Structural and Electronic Properties of an Azamacrocycle, $C_{26}H_{18}N_6$

K. Doll* and G. Zwicknagl

Institut fur Mathematische Physik, Tu Braunschweig, Mendelssohnstrasse 3, D-38106 Braunschweig, Germany

Received: February 27, 2001; In Final Form: July 2, 2001

We compute the structure of an azamacrocycle, $C_{26}H_{18}N_6$. Two approximatively planar elliptical structures with C_2 or C_i symmetry are found to be nearly degenerate. The roughly circular conformation observed in metal complexes turns out to be ∼0.6 eV higher in energy. We suggest that this difference is mainly due to electrostatic interactions. We discuss the results on various levels of theory (Hartree−Fock, local density, and gradient corrected density functional calculations).

Introduction

In recent years, the formation of metal complexes of macrocyclic ligands has become an important research field which is rapidly developing. The interest in this field originates from the possibility to build supramolecular architectures and thus to finally arrive at tailor-made materials with novel properties. The goal to design new materials with a combination of desired properties, however, requires a quantitative understanding of the properties of the individual units, their response to chemical substitutions, as well as their interactions. Of prime importance is to understand the molecular structure and the factors which determine it. The azamacrocycle, $C_{26}H_{18}N_6$, has been widely used as a ligand, for the formation of complexes with a wide variety of metals such as alkali metals,[1,2] lanthanides,[3,4] earth alkaline metals,[5] lead,[5] cadmium,[5,6] or yttrium.[4] In all of these metal complexes, the azamacrocycle is approximatively ring-like, with the metal ion bonding to the six nitrogen atoms. It was surprising, when the free ligand was synthesized and was found to be approximatively planar-elliptical.[7]

A full explanation of the difference of the two structures has not yet been given. However, modern codes and computers make ab initio calculations on the Hartree−Fock (HF) and density-functional level for these systems possible. We therefore investigated the different structures and their electronic properties. The main target of this article is a quantitative explanation of the relative stabilities of these structures. Thus, we optimized the geometry and computed the total energy, charge density, and the vibrational spectrum. In addition, we try to assess the overall validity of the methods and the approximations involved. We compare the results for HF and various density functional calculations to estimate the ambiguities introduced by the simplified description of electronic correlations. In the following section (II) we give details about the method. The results are presented in section III, and finally, we summarize the article in section IV.

Method

All of the calculations were done with the code Gaussian 98.[8] We employ the HF method, the local density approximation (LDA; with the correlation functional V from reference 9), and the gradient corrected hybrid functional B3LYP.[10] The bulk of the calculations was done with a 6-31G Gaussian basis set for C, H, and N atoms. Additional calculations with an enhanced 6-31G** basis set (i.e., with an additional *p*-polarization function for H and an additional *d*-polarization function for C and N) were performed to investigate the dependence of the results on the choice of the basis set. Because an optimization of the system in its crystal structure (monoclinic, space group $P2_1/C$) is presently prohibitive, we performed a calculation on the isolated molecule. The effects of this approximation will be discussed in section III. As a first step, a full geometry optimization with respect to all parameters and without symmetry was performed. Depending on the geometry at the beginning of the optimization process, the final optimized geometry turned out to be either C_2, C_i, or C_{2v} symmetric, the three minima considered in this article. To ensure the stability of the optimized structures, addition vibrational frequencies were calculated.

TABLE 1: Relative Energies, Computed with Respect to the Energy of the Structure with C_2 Symmetry, at Different Levels of Theory (1 E_h = 27.2114 eV)

		relative energy with respect to the structure with C_2 symmetry [E_h]	
method	basis set	structure with C_i symmetry	structure with C_{2v} symmetry
HF	6-31G	0.0003	0.043
HF	6-31G**	0.0009	0.026
LDA	6-31G	−0.0016	0.038
LDA	6-31G**	−0.0021	0.028
B3LYP	6-31G	−0.0008	0.033
B3LYP[a]	6-31G	−0.0008	0.031
B3LYP	6-31G**	−0.0016	0.022
B3LYP[a]	6-31G**	−0.0015	0.022

[a] With zero-point vibrations.

Results

The results of the calculations are summarized in Tables 1−4. First, we discuss the optimized geometries. The first calculated structure is visualized in Figure 1 using Molden.[11] This structure is approximatively planar-elliptical and has C_2 symmetry. Thus, it is the one which has the same symmetry as a single $C_{26}H_{18}N_6$ unit of the experimentally observed structure[7] (i.e., the inner hydrogens, 41 and 42 in Figure 1, are on the same face of the molecule). The second structure (structure 2) is also approximatively planar-elliptical but has C_i symmetry. In the view in Figure 1, it looks virtually identical as structure 1, and the

---

* To whom correspondence should be addressed. E-mail: k.doll@tu-bs.de.

10.1021/jp010736y CCC: $20.00

TABLE 2: Optimized Geometrical Parameters and Mulliken Populations, B3LYP, 6-31G** Basis Set, Approximatively Elliptical Structure (1) with C_2 Symmetry (i.e., simultaneously $x \rightarrow -x$ and $y \rightarrow -y$ Is a Symmetry Operation)[a]

atom number	type	x [Å]	y [Å]	z [Å]	charge $\lvert e \rvert$
1,4	N	0.352	−2.027	−0.144	−0.52
2,5	N	−3.187	−1.795	−0.022	−0.53
3,6	N	−2.939	1.147	0.275	−0.45
7,8	C	1.376	−2.890	−0.236	0.26
9,10	C	1.184	−4.269	−0.393	−0.11
11,12	C	−0.122	−4.765	−0.407	−0.06
13,14	C	−1.184	−3.877	−0.295	−0.09
15,16	C	−0.900	−2.504	−0.181	0.24
17,18	C	−1.948	−1.465	−0.114	0.12
19,20	C	−4.252	−0.889	0.112	0.24
21,22	C	−5.522	−1.494	0.104	−0.10
23,24	C	−6.692	−0.765	0.288	−0.09
25,26	C	−6.619	0.613	0.502	−0.10
27,28	C	−5.380	1.247	0.498	−0.11
29,30	C	−4.190	0.530	0.278	0.27
31,32	C	−2.738	2.313	−0.206	0.09
33,34	H	−5.315	2.312	0.696	0.09
35,36	H	−7.521	1.191	0.680	0.09
37,38	H	−7.653	−1.271	0.288	0.09
39,40	H	−5.549	−2.569	−0.035	0.10
41,42	H	−1.569	−0.443	−0.128	0.18
43,44	H	−2.218	−4.201	−0.307	0.12
45,46	H	−0.302	−5.831	−0.511	0.10
47,48	H	2.038	−4.935	−0.490	0.10
49,50	H	3.539	−2.923	−0.650	0.09

[a] Only positions of symmetry-unique atoms are given.

TABLE 3: Optimized Geometrical Parameters and Mulliken Populations, B3LYP, 6-31G** Basis Set, Approximatively Elliptical Structure (1) with C_i Symmetry (i.e., Simultaneously $x \rightarrow -x$, $y \rightarrow -y$ and $z \rightarrow -z$ Is a Symmetry Operation)[a]

atom number	type	x [Å]	y [Å]	z [Å]	charge $\lvert e \rvert$
1,4	N	0.309	−1.984	−0.414	−0.52
2,5	N	−3.220	−1.804	−0.122	−0.52
3,6	N	−2.926	1.035	0.547	−0.45
7,8	C	1.343	−2.838	−0.326	0.26
9,10	C	1.166	−4.225	−0.214	−0.11
11,12	C	−0.132	−4.738	−0.200	−0.06
13,14	C	−1.204	−3.857	−0.261	−0.08
15,16	C	−0.934	−2.479	−0.360	0.23
17,18	C	−2.005	−1.461	−0.358	0.15
19,20	C	−4.283	−0.914	0.055	0.24
21,22	C	−5.564	−1.483	−0.073	−0.10
23,24	C	−6.721	−0.752	0.162	−0.09
25,26	C	−6.625	0.580	0.576	−0.10
27,28	C	−5.375	1.172	0.712	−0.10
29,30	C	−4.192	0.464	0.425	0.26
31,32	C	−2.702	2.263	0.269	0.09
33,34	H	−5.295	2.194	1.070	0.09
35,36	H	−7.520	1.151	0.805	0.09
37,38	H	−7.693	−1.224	0.056	0.09
39,40	H	−5.611	−2.531	−0.350	0.09
41,42	H	−1.657	−0.439	−0.508	0.15
43,44	H	−2.235	−4.189	−0.220	0.12
45,46	H	−0.299	−5.808	−0.125	0.10
47,48	H	2.028	−4.882	−0.139	0.09
49,50	H	3.490	−2.942	0.088	0.09

[a] Only positions of symmetry-unique atoms are given.

difference compared to structure 1 can better be seen in Figure 3. The alternative to these flat structures is the approximatively circular structure (structure 3) which is found to be another local minimum. We display the latter structure in Figure 2. This latter structure is saddle-like; in a view from the top it appears approximatively circular (Figure 2), and when viewing from the side, we note that there is a significant bending (Figure 3).

TABLE 4: Optimized Geometrical Parameters and Mulliken Populations, B3LYP, 6-31G Basis Set, C_{2v} Symmetric (i.e., $x \rightarrow -x$ or $y \rightarrow -y$ Are Symmetry Operators)**[a]

atom number	type	x [Å]	y [Å]	z [Å]	charge
1,2,3,4	C	−1.150	3.105	0.695	0.26
5,6,7,8	C	−1.198	4.323	1.398	−0.11
9,10	C	0.000	4.942	1.744	−0.06
11,12	N	0.000	2.518	0.343	−0.47
13,14,15,16	C	2.416	2.412	0.359	0.09
17,18,19,20	N	2.436	1.347	−0.342	−0.39
21,22,23,24	C	3.628	0.711	−0.685	0.22
25,26,27,28	C	4.789	1.395	−1.079	−0.10
29,30,31,32	C	5.930	0.698	−1.473	−0.09
33,34,35,36	H	2.153	4.764	1.665	0.09
37,38	H	0.000	5.885	2.283	0.10
39,40,41,42	H	3.329	2.863	0.780	0.07
43,44,45,46	H	4.771	2.480	−1.116	0.09
47,48,49,50	H	6.810	1.244	−1.799	0.08

[a] Only positions of symmetry-unique atoms are given.

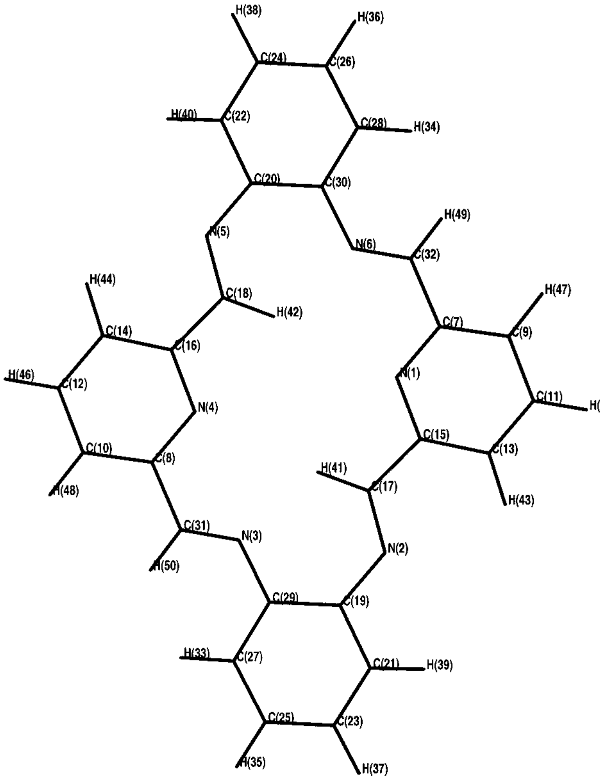


Figure 1. Optimized planar-elliptical structure with C_2 symmetry (structure 1). Structure 2 with C_i symmetry looks virtually identical in this view.

The energy differences of the structures on the HF, LDA, and B3LYP levels of theory are displayed in Table 1. We find that the saddle-like structure 3 is highest in energy at all levels of theory. HF gives the highest energy difference. This is reduced by LDA and even more by B3LYP. The calculation with the best basis set used in this article (6-31G**) gives an energy difference of 0.6 eV at the B3LYP level. Including zero-point vibrations hardly changes the energy difference, as the zero-point energy was found to be 0.384 E_h (1 E_h= 27.2114 eV) for structure 1 and 2 and 0.383 E_h for the saddle-like structure 3 (B3LYP, 6-31G** basis set). The computed vibrational frequencies were in the range from ~20 to ~3200 cm^{-1}. The energy difference is also consistent with earlier results based on molecular mechanics calculations,[2] where, depending on the approximations, an energy difference in the region from ~0 to 0.7 eV was obtained. Comparing the

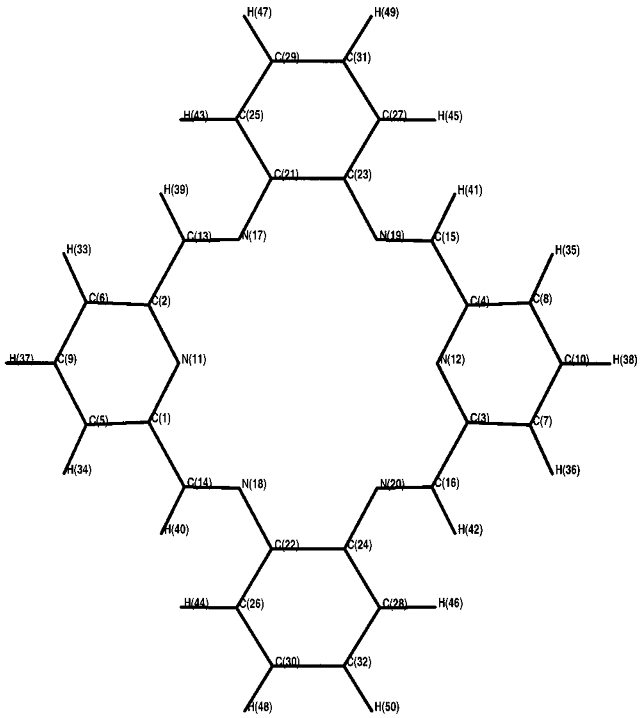
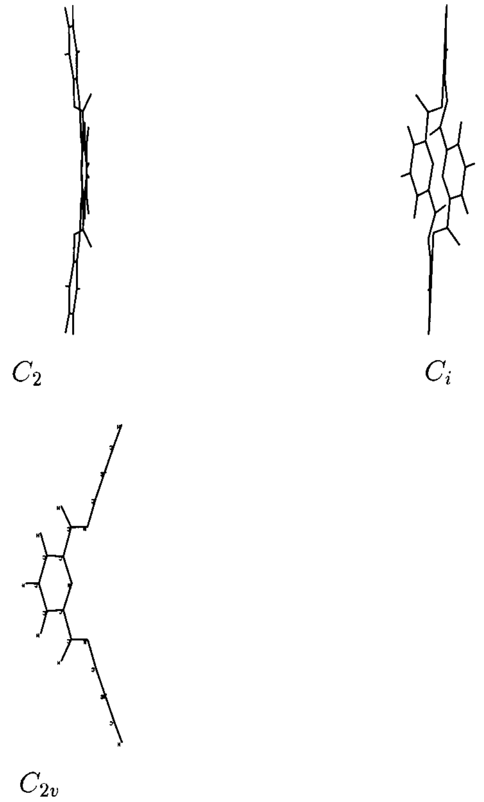


Figure 2. Optimized saddle-like structure with C_{2v} symmetry (structure 3).



C_2 C_i

C_{2v}

Figure 3. Optimized structures, side view.

results for structure 1 and 2, we note that, at the HF level, structure 1 is found to be slightly lower than structure 2. This changes when the calculations are performed at the density functional level: now, structure 2 is consistently lower than structure 1. This energy splitting ranges from $+0.0003\ E_h$ to $-0.002\ E_h$. The quality of the basis set has a minor influence, and zero-point vibrations are negligible for this splitting. Although B3LYP calculations are usually reliable, this contradiction of the various levels of theory makes the correct prediction of the molecular conformation very difficult. Concerning the molecular crystal, lattice effects may well be of the order of the magnitude of the splitting between structure 1 and structure 2. A safer prediction of the structure of the molecular crystal would thus require an optimization of the periodic system which is presently prohibitive.

TABLE 5: Error of the Distance Matrix of the Three Conformations with Respect to the Experimental Geometry

structure	method	basis set	standard deviation
1 (C_2 symmetry)	HF	6-31G	0.025
1	HF	6-31G**	0.029
1	LDA	6-31G	0.029
1	LDA	6-31G**	0.026
1	B3LYP	6-31G	0.028
1	B3LYP	6-31G**	0.024
2 (C_i)	HF	6-31G**	0.019
2	LDA	6-31G**	0.026
2	B3LYP	6-31G**	0.022
3 (C_{2v})	B3LYP	6-31G**	0.15

Structural parameters, together with Mulliken populations, are displayed in Tables 2−4. The charge distributions indicate that all of the hydrogen atoms carry charges of ~0.1 $|e|$ and the nitrogen atoms $\sim -0.5\ |e|$. The carbon atoms carry charges from ~ -0.1 to ~0.25 $|e|$; obviously they are stronger negative for those atoms with a hydrogen neighbor and positive for those atoms with a nitrogen neighbor. The charge distribution is nearly consistent for all of the structures.

We further note that the structural parameters vary only weakly when using basis sets of different quality. Similarly, the charges varied slightly by about 0.1 $|e|$. This deviation may be viewed as an error bar, and the conclusions are not affected.

A comparison with the experimental structure data was made in Table 5. We used the standard deviation of the distance matrix

$$\sqrt{\frac{2}{n(n-1)}\sum_{i=1}^{n}\sum_{j=1}^{i-1}\frac{(d_{i,j}^{\text{computed}}-d_{i,j}^{\text{exp}})^2}{(d_{i,j}^{\text{exp}})^2}}$$

as a measure for the error of the computed geometry (with n as the number of all atoms and $d_{i,j}^{\text{computed}}$ and $d_{i,j}^{\text{exp}}$ being the computed and experimental distances between the atoms i and j, respectively). We note that the standard deviation is very small both for the structure with C_2 symmetry as well as for the structure with C_i symmetry. However, the structure with the C_2 symmetry found experimentally has a slightly higher standard deviation. Finally, the structural parameters of structure 3 with C_{2v} symmetry deviate strongly.

Comparing the structures, we can thus conclude that electrostatic effects favor the approximatively planar structures 1 and 2 over structure 3: the main effect seems to be that the two inner hydrogen atoms (41 and 42 in Figure 1) have lowered the energy of the molecule by inward bending and pointing toward the negatively charge nitrogen atoms. This additional attraction would, for example, for the hydrogen 42 and nitrogen 6, be of the order 0.17 × 0.45 /4 au ~0.5 eV and thus seems to be the likely explanation for the preference of structure 1. In addition, we note that the hydrogen atoms (33, 50 and 34, 49) in structure 1 would feel a relatively strong repulsion in a strictly planar structure, and a slight distortion of the molecule thus lowers the energy. This is indeed found in the experiment and in our simulations. A similar distortion is also found in structure 2. Finally, in structure 3, the hydrogen atoms (39, 43; 41, 45; 40, 44; and 42, 46) would feel a repulsion in a planar structure, and this repulsion can be reduced by a distortion to a saddle-like structure.

In summary, we feel that the preference of the planar elliptical structures over the saddle-like one can be explained by a purely electrostatic argument. Embedding a positively charged metal ion was experimentally found to change the situation: the saddle-like structure is now the preferred one. We feel that this effect may have a similar reason: in the approximatively planar elliptical structures 1 or 2, the additional repulsion from the two inward bending hydrogen atoms would make it difficult to embed a cation, and moreover, the saddle-like structure offers more space to embed a cation. In the saddle-like structure, the metal ion feels the electrostatic attraction because of all six nitrogen atoms. However, a full quantitative analysis of a system with metal ions will be more difficult because the individual units are charged, and thus, also effects from the anions in the molecular crystal must be included.

Summary

We have demonstrated that ab initio HF and density-functional calculations can explain the relative stabilities of flat versus saddle-like conformations of the azamacrocycle $C_{26}H_{18}N_6$. The charge distribution indicates that electrostatic effects are the reason for the energy difference of ∼0.6 eV between these conformations. However, two flat structures with C_2 symmetry and C_i symmetry were found to be nearly degenerate. The distance matrixes of the structures with C_2 symmetry and with C_i symmetry are both in very good agreement with the distance matrix from experimental data. Finally, we showed that the energetically highest structure has a geometry similar to the one observed in systems with a metal embedded in the azamacrocycle. We feel that this saddle-like structure is preferable for the embedding of a metal ion because of the charge distribution and the available space.

The main limitation of these calculations was the restriction to molecules instead of molecular crystals. New code developments (for example the CRYSTAL code with analytical gradients[12]) will hopefully make calculations on the molecular crystal feasible, as well as more demanding simulations on crystals with embedded metal ions.[1−6]

Acknowledgment. The authors would like to thank Prof. S. Laschat and Dr. C. Thöne for helpful discussions.

References and Notes

(1) Bell, T. W.; Guzzo, F. *J. Am. Chem. Soc.* **1984**, *106*, 6111.

(2) Bell, T. W.; Guzzo, F.; Drew, M. G. B. *J. Am. Chem. Soc.* **1991**, *113*, 3115.

(3) Benetollo, F.; Bombieri, G.; Fonda, K. K.; Polo, A.; Quagliano, J. R.; Vallarino, L. M. *Inorg. Chem.* **1991**, *30*, 1345.

(4) Aruna, V. A. J.; Alexander, V. *Inorg. Chim. Acta* **1996**, *249*, 93.

(5) Drew, M. G. B.; Cabral, J. de O.; Cabral, M. F.; Esho, F. S.; Nelson, S. M. *J. Chem. Soc. Chem. Commun.* **1979**, 1033.

(6) Marchetti, P. S.; Bank, S.; Bell, T. W.; Kennedy, M. A.; Ellis, P. D. *J. Am. Chem. Soc.* **1989**, *111*, 2063.

(7) Bell, T. W.; Guzzo, F. *J. Chem. Soc., Chem. Commun.* **1986**, *769*,

(8) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*; Gaussian, Inc.: Pittsburgh, PA, 1998.

(9) Vosko, S. H.; Wilk, L.; Nusair, M. *Can. J. Phys.* **1980**, *58*, 1200.

(10) Stephens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M. J. *J. Phys. Chem.* **1994**, *98*, 11623.

(11) Schaftenaar, G.; Noordik, J. H. *J. Comput.-Aided Mol. Des.* **2000**, *14*, 123.

(12) Doll, K.; Saunders, V. R.; Harrison, N. M. *Int. J. Quantum Chem.* **2001**, *82*, 1.