

Conformational analysis of the core unit of crownphanes by *ab initio* calculations: 1,1-dibenzylethylene and related compounds

2 PERKIN

Seiji Tsuzuki,^{*a,b} Hirohiko Houjou,^b Yoshinobu Nagawa^b and Kazuhisa Hiratani^b

^a National Institute of Materials and Chemical Research, Tsukuba, Ibaraki 305-8565, Japan.

E-mail: tsuzuki@nimc.go.jp

^b National Institute for Advanced Interdisciplinary Research, Tsukuba, Ibaraki 305-8562, Japan

Received (in Cambridge, UK) 10th August 2000, Accepted 7th September 2000

First published as an Advance Article on the web 6th November 2000

1,1-Dibenzylethylene is the core unit of crownphanes obtained by tandem Claisen rearrangement from 1,1-bis-(phenyloxymethyl)ethylene derivatives. Although the conformational preference of this unit is important to understand, the three-dimensional structures of the crownphanes and their binding affinities with guest molecules and the relative energies of rotamers of 1,1-dibenzylethylene and its related compounds were not known. MP2/6-311G**//HF/6-311G** calculations showed that the C=C–C–C bonds of 1,1-dibenzylethylene had a skew–skew conformation in the most stable rotamer. The skew–skew conformation had been observed in the crystal form of the water–crownophane complex. The calculated relative energies of rotamers suggested that nonbonding interaction between the benzene rings (quadrupole–quadrupole interaction) stabilized the skew–skew rotamer. The calculations of 1,1-bis(2-hydroxy-3-methoxyphenylmethyl)ethylene showed that the most stable rotamer had the conformation in which the two methoxy groups are on the opposite sides, while the second most stable rotamer, in which the two methoxy groups are on the same side, was only 0.38 kcal mol⁻¹ less stable.

Introduction

Crownphanes are structurally hybridized macrocycles which have rigid aromatic moieties and flexible oxyethylene chains within the macrocyclic ring.¹ Crownphanes with phenolic moieties have several interesting properties such as being highly selective sodium ionophores.^{2–9} Recently Hiratani and co-workers reported that the tandem Claisen rearrangement^{10–13} provides a simple route to synthesize crownphanes with phenolic moieties from 1,1-bis(aryloxymethyl)ethylene with a cyclic poly(oxyethylene) chain. The crownphanes obtained by this route contain 1,1-bis(arylmethyl)ethylene groups. A crownophane obtained by this route (Fig. 1) has a strong binding affinity to a water molecule.¹⁴ They measured the binding constant to a water molecule as $K = 250 \pm 10 \text{ M}^{-1}$ in CD₂Cl₂ at 298.2 K. The water–crownophane complex in the crystal form has a characteristic structure. The complex has four hydrogen bonds. Two of them are between the water oxygen atom and hydroxy groups and the other two are between the water hydrogen atoms and oxygen atoms of the poly(oxyethylene) chain. The two C=C–C–C bonds of the crownophane have a skew–skew conformation, which enables the crownophane to have the two hydrogen bonds between the water oxygen atom and the hydroxy groups.

Knowledge of the conformational preferences of crownphanes is essential for predicting their three-dimensional structures and their binding affinities with guest molecules, since size fit and directionality are very important for molecular recognition.¹⁵ Detailed information about the conformational energies of 1,1-bis(arylmethyl)ethylene is important for the understanding of the binding affinities of the crownphanes with guest molecules and for the design of artificial host molecules. Unfortunately, however, experimental measurements of the relative energies of the rotamers of 1,1-bis(arylmethyl)ethylene molecules have not yet been reported.

Ab initio molecular orbital calculation is becoming a powerful

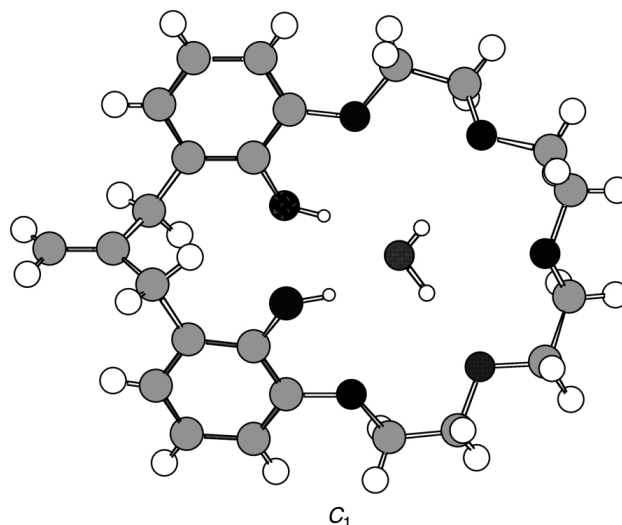


Fig. 1 The crystal structure of a water–crownophane complex.

tool for evaluating relative energies of rotamers. Recently reported calculations of small organic molecules show that *ab initio* calculation provides sufficiently accurate conformational energies, if a reasonably large basis set is used and electron correlation is appropriately corrected.^{16–21} In this paper we have calculated the relative energies of a few rotamers of 1,1-dibenzylethylene and its related compounds (1–5, Figs. 2, 4, 6–8) by high level *ab initio* methods.

Computational methods

The Gaussian 94 program²² was used for the *ab initio* molecular orbital calculations. The basis sets implemented in the program were used. Geometries were optimized at the HF/6-311G**

Table 1 Calculated relative energies of *syn* rotamers of 2-benzylprop-1-ene (**2**)^a

Basis set	BF ^b	HF	MP2
3-21G	114	0.91	0.43
6-31G	114	0.78	0.18
6-31G*	174	0.70	0.72
6-311G*	216	0.57	0.77
6-311G**	252	0.58	0.80
6-311++G**	304	0.50	0.67
6-311G(2d,2p)	338	0.47	0.54

^a Energies in kcal mol⁻¹. Calculated energies of *syn* rotamer relative to skew one (Fig. 4). ^b Number of basis functions.

level.²³ Relative energies of rotamers were calculated using the 6-311G** basis set with electron correlation correction by the second order Møller–Plesset perturbation method (MP2),^{24,25} if not otherwise noted. Electron correlation was also corrected by higher order Møller–Plesset methods²⁵ and by the coupled cluster method using single and double substitutions with non-iterative triple excitations (CCSD(T))²⁶ for selected calculations. One torsional angle was fixed and the other geometrical parameters were fully optimized in torsional potential calculations.

Results and discussion

Effects of the basis set

The relative energy of the two rotamers of 2-benzylprop-1-ene (**2**) (see Fig. 4) was calculated by HF and MP2 methods with several basis sets to evaluate the basis set effects. For all the calculations the skew rotamer is more stable than the *syn* rotamer. The relative energies of the two rotamers are summarized in Table 1. The MP2 calculations show that the basis set effects are not large if a basis set larger than the 6-31G* basis set is used. The addition of diffuse functions²⁷ and multiple polarization functions²⁸ to the 6-311G** basis set had little effect on the calculated relative energies. Similar basis set dependence was reported in the conformational energy calculations of small molecules.^{18,19,29,30}

Effects of electron correlation

The conformational energies of small molecules have been calculated with electron correlation correction by several methods.^{18,19,30} The effects of the correction beyond the MP2 level are in general not large. The relative energies of the two rotamers of **2** were calculated by the MP2, MP3, CCSD and CCSD(T) methods with the 6-31G* basis set to evaluate the effects of electron correlation beyond the MP2 level. The calculated energies of the *syn* rotamer relative to the skew rotamer with the MP2, MP3, CCSD and CCSD(T) level corrections are 0.72, 0.40, 0.52 and 0.55 kcal mol⁻¹, respectively. The effects of electron correlation beyond the MP2 level are not large (less than 0.32 kcal mol⁻¹). The MP2 level energy difference between the two rotamers (0.72 kcal mol⁻¹) is close to the CCSD(T) one (0.55 kcal mol⁻¹). Due to the good performance of the MP2 level correction, we decide to correct electron correlation with the MP2 method in further calculations.

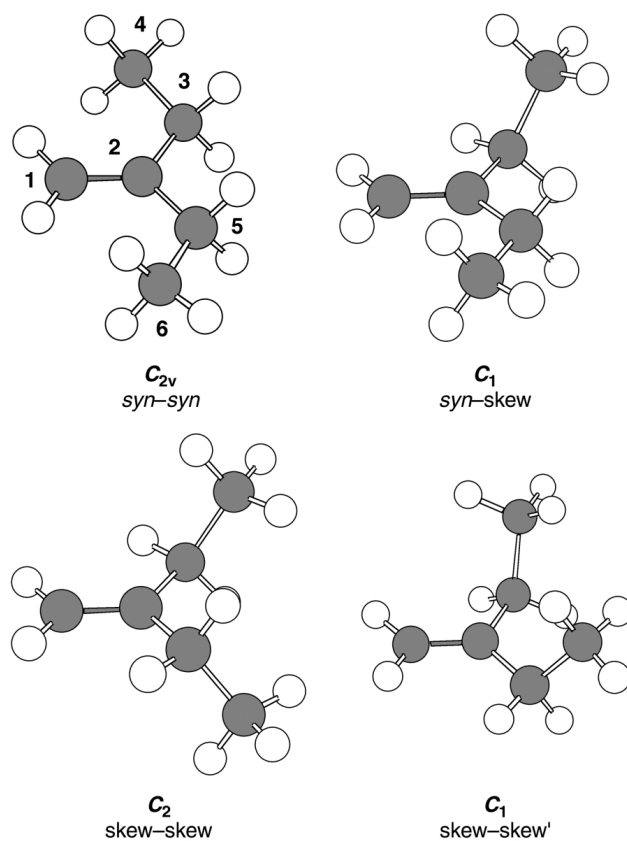
2-Ethylbut-1-ene (**1**)

It has been reported that both *syn* and skew rotamers of but-1-ene are energetically stable.^{31–34} An analysis of the microwave spectrum shows that the skew rotamer is 0.15 ± 0.15 kcal mol⁻¹ more stable than the *syn* rotamer.³¹ Liquid phase Raman data also show that the skew rotamer is 0.22 kcal mol⁻¹ more stable.³² G2 calculations³⁵ also show that the skew rotamer is 0.36 kcal mol⁻¹ more stable.³⁴ The calculations with a smaller

Table 2 Calculated relative energies of rotamers of 1–3^a

Rotamer ^b	1	2	3
HF/6-31G**			
<i>syn</i> – <i>syn</i>	0.09		1.54
<i>syn</i> –skew	0.10	0.58 ^c	0.79
skew–skew	0.00	0.00 ^d	0.00
skew–skew'	1.21		3.60
MP2/6-311G**			
<i>syn</i> – <i>syn</i>	0.46		2.80
<i>syn</i> –skew	0.33	0.80 ^c	1.59
skew–skew	0.00	0.00 ^d	0.00
skew–skew'	1.00		1.98

^a Energies in kcal mol⁻¹. The HF/6-311G** geometries were used. ^b See Figs. 2, 4 and 6. ^c *syn* rotamer. ^d Skew rotamer.

**Fig. 2** The optimized geometries of the four rotamers of 2-ethylbut-1-ene (**1**) at the HF/6-311G** level.

6-31G* basis set also showed that the skew rotamer was more stable.³⁶

Our MP2/6-311G**//HF/6-311G** calculations show that the C=C–C–C bonds of 2-ethylbut-1-ene (**1**) also prefer *syn* and skew conformations. The calculations show that the skew–skew rotamer (C¹–C²–C³–C⁴ = C¹–C²–C⁵–C⁶ = 117.3°) is the most stable among the four rotamers (Fig. 2) as summarized in Table 2. The *syn*–*syn* and *syn*–skew rotamers are 0.46 and 0.33 kcal mol⁻¹ less stable, respectively. The skew–skew' rotamer (C¹–C²–C³–C⁴ = 80.6 and C¹–C²–C⁵–C⁶ = –118.8°) has large conformational energy (1.00 kcal mol⁻¹) due to the steric repulsion between two methyl groups. The torsional potential of the C¹–C²–C³–C⁴ bond was calculated. The C¹–C²–C⁵–C⁶ bond, which was not fixed during the geometry optimization, had a skew conformation in the calculations. The calculated torsional potential of the C¹–C²–C³–C⁴ bond (Fig. 3) shows that the *gauche* and *anti* internal rotational barrier heights are about 1.5 and 4.2 kcal mol⁻¹, respectively.

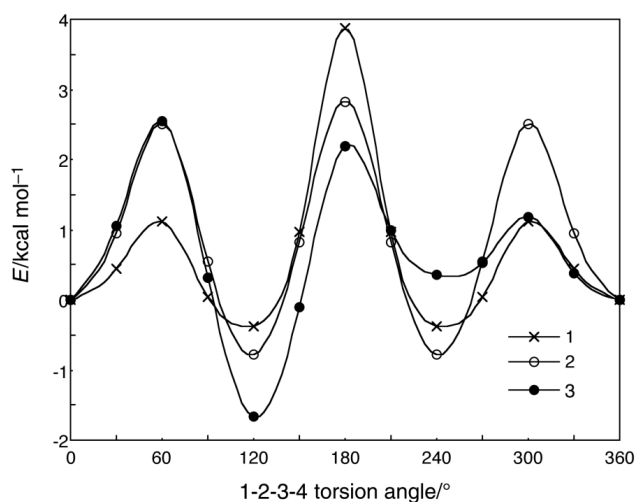


Fig. 3 The calculated torsional potentials of the $C^1-C^2-C^3-C^4$ bonds of **1-3** at the MP2/6-311G** level. The $C^2-C^3-C^4-C^5$ bonds of **2** and **3** have skew conformations.

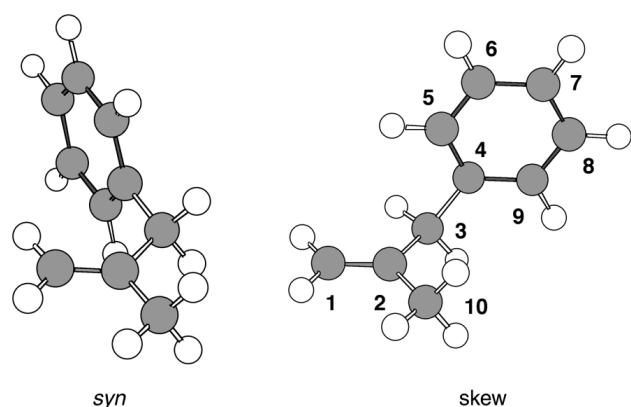


Fig. 4 The optimized geometries of the *syn* and skew rotamers of 2-benzylprop-1-ene (**2**) at the HF/6-311G** level.

2-Benzylprop-1-ene (**2**)

Our MP2/6-311G**//HF/6-311G** calculations show that the skew rotamer ($C^1-C^2-C^3-C^4 = 117.9$ and $C^2-C^3-C^4-C^5 = 118.3^\circ$) of **2** (Fig. 4) is $0.80 \text{ kcal mol}^{-1}$ more stable than the *syn* rotamer ($C^1-C^2-C^3-C^4 = 0.0$ and $C^2-C^3-C^4-C^5 = 90.0^\circ$). The $C^1-C^2-C^3-C^4$ angle of the skew rotamer is close to that of **1**. The calculated energy difference between the skew and *syn* rotamers ($0.80 \text{ kcal mol}^{-1}$) is substantially larger than that between the skew-skew and *syn*-skew rotamers of **1** ($0.33 \text{ kcal mol}^{-1}$). The steric repulsion between the C^1 methylene group and phenyl ring in the *syn* rotamer would be the cause of the larger energy difference. The distance between C^4 and a hydrogen atom attached to C^1 is only 2.6 \AA in the *syn* rotamer. The $C^2-C^3-C^4$ angle (116.7°) of the *syn* rotamer is substantially larger than that of the skew rotamer (114.1°), which indicates that the *syn* rotamer has larger steric repulsion.

The calculated torsional potential of the $C^1-C^2-C^3-C^4$ bond is shown in Fig. 3. The $C^2-C^3-C^4-C^5$ angle was $72-118^\circ$ in the optimized structures. The calculated potential shows that *gauche* and *anti* barrier heights are about 3.3 and $3.6 \text{ kcal mol}^{-1}$, respectively. The torsional potential of the $C^2-C^3-C^4-C^5$ bond in the skew rotamer was calculated as shown in Fig. 5. The calculated internal rotational barrier height of the phenyl group is about $3.4 \text{ kcal mol}^{-1}$. The torsion angle of the $C^2-C^3-C^4-C^5$ bond is not too different from 90° in the stable conformation as in the case of ethylbenzene. MP2/6-311G**//HF/6-311G** calculations of ethylbenzene show that the perpendicular rotamer is $1.43 \text{ kcal mol}^{-1}$ more stable than the coplanar rotamer.

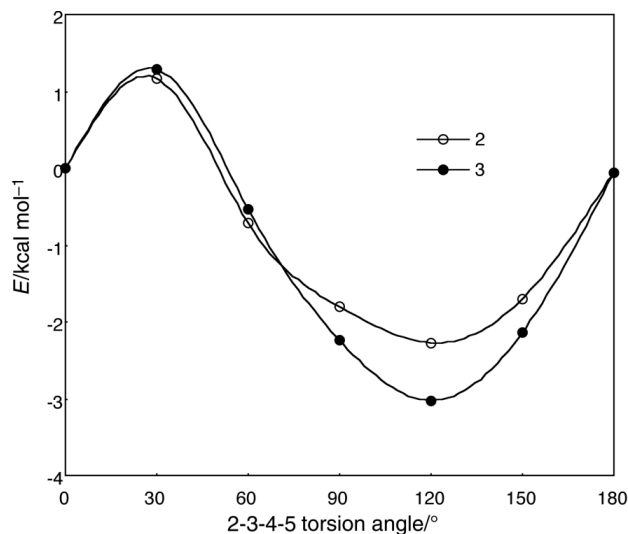


Fig. 5 The calculated torsional potentials of the $C^2-C^3-C^4-C^5$ bonds of **2** and **3** at the MP2/6-311G** level. The $C^1-C^2-C^3-C^4$ bonds of **2** and **3** have skew conformations.

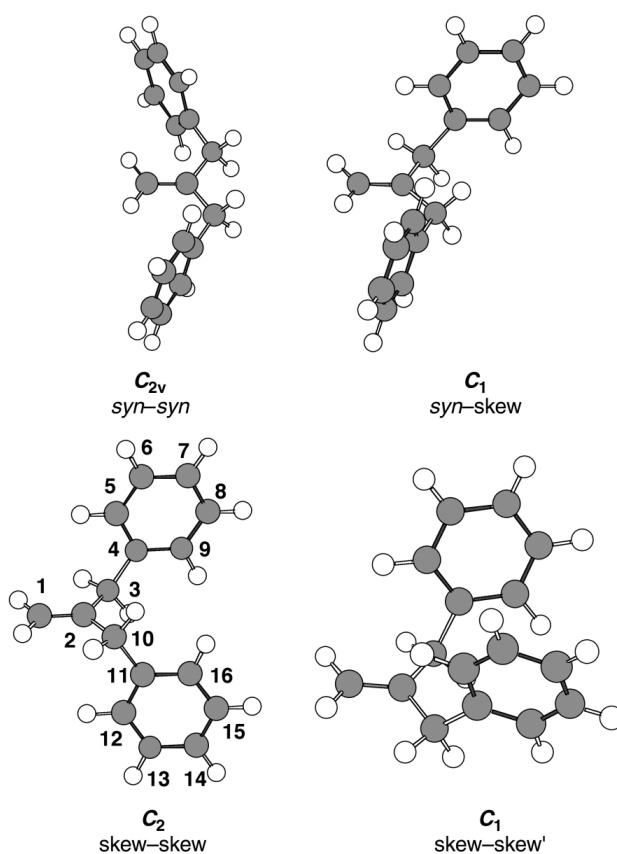


Fig. 6 The optimized geometries of the four rotamers of 1,1-dibenzylethylene (**3**) at the HF/6-311G** level.

1,1-Dibenzylethylene (**3**)

Conformational analysis of **2** shows that the benzyl group prefers the *syn* and skew conformations with respect to the $C=C$ bond. We have calculated the relative energies of the four rotamers of 1,1-dibenzylethylene (**3**) (Fig. 6). The benzyl groups take the *syn* or skew conformations in these rotamers. MP2/6-311G**//HF/6-311G** calculations show that the skew-skew rotamer is the most stable among the four rotamers as shown in Table 2. The $C^1-C^2-C^3-C^4$ and $C^1-C^2-C^{10}-C^{11}$ torsion angles are both 116.7° in this rotamer. The relative energies of the *syn*-*syn*, *syn*-skew and skew-skew' conformations are 2.80 , 1.59 and $1.98 \text{ kcal mol}^{-1}$, respectively. Compound **3** is the core

unit of the crownphanes obtained by the tandem Claisen rearrangement. Crystal structures of the six crownphanes obtained by the rearrangement have been analyzed.^{13,37} The 1,1-dibenzylethylene unit takes the skew-skew conformation in these crystals. The calculated conformational preference of this group agrees well with the experimental observation.

The energy difference between the *syn*-skew and skew-skew rotamers (1.59 kcal mol⁻¹) is considerably larger than that of the *syn* and skew rotamers of **2** (0.80 kcal mol⁻¹). The C¹-C²-C³-C⁴ torsional potential of **3** is very close to that of **2** when the C¹-C²-C³-C⁴ torsion angle is 0–60° (Fig. 3), while the potential of **3** has a deeper minimum than that of **2** when the torsion angle is 120° (skew-skew). These results indicate that the second phenyl group stabilizes the skew-skew rotamer. The larger stability of the skew-skew rotamer suggests that this conformer is stabilized by the nonbonding interaction between phenyl groups. The two benzene rings take the slipped-parallel geometry in this rotamer. It has been reported that the slipped-parallel structure is a stable structure of the benzene dimer and that this structure is stabilized with attractive quadrupole-quadrupole interactions.^{38–41} Hobza *et al.* reported that the binding energy of the slipped-parallel benzene dimer is about 2.0 kcal mol⁻¹ at the equilibrium geometry from their CCSD(T) calculations using a modified aug-cc-pVDZ basis set.⁴⁰ This attractive interaction between the two phenyl groups would be the cause of the large stability of the skew-skew rotamer. The skew-skew' rotamer is considerably less stable than the skew-skew rotamer. In this rotamer the two phenyl rings have close contact. The C₄⋯C₁₁ distance is only 3.43 Å in this rotamer. Steric repulsion between the two phenyl groups is apparently one of the causes of the high energy of this rotamer. The calculated torsional potential of the C¹-C²-C³-C⁴ bond is shown in Fig. 3. The C²-C³-C⁴-C⁵ torsional angle is not too different from 90°. The calculated torsional potential of the C²-C³-C⁴-C⁵ bond is shown in Fig. 5. The torsional angle of this bond is close to 120° in the energy minimum structure. The difference between the potentials of **2** and **3** also suggests that the energy minimum structure (skew-skew) is stabilized by the interaction between the two phenyl groups.

1,1-Bis(*o*-hydroxyphenylmethyl)ethylene (**4**)

The relative energies of the four rotamers of 1,1-bis(*o*-hydroxyphenylmethyl)ethylene (**4**) (Fig. 7) were calculated to evaluate the effects of the *ortho*-hydroxy groups. The C¹-C²-C³-C⁴ and C¹-C²-C¹⁰-C¹¹ bonds have the skew conformation in these rotamers. The conformations of the phenyl rings and hydroxy groups are different. The rotamer D was the most stable among the four rotamers. The calculated relative energies of the rotamers A–C are 3.21, 2.43 and 3.41 kcal mol⁻¹, respectively, as shown in Table 3. One hydroxy group has an intramolecular hydrogen bond with the oxygen atom of the other hydroxy group in the rotamer D. Apparently this hydrogen bond is the cause of the large stability of the rotamer D. The rotamer A, which does not have this hydrogen bond, is 3.21 kcal mol⁻¹ less stable. The relative stability of the rotamer C is close to that of the rotamer A. The rotamer B is more stable than the rotamers A and C.

1,1-Bis(2-hydroxy-3-methoxyphenylmethyl)ethylene (**5**)

The relative energies of the three rotamers of 1,1-bis(2-hydroxy-3-methoxyphenylmethyl)ethylene (**5**) (Fig. 8) were calculated. The two hydroxy groups of this molecule have intramolecular hydrogen bonds with the oxygen atoms of the neighboring methoxy groups in these three rotamers. A rotamer which has a hydrogen bond between the two hydroxy groups, as in the case of the rotamer D of **4**, was not an energy minimum structure. The rotamer B was the most stable among the three rotamers as shown in Table 3, while the energy difference between the rotamers A and B is only 0.38 kcal mol⁻¹. The energy difference

Table 3 Calculated relative energies of rotamers of **4** and **5**^a

Rotamer	4	5
HF/6-311G**		
A	0.60	0.52
B	0.00	0.00
C	1.09	1.44
D	-1.54	
MP2/6-311G**		
A	0.78	0.38
B	0.00	0.00
C	0.98	1.20
D	-2.43	

^a Energies in kcal mol⁻¹. The 6-311G** basis set was used. See Figs. 7 and 8.

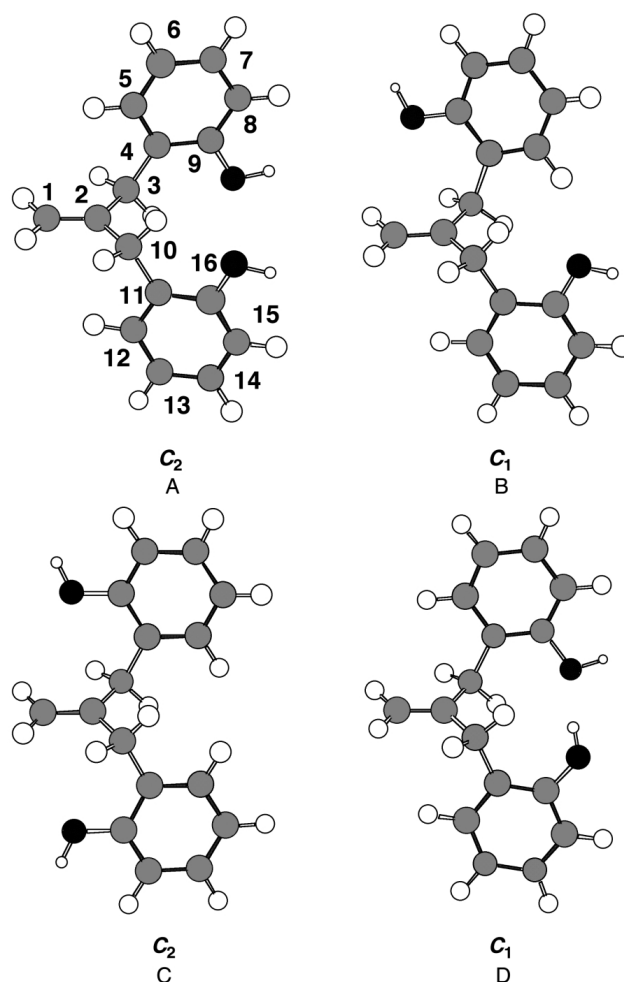


Fig. 7 The optimized geometries of the four rotamers of 1,1-bis(*o*-hydroxyphenylmethyl)ethylene (**4**) at the HF/6-311G** level.

is smaller than that of **4** (0.78 kcal mol⁻¹), which indicates that the methoxy groups increase the relative stability of the rotamer A.

Compound **5** is the core unit of the crownphanes obtained by the tandem Claisen rearrangement. The conformational analysis of **5** by *ab initio* calculations shows that the conformation B is more stable than the conformation A, while the energy difference between the two conformations is very small (0.38 kcal mol⁻¹). The order of the stability of the two conformations will be changed very easily by additional effects such as geometrical constraints and host-guest interaction. It is not surprising that this unit adopts conformation A in the water-crownphane complex (Fig. 1).

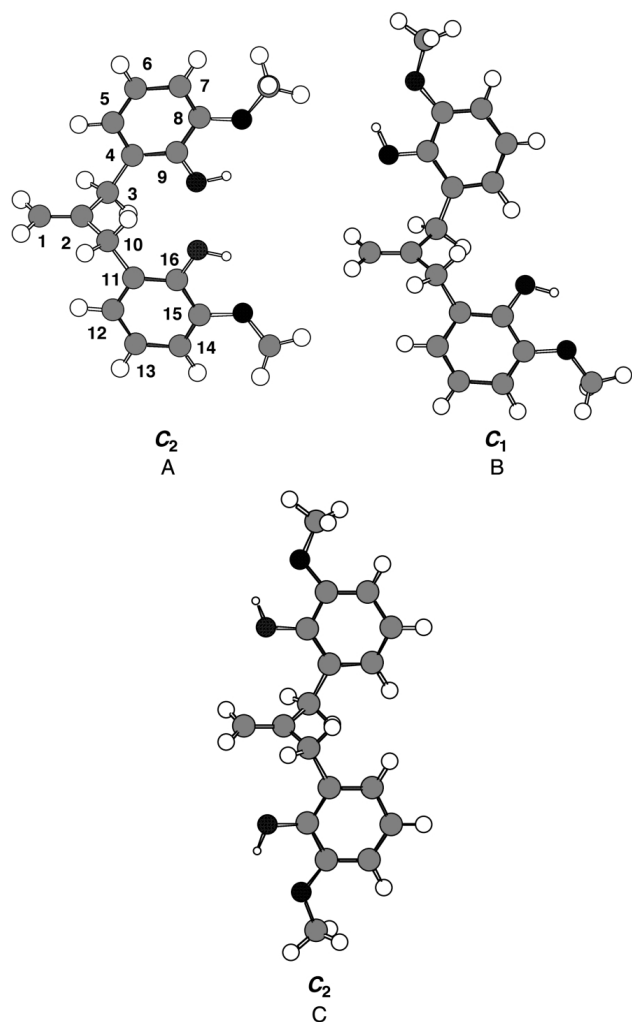


Fig. 8 The optimized geometries of the three rotamers of 1,1-bis(2-hydroxy-3-methoxyphenylmethyl)ethylene (**5**) at the HF/6-311G** level.

Conclusions

The C=C–C–C bonds of 1,1-benzylethylene units of crownphanes take the skew–skew conformation in the crystal form. Our calculations indicate that the C=C–C–C bonds prefer the skew conformation to the *syn*. The calculated conformational energies suggest that the skew–skew conformation is further stabilized by the nonbonding interaction between the phenyl groups (quadrupole–quadrupole interaction).

Our calculations show that the most stable rotamer of the 1,1-bis(2-hydroxy-3-methoxyphenylmethyl)ethylene has the conformation in which the two methoxy groups are on opposite sides. The rotamer in which the two methoxy groups are on the same side is the second most stable rotamer. This rotamer, which corresponds to the conformation observed in the crystal, is only 0.38 kcal mol⁻¹ less stable than the most stable one.

Acknowledgements

We thank the Tsukuba Advanced Computing Center for the provision of the computational facilities.

References

- 1 S. Inokuma, S. Sakaki and J. Nishimura, *Top. Curr. Chem.*, 1994, **172**, 87.

- 2 K. Koenig, G. M. Lein, P. Stuckler, T. Kaneda and D. J. Cram, *J. Am. Chem. Soc.*, 1979, **101**, 3553.
- 3 R. C. Helgeson, T. L. Tarnowski and D. J. Cram, *J. Org. Chem.*, 1979, **44**, 2538.
- 4 G. M. Lein and D. J. Cram, *J. Am. Chem. Soc.*, 1985, **107**, 448.
- 5 Y. Sun, A. E. Martell and R. J. Motekaitis, *Inorg. Chem.*, 1986, **25**, 4780.
- 6 T. Kaneda, S. Umeda, Y. Ishizaki, H. S. Kuo, S. Misumi, Y. Kai, N. Kanehisa and N. Kasai, *J. Am. Chem. Soc.*, 1989, **111**, 1881.
- 7 T. Kaneda, K. Hirose and S. Misumi, *J. Am. Chem. Soc.*, 1989, **111**, 742.
- 8 A. R. van Doorn, M. Bos, S. Harkema, J. van Eerden, W. Verboom and D. N. Reinhoudt, *J. Org. Chem.*, 1991, **56**, 2371.
- 9 A. R. van Doorn, R. Schaafstra, M. Bos, S. Harkema, J. van Eerden, W. Verboom and D. N. Reinhoudt, *J. Org. Chem.*, 1991, **56**, 6083.
- 10 K. Hiratani, T. Takahashi, K. Kasuga, H. Sugihara, K. Fujiwara and K. Ohashi, *Tetrahedron Lett.*, 1995, **36**, 5567.
- 11 K. Hiratani, K. Kasuga, M. Goto and H. Uzawa, *J. Am. Chem. Soc.*, 1997, **119**, 12677.
- 12 H. Uzawa, K. Hiratani, N. Minoura and T. Takahashi, *Chem. Lett.*, 1998, 307.
- 13 K. Hiratani, T. Uzawa, K. Kasuga and H. Kobayashi, *Tetrahedron Lett.*, 1997, **38**, 8993.
- 14 K. Hiratani, M. Goto, Y. Nagawa, K. Kasuga and K. Fujiwara, *Chem. Lett.*, in the press.
- 15 *Host–Guest Chemistry*, eds. F. Vogtle and E. Weber, I, II and III, Springer-Verlag, Berlin, 1981 (I), 1982 (II) and 1984 (III).
- 16 K. Raghavachari, *J. Chem. Phys.*, 1984, **81**, 1383.
- 17 K. B. Wiberg and M. A. Murcko, *J. Am. Chem. Soc.*, 1988, **110**, 8029.
- 18 N. L. Allinger, R. S. Grev, B. F. Yates and H. F. Schaefer III, *J. Am. Chem. Soc.*, 1990, **112**, 114.
- 19 G. D. Smith and R. L. Jaffe, *J. Phys. Chem.*, 1996, **100**, 18718.
- 20 N. L. Allinger, J. T. Fermann, W. D. Allen and H. F. Schaefer III, *J. Chem. Phys.*, 1997, **106**, 5143.
- 21 S. Tsuzuki, T. Uchimaru, K. Tanabe and T. Hirano, *J. Phys. Chem.*, 1993, **97**, 1346.
- 22 M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. J. P. Stewart, M. Head-Gordon, C. Gonzalez and J. A. Pople, *Gaussian 94*, Gaussian, Inc., Pittsburgh, PA, 1994.
- 23 R. Krishnan, J. S. Binkley, R. Seeger and J. A. Pople, *J. Chem. Phys.*, 1980, **72**, 650.
- 24 C. Møller and M. S. Plesset, *Phys. Rev.*, 1934, **46**, 618.
- 25 R. Krishnan and J. A. Pople, *Int. J. Quantum Chem.*, 1978, **14**, 91.
- 26 J. A. Pople, M. Head-Gordon and K. Raghavachari, *J. Chem. Phys.*, 1987, **87**, 5968.
- 27 T. Clark, J. Chandrasekhar, G. W. Spitznagel and P. v. R. Schleyer, *J. Comput. Chem.*, 1983, **4**, 294.
- 28 M. J. Frisch, J. A. Pople and J. S. Binkley, *J. Chem. Phys.*, 1984, **80**, 3265.
- 29 S. Tsuzuki and K. Tanabe, *J. Chem. Soc., Perkin Trans. 2*, 1991, 1255.
- 30 S. Tsuzuki and K. Tanabe, *J. Chem. Soc., Faraday Trans.*, 1991, **87**, 3207.
- 31 S. Kondo, E. Hirota and Y. Morino, *J. Mol. Spectrosc.*, 1968, **28**, 471.
- 32 K. S. Pitzer, *J. Chem. Phys.*, 1946, **14**, 239.
- 33 D. Van Hemelrijk, L. Van den Enden, H. J. Geise, H. L. Sellers and L. Schafer, *J. Am. Chem. Soc.*, 1980, **102**, 2189.
- 34 M. A. Murcko, H. Castejon and K. B. Wiberg, *J. Phys. Chem.*, 1996, **100**, 16162.
- 35 L. A. Curtiss, K. Raghavachari, G. W. Trucks and J. A. Pople, *J. Chem. Phys.*, 1991, **94**, 7221.
- 36 K. B. Wiberg and E. Martin, *J. Am. Chem. Soc.*, 1985, **107**, 5035.
- 37 K. Hiratani, unpublished results.
- 38 P. Hobza, H. L. Selzle and E. W. Schlag, *J. Am. Chem. Soc.*, 1994, **116**, 3500.
- 39 G. D. Smith and R. L. Jaffe, *J. Phys. Chem.*, 1996, **110**, 9624.
- 40 P. Hobza, H. L. Selzle and E. W. Schlag, *J. Phys. Chem.*, 1996, **100**, 18790.
- 41 A. J. Stone, *The theory of intermolecular forces*, Clarendon Press, Oxford, 1996.