3.13	1.99	3.04	3.01	3	− + 0 + − 0 − − 0 − − 0
6	C_1	5	7.60	6.26	6.60					− + 0 + − 0 − − 0 − − 0
7	C_1	5	4.97	11.34	10.5					− + 0 + − 0 − − 0 − − 0
8	C_1	2.68	3.57	2.65	2.67	2.02	2.83	2.89	10	+ − 0 0 + 0 + + − − 0 0
9	C_i	2.69	2	2					2	0 − − 0 − + 0 + + 0 + −
10	C_1	9	7.12	5.34	5.65	4.86	5.29	5.30		0 − − 0 − + 0 + + 0 + −
11	C_1	2.78	5.29	2.48	3.22	1.83	3.35	3.43	9	0 − + 0 + + − + 0 + + 0
12	C_1	11	10	10						0 − + 0 + + − + 0 + + 0
13	C_1	3.21	6.22	5.50	5.31	4.74	5.33	5.24		0 − + − 0 0 + − 0 − − −
14	C_1	3.22	5.51	4.40	3.82	3.52	4.43	4.38	13	− + + 0 + + − + 0 + + −
15	C_1	3.31	5	2.41	3.47	1.97	6.90	ftc[f]	4	+ + 0 + + 0 + − 0 0 + 0
16	C_1	3.61	7.05	3.62	4.86	3.00	5.07	5.16	12	0 + + − − 0 0 + − 0 − +
17	C_1	17	4	4						0 + + − − 0 0 + − 0 − +
18	C_1	3.74	11	11						0 − + − + + 0 + − + + 0
19	C_s	3.79	9.00	3.03	4.36	2.89	4.69	4.65	5	0 − − 0 − 0 0 + 0 + + 0
20	C_1	3.86	10.51	6.42	6.13					− + 0 + + + 0 + + − + 0
21	D_2d	3.88	7.46	ftc[f]					11	0 + 0 0 − 0 0 + 0 0 − 0
22	C_2	21	1	2.87	5.66					− 0 0 0 − + − 0 0 0 − +
23	C_1	4.05	8.15	5.71	5.78				20	+ + 0 + + 0 0 − + 0 0 −
24	C_1	23	14	4.51	4.46	3.80	4.64	4.63		+ + 0 + + 0 0 − + 0 0 −
25	C_1	23	11.52	9.87	9.41					+ + 0 + + 0 0 − + 0 0 −
26	C_1	4.16	7.63	19						0 − − + 0 + − + + 0 + −
27	C_1	4.25	6.63	6.12	5.15	4.75	5.42	5.17	14	− + + 0 + 0 + + − − 0 −
28	C_1	4.25	8.49	7.58	6.78					+ − − 0 0 + − + 0 0 − +
29	C_1	28	5.71	6.10		ftc[f]		ftc[f]		0 + − + 0 0 − + + − − 0
30	C_1	28	28	29	5.50	6.39	7.94	6.81		0 + − + 0 0 − + + − − 0
31	C_2	4.35	8.54	6.23	5.54	5.32	5.61	5.54		+ + − + 0 + − + + 0 + 0
32	C_1	4.38	8.29	5.34	5.87				19	0 − − 0 − − 0 0 + − + 0
33	C_1	4.47	6.34	4.73	3.84	4.25	5.59	5.64	16	+ + 0 + − 0 − − + + − −
34	C_1	4.48	33	33						+ − 0 0 + + − − + + − −
35	C_1	4.53	7.08	5.03	4.95	4.30	5.08	5.07	15	0 + − − 0 0 + + 0 + − 0
36	C_1	4.54	26	19						0 − − 0 − + 0 0 − + + 0
37	C_1	36	7.18	19						0 − − 0 − + 0 0 − + + 0
38	C_1	4.54	9.28	6.63	6.87					0 − − 0 − + 0 0 − + + 0
39	C_1	4.71	10	10					21	− − 0 − + 0 + + − 0 0 +
40	C_1	4.72	10.65	7.05	6.59					+ + + 0 + + − − + − + 0
41	C_2	4.76	4.40	3.91	3.88	3.29	3.98	4.05		− − + − 0 − + − − 0 − 0
42	C_1	4.76	7	24					17	− + + 0 + 0 0 − + + 0 +
43	C_1	4.89	8.14	7.68	6.25					+ + + 0 + − + 0 + + − −
44	C_1	4.89	7.76	16					8	+ − 0 0 + − 0 − − + + 0
45	C_1	4.91	8.09	7.62	7.22					0 0 + − + 0 + − 0 − − −
46	C_2	4.93	6.15	6.37	5.90					+ 0 + + − 0 0 + − 0 − +
47	C_1	5.09	9.80	6.23	5.54	5.18	5.70	5.62		− − − 0 − + 0 + + 0 + +
48	C_1	5.14	48	6.30	6.31					0 − + + 0 0 − + 0 + + 0
49	C_1	48	9.40	37						0 − + + 0 0 − + 0 + + 0
50	C_1	5.20	44	16						− − + − + 0 0 − + − + 0
51	C_1	5.28	7	24						0 − − + − 0 − + − − 0 −
52	C_1	51	8.53	48						0 + − + − 0 + + − + − 0
53	C_4	5.38	15.05	6.95	7.85	5.65	8.07	8.22	6	0 + − − + + 0 0 − − + 0
54	C_1	5.54	8.29	8.41	6.79					+ 0 0 0 + − 0 − 0 0 − +
55	C_1	5.63	7.84	6.75	6.91					− − − 0 0 − + − − + − 0
56	C_1	5.65	10.02	9.86	8.56					− − − 0 − − + − 0 − − 0
57	C_i	5.74	10.51	7.89	7.64					− − − 0 − − + − 0 − − 0
58	C_1	5.77	10.96	8.26	7.93					− 0 − − + + 0 + + 0 + +
59	C_1	5.78	9.70	8.72	6.76					0 + + − − − + + − − + 0
60	C_1	5.79	7.97	7.49	6.80					− 0 − + − 0 0 + − − 0 −
61	C_1	5.92	4	4						− 0 − − − 0 − + 0 0 − +
62	C_1	6.00	7	24						+ + − + 0 + + − 0 0 + 0
63		6.08	5	5						
MAD[g]		0.98 ± 0.70	0.2.18 ± 1.66	0.68 ± 0.54	0.34 ± 0.54 0.20 ± 0.14[h]	1.02 ± 0.64	0.13 ± 0.25 0.06 ± 0.04[i]			

[a] For conformation **1**, the energy at the HF/STO-3G level is −603.964 55, at the HF/4-31G level it is −610.751 65, at the HF/6-31+G* level it is −611.663 09, at the MP2/6-31+G*//HF/6-31+G* level it is −613.426 456 9, at the B3LYP/6-31+G* level it is −615.340 54, at the MP2/6-31+G*//B3LYP /6-31+G* level it is −613.432 16, and at the MP2/6-31+G* level it is −613.433 522 5. The number given instead of the energy difference is the conformation number to which conformations converge. [b] MP2/6-31+G* relative energy at the HF/6-31+G* optimized geometry, or MP2/6-31+G*//HF/6-31+G* relative energy. [c] MP2/6-31+G* relative energy at the B3LYP/6-31+G* optimized geometry, or MP2/6-31+G*//B3LYP/6-31+G* relative energy. [d] Conformation number assigned in Bultinck et al.[22] Qualitative description of the torsion angles of the four C−O−C−C−O−C groups based on the HF/STO-3G geometry. Angles between 0 and $2/3\pi$ are designated as (+), angles between 0 and $-2/3\pi$ are designated as (−), and angles between $2/3\pi$ and $4/3\pi$ are designated as (0). [f] Failed to converge. [g] Mean absolute deviation of the relative energies compared to the MP2/6-31+G* relative energies of the 20 lowest conformations, according to the MP2/6-31+G*//HF/6-31+G* energy order and the C_4 conformation. See text. [h] Excluding conformations **30** and **33**. [i] Excluding conformations **27** and **30**.

of the former will be typed in bold face. Also, since Bultinck et al.,[22] and Hay et al.[26] will be mentioned quite frequently, these two references will be referred to as BGV and HRZW, respectively.

Several observations can be made about the data in Table 1 in comparison to those previously reported by BGV and HRZW. Since the strain energy is not calculated by the CAChe program and in the HRZW report only MM3 strain energy is reported, comparison between the conformations predicted in this work and the 30 conformations reported by HRZW is not possible. BGV reported HF/STO-3G energy differences, in addition to MM3 strain energy differences between each of the 23 predicted conformations and the lowest energy S_4 conformation. It is possible then to compare these conformations with those predicted in this work. Notice that the 23 conformations predicted by BGV are the same as the first 23 conformations predicted by HRZW with only one exception, which will be mentioned shortly. From this comparison, it is apparent that all conformations predicted by BGV at the HF/STO-3G level were located in the current work, which is a support of the conformational search methodology implemented in the CAChe program. This is with the exception of conformations 18 and 22 in the BGV work, where no HF/STO-3G relative energies were reported, prohibiting allocating these conformations to the same conformations predicted in the current publication. It is interesting to notice that in this report where a thorough conformational search was preformed, no conformation of lower energy than the known S_4 conformation, conformation **1**, could be located. In the BGV work, computations were also performed at the HF/3-21G and HF/6-31G** levels, with basis sets that are different from those used in the current report. Consequently, further comparison is not possible. The only difference between the BGV and HRZW assignments is that in the BGV assignment, conformation 8 is assigned a C_s symmetry and conformation 10 is assigned a C_1 symmetry. In the HRZW assignment, the symmetry of these two conformations is reversed. Clearly, the data in Table 1 support the HRZW assignment.

On the other hand, it can be noticed from the data in Table 1 that, although most of the low energy conformations, according to the HF/STO-3G energy order, of 12c4 were predicted by BGV, some of the low energy conformations, such as conformations **3**, **6**, **7**, **10**, and **13**, were not predicted. In fact, conformations **10** and **13** are two of the 20 lowest energy conformations, according to the MP2/6-31+G*//HF/6-31+G* energy order. Notice that there are two conformations in the BGV work for which no minima could be located at the HF/STO-3G level. Comparison of the description of the torsion angles of these two conformations with those predicted in the current work, at either the MM3 or HF/STO-3G levels, could not conclude that any of these two conformations correspond to any of the conformations mentioned above. In fact, conformations **10** and **13** had a high MM3 steric energy and probably were not considered in the BGV report since they considered only conformation with strain energy higher by 6.0 kcal/mol from the lowest energy conformation. This indicates the necessity of performing a thorough conformational search, taking into consideration the energy order at the HF/STO-3G level and addition of the correlation energy, to have an accurate prediction of the energy order. Notice that conformation 2 in the BGV work corresponds to conformation **9** in the current publication and converges, at the HF/4-31G and HF/6-31+G* levels, to the experimentally known conformation **2**. Notice also that problems with locating minima at different levels were also observed by BGV and Feller et al.[16]

The work presented in this publication is characterized by a significantly large number of conformations of 12c4 considered, and at high levels of theory as well. It is rational, then, to compare the performance of the different computational methods used. It should be mentioned first that, although the B3LYP method scales formally as N^4 (N^2 for large molecules), where N is the number of basis functions, and the MP2 method scales as N^5, geometry optimization at both levels required practically almost the same computational time. This is due to the faster convergence of the MP2 method, or rather the lower number of geometry optimization steps to meet the geometry optimization criteria, than the B3LYP method.

An examination of relative energies in Table 1 shows that the 20 conformations for which computations were performed at the MP2/6-31+G* level are among the lowest energy conformations at all levels. The agreement is the worst at the lower HF/STO-3G and HF/4-31G levels. Also, the magnitude of the relative energies is comparable at all levels, except at the HF/4-31G level where the magnitude of the relative energies is larger. This was also reported by BGV at the HF/3-21G level.[22]

Since energies predicted at the MP2/6-31+G* level are expected to be more accurate than all other levels used in this work, it is reasonable to judge the performance of other methods relative to this method. To facilitate this comparison, the mean absolute deviations (MADs) of the difference of the relative energies at any level and that at the MP2/6-31+G* level for the 20 lowest energy conformations, according to the MP2/6-31+G*//HF/6-31+G* energy order, in addition to the C_4 conformation, were calculated and appended in Table 1. Since it was not certain how to calculate the differences between the relative energies of conformations converging to others, these were excluded in the calculation of the MADs. Conformation **1** was also excluded, since it is the reference conformation in the calculation of the relative energies. Consequently, 19 conformations were considered at all levels except at the HF/STO-3G level, where 16 conformations were considered; at the HF/3-21G level 17 conformations were considered and at the HF/6-31+G* level 18 conformations were considered. The calculated MADs are 0.98 ± 0.70 at the HF/STO-3G level, 2.18 ± 1.66 at the HF/3-21G level, 0.68 ± 0.54 at the HF/6-31+G* level, 0.34 ± 0.54 (0.20 ± 0.14 excluding conformations **30** and **33**) at the MP2/6-31+G*//HF/6-31+G* level, 1.02 ± 0.64 at the B3LYP/6-31+G*level, and 0.13 ± 0.25 (0.06 ± 0.04 excluding conformations **27** and **30**) at the MP2/6-31+G*//B3LYP/6-31+G* level. These data show that the relative energies, in addition to the energy order, at the MP2/6-31+G*//B3LYP/6-31+G* level are the closest to that at the MP2/6-31+G* level, followed by that at the MP2/6-31+G*//HF/6-31+G* level, with the performance of both levels quite close.

Notice that the magnitude of the relative energies at the MP2/6-31+G*//B3LYP/6-31+G* level is quite close to that at the MP2/6-31+G* level, to less than 0.1 kcal/mol. This is with the exception of conformations **27** and **30** where the differences are 0.25 and 1.13 kcal/mol, respectively. This is a quite important observation, since for larger molecules such as 18c6 where the MP2/6-31+G* calculations are prohibitively expensive, especially for conformations with C_1 symmetry, the affordable MP2/6-31+G*//B3LYP/6-31+G* level can be used instead. It can be assumed that the closeness of the relative energies at the MP2/6-31+G* and MP2/6-31+G*//B3LYP/6-31+G* levels is a reflection of the closeness of the MP2/6-31+G* and B3LYP/6-31+G* geometries, but not for

TABLE 2: Ring Dihedral Angles of Some Conformations of 12c4[a]

conformation coordinate	method[b]	**1** S_4	**2** C_i	**4** C_1	**5** C_1	**19** C_s	**27** C_1	**30** C_1	**53** C_4
$C_{12}O_1C_2C_3$	HF	96.8	−102.3	118.1	156.0	160.1	−143.1	77.0	161.7
	B3LYP	92.3	−97.2	111.3	156.0	159.7	−140.8	66.9	161.1
	MP2	92.2	−97.1	110.5	152.8	162.6	−130.6	71.3	162.8
$O_1C_2C_3O_4$	HF	−70.9	72.2	−170.8	−68.0	−71.0	74.0	−78.0	−62.0
	B3LYP	−73.1	75.3	−173.7	−70.1	−72.8	77.1	−89.9	−63.5
	MP2	−72.5	74.0	−176.2	−70.7	−72.1	75.4	−79.7	−62.5
$C_2C_3O_4C_5$	HF	157.2	−152.3	149.5	−83.8	133.2	−135.0	−99.4	−77.2
	B3LYP	155.9	−153.7	152.9	−82.0	131.2	−155.0	−85.2	−75.1
	MP2	157.3	−153.2	155.6	−84.4	130.0	−166.5	−75.6	−76.3
$C_3O_4C_5C_6$	HF		91.7	−87.2	155.2	−71.8	89.2	110.3	
	B3LYP		90.0	−84.6	149.7	−69.8	87.0	159.7	
	MP2		91.2	−86.8	152.4	−69.1	88.5	169.4	
$O_4C_5C_6O_7$	HF		73.0	70.6	−67.3	−62.4	78.0	−78.4	
	B3LYP		76.2	73.5	68.9	−63.7	78.9	−103.4	
	MP2		79.9	72.3	−68.6	−63.2	79.6	−141.6	
$C_5C_6O_7C_8$	HF		−163.2	−150.6	−81.7	159.8	60.6	158.0	
	B3LYP		−159.6	−147.9	−81.4	159.4	−61.6	120.3	
	MP2		−163.3	−147.1	−80.9	162.7	−55.4	104.4	
$C_6O_7C_8C_9$	HF			149.8	154.7		−71.2	−103.7	
	B3LYP			145.5	157.5		−70.6	−101.1	
	MP2			149.2	158.5		−65.6	−74.5	
$O_7C_8C_9O_{10}$	HF			−68.6	−67.1		174.2	58.1	
	B3LYP			−70.4	−65.7		175.8	64.4	
	MP2			−71.1	−65.9		177.3	64.2	
$C_8C_9O_{10}C_{11}$	HF			160.2	114.5		−76.8	−161.9	
	B3LYP			160.1	104.2		−77.1	177.0	
	MP2			159.3	100.0		−83.0	161.6	
$C_9O_{10}C_{11}C_{12}$	HF			−170.6	−168.6		−67.9	130.1	
	B3LYP			−171.6	−167.3		−70.1	170.9	
	MP2			−174.4	−171.3		−76.8	174.5	
$O_{10}C_{11}C_{12}O_1$	HF			70.2	78.1		77.7	−88.9	
	B3LYP			72.5	82.4		77.9	−91.9	
	MP2			73.2	86.4		77.8	−95.4	
$C_{11}C_{12}O_1C_2$	HF			−80.3	−88.3		86.0	70.6	
	B3LYP			−78.6	−81.6		84.6	64.8	
	MP2			−76.2	−77.6		81.3	60.6	

[a] Bond lengths in Å and angles in degrees. [b] Optimized geometries at the HF, B3LYP, and MP2 levels using the 6-31+G* basis set.

conformations **27** and **30**. Notice that conformation **30** has the largest difference between the MP2/6-31+G*//B3LYP/6-31+G* and MP2/6-31+G* relative energies. To further clarify this point, the ring dihedral angles of conformations **1**, **2**, **4**, **5**, **19**, **27**, **30**, and **53** are given in Table 2. A clear feature in Table 2 is the difference between the B3LYP and MP2 dihedral angles of coordinates $O_4C_5C_6O_7$, $C_5C_6O_7C_8$ and $C_6O_7C_8C_9$ of conformation **30**. While the B3LYP and MP2 dihedral angles differ by not more than 5° for the other conformations, the difference is as high as about 40° for the $O_4C_5C_6O_7$ angle of conformation **30**. Interestingly, conformation **30** converges to conformation **28** at the HF/STO-3G and HF/4-31G levels and to conformation **29** at the HF/6-31+G* level, for which convergence could not be achieved even after restarting the computations at either the B3LYP or MP2 levels. For conformation **27**, the B3LYP and MP2 dihedral angles of coordinates $C_{12}O_1C_2C_3$ and $C_2C_3O_4C_5$ differ by about 10°. Consequently, it has a smaller difference between the MP2/6-31+G* and MP2/6-31+G*//B3LYP/6-31+G* relative energies than conformation **30** but higher than the other conformations. It is worth mentioning that the bond lengths and angles of conformations **27** and **30** showed no abnormalities compared to those of the other conformations given in Table 2.

On the other hand, the magnitude of the difference of the relative energies at the MP2/6-31+G* and MP2/6-31+G*//HF/6-31+G* levels is as high as 0.56 kcal/mol for conformation **14**. This is with the exception of conformations **30** and **33**, where the differences are unusually high, 1.31 and 1.80 kcal/mol, respectively. The performance of the B3LYP/6-31+G* and HF/6-31+G* levels, compared to that at the MP2/6-31+G* level, is quite close to each other, with the performance at the B3LYP/6-31+G* level only slightly better, but both are worse than that at the MP2/6-31+G*//HF/6-31+G* or MP2/6-31+G*//B3LYP/6-31+G* levels. Those predicted at the HF/STO-3G, HF/4-31G, and HF/6-31+G* levels are the worst but are in good qualitative agreement with that at the MP2/6-31+G* level. BGV concluded that, and in agreement with what was also concluded by Anderson et al.,[50] based on MP2/6-31G**//HF/6-31G** energies the MP2 energy does not substantially influence the energy order of the different minima. The data in Table 1 and the above discussion clearly do not support this conclusion. Addition of a polarization function on the hydrogen atoms as presented by the HF/6-31G** results reported by BGV did not have a significant improvement of the energy order compared to that at the MP2/6-31+G* level over that at the HF/6-31+G* level.

It is noticed from Table 1 that the trend of conformations to converge to other conformations increases as the conformational relative energies increase. Notice also that not only conformations with the C_1 symmetry converged to other conformations; conformations of higher symmetry did also. For example, conformation **9** of C_i symmetry converged to conformation **2** of the same symmetry, and conformation **22** of C_2 symmetry converged to conformation **1** of S_4 symmetry.

It is known that optimized geometries calculated at the B3LYP and MP2 levels are of high accuracy compared to those predicted at the HF level. Johnson et al.[51] reported that, compared to the experimental bond lengths, bond lengths

TABLE 3: CH···O Distances, in angstroms, of Less than 3.00 Å for Six and Seven-Membered Rings of Some Selected Conformations of 12c4[a]

conf. no.[b]	MM3	HF/6-31+G*	B3LYP/6-31+G*	MP2/6-31+G*
1	2.45 (4)	2.5 (4)	2.50 (4)	2.39 (4)
2	2.47 (2)	2.6 (2)	2.63 (2)	2.51 (2)
4	2.33	2.38	2.35	2.28
	2.57	2.55	2.58	2.51
	2.70	2.72	2.64	2.51
5	2.45	2.50	2.42	2.34
	2.60	2.90	2.68	2.47
8	2.39	2.42	2.43	2.36
	2.57	2.56	2.52	2.45
	2.89	2.68	2.70	2.60
33	2.41	2.51	2.51	2.4
	2.51	2.52	2.52	2.45
	2.53	2.58	2.57	2.47
		2.71	2.70	2.53
53	–	–	–	–

[a] Number in parentheses is the number of these interactions due to symmetry. [b] Conformation number.

determined at the HF level are underestimated by 0.011 Å and those determined at the MP2 level are overestimated by 0.010 Å. Previous results for furan and thiophene concluded that the B3LYP optimized geometries, compared to the experimental geometries, are slightly better than those predicted at the MP2 level.[45] The only known experimental geometry of free 12c4 is for the C_i conformation determined by X-ray for the solid phase at −150 °C. This conformation corresponds to conformation **2** in the current study. The calculated geometries at the three HF, B3LYP, and MP2 levels using the 6-31+G* basis set are in good qualitative agreement with the experimental geometry of this conformation. The C−O bond lengths are calculated to be within a few tenths of an angstrom at the MP2 and B3LYP levels and 0.3 Å too short at the HF level. The C−C bond lengths are predicted to be 0.1 and 0.2 Å too short at the MP2 and B3LYP levels, respectively, and 0.1 Å too long at the HF level. The bond angles and dihedral angles are predicted with a difference of 2° in most of the cases, at the three MP2, B3LYP, and HF levels. The same observations can be made about the C_s and C_4 conformations, conformations **19** and **53**, respectively, except that the available experimental data are for the cation metal complexes rather than free 12c4.

It is important to discuss how the CH···O interactions may affect the energy order of the conformations at any level of theory. These interactions were considered in detail for 12c4[22] and similar molecules by Bultinck et al.[52,53] It was pointed out that there is some degree of uncertainty for whether the 1,5-CH···O interaction is one of the factors that determines the conformational stability and structure.[22] To further investigate this point, the CH···O distances of less than 3.00 Å of the possible six- and seven-membered rings for the five lowest energy conformations, according to the MP2/6-31+G* energy order, in addition to some selected conformations of 12c4, are depicted in Table 3. It is interesting to notice that the CH···O distances increase on going from the MM3 level to the HF/6-31+G* level. At the B3LYP/6-31+G* level, they are slightly shorter by a few tenths of an angstrom than that at the HF/6-31+G* level and shorter at the MP2/6-31+G* level by 0.1−0.2 Å in most of the cases. The difference in the CH···O distances at the MM3, HF, and MP2 levels can be rationalized by noting that these weak interactions are not well parameterized in the MM3 method compared to that at the HF level and the inclusion of the electron correlation at the MP2 level.

It is clear from the data in Table 3 that the lowest energy S_4 conformation has the highest number of the CH···O interactions at relatively short distances of only 2.5 Å, rationalizing that it is the lowest energy conformation. On the other hand, these interactions are almost absent for conformation **53**, which may rationalize its high energy at the ab initio level, although it has a low relative energy at the MM3 level. Also, for conformations **2** and **4**, the former has lower energy at the MM3 level while the later has lower energy at the HF level. While the CH···O distances of the later remained almost the same at the MM3 and ab initio levels, that of the former increased by about 0.2 Å, in agreement with the increase of the relative energy of conformation **2** compared to that of conformation **4**. On the other hand, conformation **33** has four of the CH···O interactions at distances that are comparable to those of conformation **8**, but its energy is higher by about 1.8 kcal/mol at the MP2/6-31+G* level. It can be concluded from the former discussion that the CH···O interactions play an important role in the stabilization of some conformations, but it is natural to assume that other factors also affect the conformational stablility.[22]

Conclusion

In the current report, a thorough conformational search of 12c4 was performed and more conformations of 12c4 were considered at higher levels of theory than those reported before.[13−28] The predicted conformations were correlated to the previously known conformations of 12c4 where comparable energies are available. It was found that some of the conformations with a high MM3 steric energy order had a low energy order at the correlated MP2/6-31+G*//B3LYP/6-31+G* and MP2/6-31+G*//HF/6-31+G* levels. This shows the success of the methodology of the conformational search method used in this report and the need to include the correlation energy to get a more accurate energy order of the predicted conformations. This is in fact contrary to earlier reports.[22,50]

It is also concluded that, with the exception of only two conformations, the relative energies of the conformations at the MP2/6-31+G*//B3LYP/6-31+G* and MP2/6-31+G* levels are quite close to each other, to within 0.1 kcal/mol at the highest. This was shown to be merely a reflection of the closeness of the MP2 and B3LYP optimized geometries. For the two excluded conformations, large differences, of as much as 40°, were found between some of the MP2 and B3LYP ring torsional angles. This is a quite significant observation, especially for molecules as large as 18c6 where the computations at the MP2/6-31+G* level are not practical with the present computational speed. A good agreement between the energy orders was obtained at the MP2/6-31+G*//HF/6-31+G* and MP2/6-31+G*//B3LYP/6-31+G* levels, and that at the MP2/6-31+G* level, the highest level of computations considered in this work. Also, a good qualitative agreement was obtained between the energy orders at the HF/STO-3G, HF/4-31G, and HF/6-31+G* levels and that at the MP2/6-31+G* level.

It is observed that the lowest energy S_4 conformation is stabilized by four of the CH···O interactions of distances of about 2.5 Å, which may rationalize its low energy. Other factors, such as the value of the dihedral angles, are important for the determination of the conformational energy order, as some of the high energy conformations also include these CH···O interactions.

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