

A quantum chemistry study on the structure and properties of a novel stable strained cyclophane

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Abstract—Different levels of theoretical methods have been used to study a novel stable cyclophane 1,8-[1,8-naphthalenediylbis(4',4-biphenyldiyl)]naphthalene. It was concluded that HF/3-21g* was the most efficient method for the system, which could well reproduce the experimental structure. In addition, HF/3-21g*//B3LYP/3-21g* calculations explained the experimental observation that the cyclophane was much easier to be oxidized to the corresponding radical cation than its related compound 1,8-bisphenyl-naphthalene. It was proposed that the more effective $\pi-\pi$ and π -cation interactions in the radical cation of the cyclophane caused the above behavior.

INTRODUCTION

Cyclophanes are interesting to theoretical chemists because of their unique structures and unusual intramolecular interactions [1]. To date, theoretical methods including molecular mechanics [2], HMO [3], CNDO [4], MNDO [5], AM1 [6], PM3 [7], MS-X α [8], and *ab initio* calculations [9] have been used on various cyclophanes, whose major aim is usually to know whether or not a particular theoretical method can reproduce the experimental structure and predict the corresponding physicochemical properties.

Recently, Iyoda *et al.* successfully synthesized 1,8-[1,8-naphthalenediylbis(4',4-biphenyl-diyl)]naphthalene **1** (Fig. 1), which is a very stable strained cyclophane and represents the first example in which two biphenyl rings are held so rigidly that they strongly interact with each other *via* a $\pi-\pi$ stacking [10]. Interestingly, it was also found that though **1** was fairly easily oxidized, smaller related compounds such as 1,8-bisphenyl-naphthalene **2** were not.

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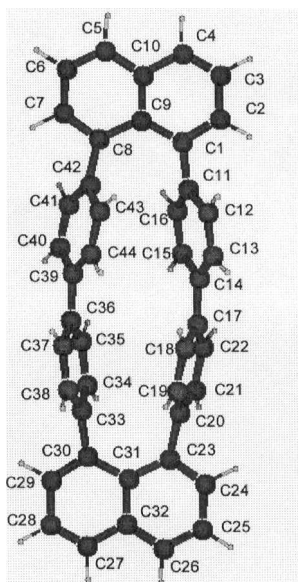


Figure 1. 1,8-[1,8-naphthalenedylbis(4',4-biphenyldiyl)]naphthalene **1**.

Herein, we performed a systematic quantum chemistry study on the above cyclophane to see which theoretical method is the most appropriate for the present system, whether the strong strain and $\pi-\pi$ interaction can be well reproduced, and whether the observed electrochemical behaviors can be satisfactorily interpreted.

METHODS

All the calculation was performed with GAUSSIAN 98 [11]. The initial geometries of the neutral **1** and **2** and their radical cations were constructed with the help of Molden. The standard CNDO, MNDO, AM1, PM3, HF/sto-3g, HF/3-21g*, HF/6-31g*, and B3LYP/3-21g* methods using the Bery analytical gradient algorithm were employed in the calculation. In the case of the radical cation, the spin-unrestricted approximation, where electrons with different spins occupy different sets of orbitals, was employed. As all the structures were found to be true energy minima, no constraints were used in the optimization.

RESULTS AND DISCUSSION

The structure of the cyclophane

In Table 1 are listed some intramolecular distances and out-of-plane deformation angles of the experimental and theoretical structures of **1**. These values are the most important in determining the shape and hence the molecular strain of the cyclophane.

Table 1.

Some intramolecular distances and deformation angles of the experimental and theoretical structures of **1**

	Crystal	CNDO	MNDO	AMI	PM3	HF/ sto-3g	HF/ 3-21g*	HF/ 6-31g*	B3LYP/ 3-21g*
Intramolecular distances (Å)									
C11–C42	3.03	2.58	3.10	2.96	2.96	3.01	3.02	3.08	3.02
C20–C33	2.99	2.57	3.10	2.96	2.96	3.01	3.02	3.08	3.02
C14–C39	3.66	2.69	4.07	3.82	3.75	3.78	3.86	3.96	3.84
C17–C36	3.65	2.69	4.07	3.82	3.75	3.78	3.86	3.96	3.84
C4–C5	2.44	2.48	2.47	2.44	2.44	2.46	2.43	2.43	2.45
C26–C27	2.45	2.48	2.47	2.44	2.44	2.46	2.43	2.43	2.45
C1–C8	2.59	2.49	2.61	2.55	2.56	2.59	2.58	2.59	2.58
C23–C30	2.58	2.49	2.61	2.55	2.56	2.59	2.58	2.59	2.59
relative errors	—	11.5%	4.1%	1.9%	1.4%	1.2%	1.8%	2.9%	1.6%
Out-of-plane deformation angles of C–C bonds (deg)									
Between benzene and naphthalene rings	2.2	2.3	1.1	1.3	0.3	0.9	1.0	1.3	1.3
Between two benzene rings	4.2	2.0	10.8	9.0	8.2	8.0	8.8	9.2	9.2

As seen from the table, CNDO does a very poor optimization. The distances between C11 and C42, between C20 and C33, between C14 and C39, and between C17 and C36 given by CNDO are much shorter than the experimental values. Since the above four distances are related to the strength of the $\pi-\pi$ interaction between the two layers of phenyl rings, the results indicate that CNDO overestimates the strength of the $\pi-\pi$ stacking. As the deviation is too large (the relative error from the crystal structure is 11.5%), it seems that CNDO is not reliable for the system.

In comparison, MNDO offers a much better optimization than CNDO. The relative error from the crystal structure (4.1%) is much smaller than that obtained from CNDO (11.5%). In fact, the results given by the modified MNDO methods such as AM1 and PM3 are so good that they are comparable to *ab initio* calculations. Thus, it can be concluded that AM1 and PM3 can reasonably estimate the $\pi-\pi$ interaction and hence are applicable to the present system.

Nevertheless, it is more desirable to perform *ab initio* calculations as long as the CPU requirement of the calculation can be satisfied. Interestingly, though it is expected that the HF/sto-3g result is too crude, the relative errors from the crystal structure are so small (1.2%) that it is still able to well reproduce the experimental values. As the method becomes HF/3-21g*, the theoretical values are so close to the experimental ones that higher-level methods such as HF/6-31g* or B3LYP/3-21g* cannot offer a significantly better optimization. In fact, as the system is so large that the HF/6-31g* or B3LYP/3-21g* method requires unreasonably long CPU time, it is concluded that HF/3-21g* is the most efficient method for the present system.

According to Table 1, both the experimental and the HF/3-21g* optimized structures show that the cyclophane has its opposite phenyl rings approximately parallel to each other, which apparently maximizes the $\pi-\pi$ stacking interaction. Meanwhile, the naphthalene parts have a splayed structure, indicated by the shorter distance between C26 and C27 than that between C23 and C30. Presumably, this pattern of structure relieves the cyclic strain of **1**.

It is noteworthy that the theoretical distances between the two layers of phenyl rings are somewhat larger than the experimental ones. As the HF/6-31g* or B3LYP/3-21g* calculation also gives similar results, it is unlikely that the theoretical estimations are wrong. In fact, the theoretical calculations are done in the gas phase and the experimental values correspond to the structure in the crystal. Therefore, the smaller experimental distances between the two layers of phenyl rings might be caused by the crystalline packing, which pushes the two layers of phenyl rings towards each other. The same reason explains why the theoretical out-of-plane deformation angles are somewhat different than the experimental ones. Nevertheless, as all the deformation angles are very small, the difference between them is insignificant. Meanwhile, the same reason also explains why the relative errors from the crystal structure of HF/3-21g*, HF/6-31g* or B3LYP/3-21g* are larger than those obtained from HF/sto-3g.

The electrochemical property of the cyclophane

The reason that the cyclophane **1** is interesting lies in its unusual electrochemical property. Compared to its related compounds such as 1,8-bisphenyl-naphthalene **2**, **1** has a much lower first oxidation potential. From the viewpoint of thermodynamics, the above behavior means that the radical cation of **1** is much more stable than that of **2**, or in other words, the energy difference between the neutral species and its radical cation is much smaller for **1** than for **2**.

Herein, the structure of **2** is also optimized with the HF/3-21g* method, and the radical cations of **1** and **2** are optimized with the UHF/3-21g* method. In order to take the electron correlation effect into account, B3LYP/3-21g* or UB3LYP/3-21g* single-point calculation is performed on the optimized species. Interestingly, the calculated energy difference here between the neutral species and its radical cation is 6.48 eV and 7.01 eV for **1** and **2**, respectively. Accordingly, **1** is truly easier to oxidize than **2**, which agrees with the experimental observation.

The above result is reasonable, because in **1** the two layers of phenyl rings are so rigidly arranged face to face that the interaction between them is expected to be very effective. When **1** loses an electron, in addition to an enhanced $\pi-\pi$ interaction, a π -cation interaction [12] will also be turned on. Apparently, these two interactions can greatly stabilize the corresponding radical cation. On the other hand, due to the steric effect, the two layers of phenyl rings in **2** are not rigidly face-to-face arranged. As a result, the interaction between them cannot be very effective. Therefore, the $\pi-\pi$ and π -cation interactions are not as beneficial as those in **1** in stabilizing the radical cation of **2**, which makes **2** more difficult to oxidize.

Nevertheless, it should be noted that the calculated energy difference between the neutral species and the radical cation is much larger than the observed oxidation potential (0.85 V). Obviously, disregarding the solvation effect leads to such a result, because the solvent molecules can stabilize the radical cation more effectively than they do the neutral species. However, the inclusion of the solvation effect is very difficult to model at the present stage, as the available continuum solvation model has been shown to be questionable in dealing with the solvent reorganization [13]. In fact, we have also used SCRF model in the B3LYP/3-21g* or UB3LYP/3-21g* single-point calculation. Compared with calculations in the gas phase (6.48 eV and 7.01 eV, respectively), the calculated energy difference here between the neutral species and its radical cation is 6.48 eV and 6.94 eV for **1** and **2**, respectively. Apparently, there is no significantly better result when we include the solvation effect. This result also proves our supposition regarding the solvation effect model at the present stage. Thus, the calculations without the inclusion of the solvation effect are reasonable.

CONCLUSION

The structure of 1,8-[1,8-naphthalenediylbis(4',4'-biphenyldiyl)]naphthalene **1** was investigated systematically with various semiempirical and *ab initio* calculations. It was found that the HF/3-21g* method was the most efficient for the above system. Calculations also reproduced the experimental observation that **1** was much easier to oxidize than its related compounds, such as 1,8-bisphenyl-naphthalene. It was proposed that the more effective $\pi-\pi$ and π -cation interactions in the radical cation of **1** caused the above behavior.

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REFERENCES

- (a) D. J. Cram and J. M. Cram, *Acc. Chem. Res.* **4**, 204 (1971);
(b) F. Bickelhaupt, *Pure Appl. Chem.* **62**, 373 (1990);
(c) Z. Shi and J.-H. Wang, *Chin. J. Org. Chem.* **13**, 113 (1993);
(d) Y. Tobe, *Top. Curr. Chem.* **172**, 1 (1994).
- (a) R. H. Boyd, *J. Chem. Phys.* **49**, 2574 (1968);
(b) H. J. Lindner, *Tetrahedron* **32**, 753 (1976);
(c) U. Norinder and O. Wennerstroem, *J. Phys. Chem.* **89**, 3233 (1985).
- H. Vogler, G. Ege and H. A. Staab, *Mol. Phys.* **33**, 923 (1977).
- K. Tokita, S. Kondo and N. Mori, *Bull. Chem. Soc. Jpn.* **53**, 3371 (1980).
- L. W. Jenneskens, F. J. de Kanter, W. H. de Wolf and F. Bickelhaupt, *J. Comput. Chem.* **8**, 1154 (1987).
- L. Turker, *J. Mol. Struct. (Theochem)* **530**, 119 (2000).

7. R. Castro, P. D. Davidov, K. A. Kumar, A. P. Marchand, J. D. Evanseck and A. E. Kaifer, *J. Phys. Org. Chem.* **10**, 369 (1997).
8. (a) H.-X. Liu, B.-F. Li, Z.-Z. Yang and J.-Z. Sun, *Acta Chim. Sin.* **52**, 29 (1994);
(b) H.-X. Liu and J.-Z. Sun, *Acta Chim. Sin.* **53**, 125 (1995);
(c) H.-X. Liu, *Acta Chim. Sin.* **53**, 543 (1995);
(d) H.-X. Liu, *Acta Phys.-Chim. Sin.* **11**, 896 (1995).
9. (a) H. F. Bettinger, P. v. R. Schleyer and H. F. Schaefer, *J. Am. Chem. Soc.* **120**, 1074 (1998);
(b) B. H. Hong, J. Y. Lee, S. J. Cho, S. Yun and K. S. Kim, *J. Org. Chem.* **64**, 5661 (1999);
(c) C. Kind, M. Reiher, J. Roder and B. A. Hess, *Phys. Chem. Chem. Phys.* **2**, 2205 (2000);
(d) D. Henseler and G. Hohlneicher, *J. Mol. Struct. (Theochem)* **497**, 145 (2000);
(e) R. Salcedo, L. E. Sansores, A. Martinez, L. Alexandrova and M. Garcia, *J. Organomet. Chem.* **603**, 225 (2000);
(f) P. Saarenketo, R. Suontamo, T. Jodicke and K. Rissanen, *Organometallics* **19**, 2346 (2000).
10. M. Iyoda, T. Kondo, K. Nakao, K. Hara, Y. Kuwatani, M. Yoshida and H. Matsuyama, *Org. Lett.* **2**, 2081 (2000).
11. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, A. G. Baboul, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle and J. A. Pople, *Gaussian 98, Revision A.7*, Gaussian, Inc., Pittsburgh, PA (1998).
12. J. C. Ma and D. A. Dougherty, *Chem. Rev.* **97**, 1030 (1997).
13. P. Vath, M. B. Zimmt, D. V. Matyushov and G. A. Voth, *J. Phys. Chem. B* **103**, 9130 (1999).