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Effects of CH–O and CH–π interactions on the conformational preference of a crownophane core unit †

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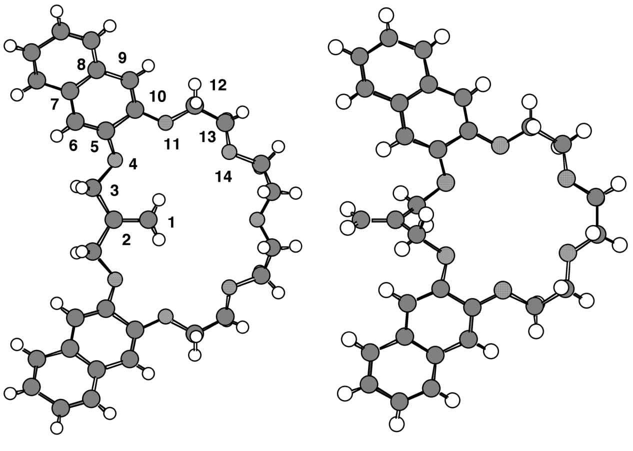
Relative energies of the rotamers of prop-2-enyl *o*-methoxyphenyl ether and related compounds (CH_2=CH–CH_2–X–R, X = O or CH_2, R = CH_3, C_6H_5 or *o*-$CH_3OC_6H_4$) were calculated at the MP2/6-311G**//HF/6-311G** level as models of the crownophane core unit [1,1-bis(aryloxymethyl)ethylene]. The calculations show that CH–O and CH–π interactions play important roles in determining the conformational preference of the core unit. The terminal methylene unit of the crownophane, which consists of the core unit and a –O–(CH_2–CH_2–O)$_n$– chain ($n = 4$), points towards the inside of the ring cavity (in-conformation) in the crystal. The C=C–C–O and C–C–O–C bonds of the crownophane have an eclipse-*trans* conformation. Conformational analysis of model compounds shows that the eclipse-*trans* conformation is stabilized by a CH–O interaction. The methylene unit of the crownophane which has a shorter oxyethylene chain ($n = 3$) points toward the outside (out-conformation) in the crystal. The C=C–C–O and C–C–O–C bonds of this crownophane adopt a skew-*gauche'* conformation that is stabilized by a CH–π interaction. Conformational analysis of model compounds shows that the C=C–C–O and C–C–O–C bonds of the core unit prefer the eclipse-*trans* conformation and that the skew-*gauche'* conformation is slightly less stable. Calculations on the in- and out-conformations of the crownophane ($n = 3$) show that the out-conformation is more stable and that the in-conformation has significant strain due to the short oxyethylene chain, suggesting that this strain is the cause of the observed out-conformation in the crystal.

Introduction

Crownophanes are structurally hybridized macrocycles which have rigid aromatic moieties and a flexible oxyethylene chain within the macrocyclic ring.[1] Crownophanes with phenolic moieties have several interesting properties such as being a highly selective sodium ionophore.[2–9] Recently reported tandem Claisen rearrangement reactions[10–13] have attracted much interest, since this type of reaction provides a simple route to crownophanes with phenolic moieties from macrocyclic 1,1-bis(aryloxymethyl)ethylene derivatives with an oxyethylene chain. The conformational preference of macrocyclic 1,1-bis(aryloxymethyl)ethylene derivatives, which are also crownophanes, is important for the understanding of their three dimensional structures, host–guest binding affinities as well as for the control of tandem Claisen rearrangement reaction.

Recently Nagawa and coworkers reported that two crownophanes [macrocyclic 1,1-bis(2-naphthyloxymethyl)ethylene derivatives **1** and **2**, see Fig. 1] have completely different conformations in their crystal forms.[14] The terminal methylene unit of **1** directs toward the inside of the ring cavity (in-conformation), while that of **2** directs to the outside (out-conformation). The only difference between the two crownophanes is the ring size; the crownophane **1** has one additional oxyethylene unit. The crystal structures of the crownophanes suggest that the ring size of **2** is too small to have the in-conformation. On the other hand it is still not certain why **1** prefers the in-conformation. They reported that the crownophane **1** has short CH–O contacts in the crystal and that the short contacts suggest that CH–O interactions[15–20] play an important role in the determination of the conformational preference of crownophane **1**. Detailed information on the conformational energies of the crownophane core unit [1,1-bis(aryloxymethyl)ethylene] is important for the understanding of three dimensional structures of crownophanes and the role of weak nonbonding interactions such as the CH–O interaction. It is not an easy task to measure small energy differences among rotamers by experimental methods. Fortunately, however, it has been reported that high level *ab initio* calculations provide sufficiently accurate conformational energies of small organic molecules.[17,21,22] In this study we have calculated relative energies of rotamers of model compounds (Fig. 2, **3**–**7**) to understand the conformational preference of the crownophane core unit. We have also discussed the roles of weak nonbonding interactions such as the CH–O and CH–π[23–27] interactions for the conformational preference of the core unit. In



1 **2** (out-conformation)

Fig. 1 The crystal structures of crownophanes **1** and **2** (see Ref. 14).

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† Electronic supplementary information (ESI) available: conformational details. See http://www.rsc.org/suppdata/p2/b1/b104199c

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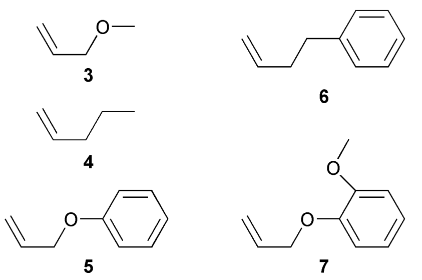


Fig. 2 Model compounds of the crownophane core unit (**3**–**7**) considered in this work.

addition we have carried out HF and DFT calculations of in- and out-conformations of crownophane **2** to understand why this crownophane prefers the out-conformation. Although these calculations cannot evaluate environmental effects, they provide useful information for the understanding of the conformations of crownophanes.

Computational methods

The Gaussian 98 program[28] was used for the *ab initio* molecular orbital calculations. The basis sets implemented in the program were used. The rotamer geometries of the model compounds were optimized at the HF/6-311G** level.[29] Electron correlation was corrected by the second order Møller–Plesset perturbation (MP2) method[30,31] and by the coupled cluster method using single and double substitutions with non-iterative triple excitations (CCSD(T)).[32] The relative energies of the rotamers were calculated at the MP2/6-311G** level, unless otherwise noted. The contributions of the zero-point energy, the thermal energy and entropy were not considered.[33–36] The geometries of the in- and out-conformations of crownophane **2** and 1,1-bis(3-methoxy-2-naphthyloxymethyl)ethylene were optimized at the HF/6-31G* level. Density functional theory (DFT) calculations with Becke's 3 parameter functional combined with Lee, Yang and Parr's correlation functional (B3LYP)[37,38] and with Perdew and Wang's exchange and correlation functionals (PW91)[39] were carried out for the evaluation of the relative stability of the two conformations of **2**. Atomic charge distributions were calculated by electrostatic potential fitting according to the scheme of Merz–Singh–Kollman[40,41] using the MP2/6-311G** wave functions.

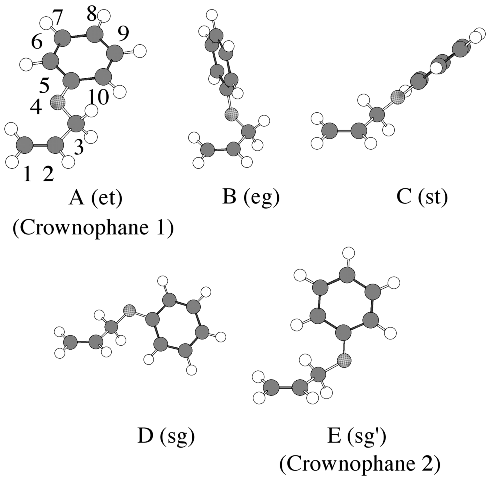
Results and discussion

Effects of basis set and electron correlation

The relative energy of the rotamers B and D of prop-2-enyl phenyl ether **5** (Fig. 3) was calculated by the HF and MP2 methods using several basis sets to evaluate basis set effects. For all the calculations the rotamer B is more stable than the rotamer D. The calculated energy differences at the HF level using 6-31G*, 6-311G*, 6-311G** and 6-311G(2d,2p) basis sets are 0.76, 0.79, 0.77 and 0.76 kcal mol^{-1}, respectively. Those calculated at the MP2 level are 0.88, 0.99, 0.85 and 1.17 kcal mol^{-1}, respectively. The basis set effects are not large (less than 0.4 kcal mol^{-1}). Electron correlation slightly increases the energy difference. The effects of higher electron correlation correction beyond MP2 are very small. The CCSD(T)/6-31G* level energy difference (0.90 kcal mol^{-1}) is close to the MP2/6-31G* one (0.88 kcal mol^{-1}).

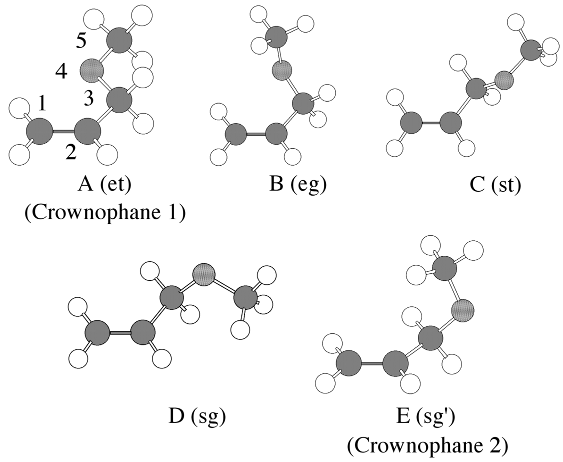
3-Methoxyprop-1-ene (3) and pent-1-ene (4)

The geometries of the five rotamers of 3-methoxyprop-1-ene **3** (Fig. 4) were optimized. The C1=C2–C3–O4 bond has eclipse or skew conformations in these equilibrium rotamers as in the case of the stable conformations of but-1-ene.[42–44] The calculated torsional angles of the C1=C2–C3–O4 bond in the rotamers A–E are 0.0°, 10.2°, 130.6°, 125.0° and 130.2°, respectively. The torsional angles of the C2–C3–O4–C5 bond are 180.0°, 86.8°, 177.1°, 83.5° and −74.0°, respectively. The calculated relative energies of the rotamers are summarized in Table 1. Although rotamer **E** is the most stable of the five rotamers, the calculated energy differences of the four rotamers **A**, **B**, **C** and **E** are very small.



A (et)
(Crownophane 1)
B (eg)
C (st)
D (sg)
E (sg')
(Crownophane 2)

Fig. 3 The optimized geometries of five rotamers of prop-2-enyl phenyl ether **5** at the HF/6-311G** level. The conformation of rotamer **A** is the same as that of crownophane **1**. The conformation of rotamer **E** is the same as that of crownophane **2**.



A (et)
(Crownophane 1)
B (eg)
C (st)
D (sg)
E (sg')
(Crownophane 2)

Fig. 4 The optimized geometries of the five rotamers of 3-methoxyprop-1-ene **3** at the HF/6-311G** level. The conformation of rotamer **A** is the same as that of crownophane **1**. The conformation of rotamer **E** is the same as that of crownophane **2**.

The C1=C2–C3–O4 bonds of the rotamers **C**–**E** have *gauche* conformation. The major difference among the rotamers **C**–**E** are the torsional angles of the C2–C3-O4–C5 bond (*trans*, *gauche* and *gauche′*, respectively). The rotamer **D** (*gauche*) is 1.32 kcal mol^{-1} less stable than **C** (*trans*). This energy difference is close to the *trans*/*gauche* energy difference of ethyl methyl ether (about 1.5 kcal mol^{-1}).[45–47] Surprisingly, the rotamer **E** (*gauche′*) is 1.72 kcal mol^{-1} more stable than **D**. The major difference between these rotamers is the sign of the torsional angles of the C2–C3–O4–C5 bonds (83.5° and −74.0°, respectively), which shows that the torsional energy of this bond is not the cause of the energy difference. The rotamer **E** has a short contact between the methyl group and the C=C bond. The distance between the C2 and H5 (a hydrogen attached to C5) is 2.77 Å; this short contact suggests that the attractive CH–π interaction stabilizes this rotamer. The H5–C2–C1 angle is 104°. The conformer **B** also has a short CH–π contact. The C2 · · · H5 distance is 2.95 Å and the H5–C2–C1 angle is 80.0°.

Table 1 Calculated relative energies of the rotamers of **3**–**7**[a]

Molecule		**A** (et)[b]	**B** (eg)	**C** (st)	**D** (sg)	**E** (sg′)[c]
3-Methoxyprop-1-ene	**3**	0.07	0.43	0.40	1.72	0.0
Pent-1-ene	**4**	0.78	1.61	0.12	0.60	0.0
Prop-2-enyl phenyl ether	**5**	0.15	0.0	0.03	0.85	0.22
4-Phenylbut-1-ene	**6**	0.89	2.19	0.38	0.0	0.41
Prop-2-enyl *o*-methoxyphenyl ether	**7**	0.0	0.62	0.43	1.34	0.67

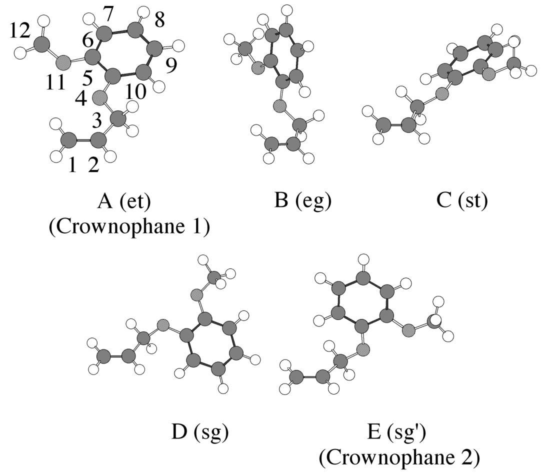
[a] Energies in kcal mol^{-1}. Relative energies were calculated at the MP2/6-311G**//HF/6-311G** level. [b] The conformation of rotamer **A** (eclipse-*trans*) is the same as that of crownophane **1**. [c] The conformation of rotamer **E** (skew-*gauche′*) is the same as that of crownophane **2**.

The energy difference between the rotamers **A** and **B** is 0.43 kcal mol^{-1}, the major difference between the two rotamers again being the conformation of the C2–C3–O4–C5 bond (*trans* and *gauche*, respectively). The energy difference is substantially smaller than the *trans*/*gauche* energy difference of ethyl methyl ether (about 1.5 kcal mol^{-1}),[45–47] which suggests that the CH–π interaction also stabilizes the rotamer **B**. *Ab initio* calculations of model systems of the CH–π interaction have been reported.[26,27] Recently reported high level *ab initio* calculations show that the interaction energies of benzene–methane and benzene–ethylene complexes are −1.45 and −2.06 kcal mol^{-1}, respectively.[27]

The relative energies of the five rotamers (**A**–**E**) of pent-1-ene **4** were compared to those of **3** in order to evaluate the effects of the oxygen atom of **3**. The calculated relative energies of **4** are summarized in Table 1. The calculated C1=C2–C3–C4 torsional angles of **4** are 0°, 10.8°, 119.6°, 115.4° and 122.5°, respectively. The C2–C3–C4–C5 torsional angles are 180°, 72.9°, 178.4°, 64.8° and −66.9°, respectively. The rotamers **A** and **B** of **4** are substantially less stable than rotamers **C** and **E**, while the energy differences among rotamers **A**, **B**, **C** and **E** of **3** are very small. These results indicate that the oxygen atom of **3** stabilizes the rotamers **A** and **B**. The distances between O4 and H1 in the rotamers **A** and **B** of **3** are 2.46 and 2.56 Å, respectively. The distances between C4 and H1 in the two rotamers of **4** are 2.71 and 2.77 Å, respectively. The shorter interatomic distances in the two rotamers of **3** suggest the existence of an attractive CH–O interaction. The calculated charge distribution in **3** indicates the existence of an attractive electrostatic interaction between O4 and H1. The calculated atomic charge distributions of O4 in the rotamers **A** and **B** are −0.25 and −0.35 e (1 e = 1.602 × 10^{-19} C), respectively. Those of H1 are 0.13 and 0.18 e, respectively. Recently Gu *et al.* reported *ab initio* calculations of model systems of the CH–O interaction.[20] From MP2/aug-cc-pVDZ level calculations the interaction energies of H_2O–CH_4, H_2O–CH_3F and H_2O–CH_2F_2 complexes were determined to be −0.43, −1.23 and −2.24 kcal mol^{-1}, respectively.

Prop-2-enyl phenyl ether (5) and 4-phenylbut-1-ene (6)

The calculated relative energies of the five rotamers of prop-2-enyl phenyl ether **5** (Fig. 3) are summarized in Table 1. The energy differences among the rotamers are very small. The calculated C1=C2–C3–C4 torsional angles are 0.0°, 3.6°, 129.4°, 127.4° and 141.4°, respectively, whilst the C2–C3–C4–C5 torsional angles are 180.0°, 92.4°, 177.2°, 84.4° and −81.2°, respectively. The phenyl ring is nearly coplanar with the C3–O4 bond in these rotamers as in the case of stable conformation of anisole.[48–50] The rotamers **B** and **E** have a short C2 · · · H6 contact as in the case of the short C2 · · · H5 contact in **3**. The C2 · · · H6 distances in the rotamers **B** and **E** of **5** are 2.86 and 2.83 Å, respectively. The rotamers **B** and **D** have additional short CH–π contacts. The H1 · · · C5 distance of the rotamer **B** and the H2 · · · C6 distance of the rotamer **D** are 3.05 and 2.98 Å, respectively. Comparison of the calculated relative energies of the rotamers of **5** with those of **3** indicates that the phenyl group of **5** stabilizes the rotamers **B** and **D**. The calculated energy difference between the rotamer **C** and **E** of **5** is only 0.19 kcal mol^{-1}, which is considerably smaller than the *trans*/*gauche* energy difference of ethyl methyl ether (about 1.5 kcal mol^{-1}).[45–47] These results indicate that CH–π interaction plays an important role in the determination of relative stability of rotamers.



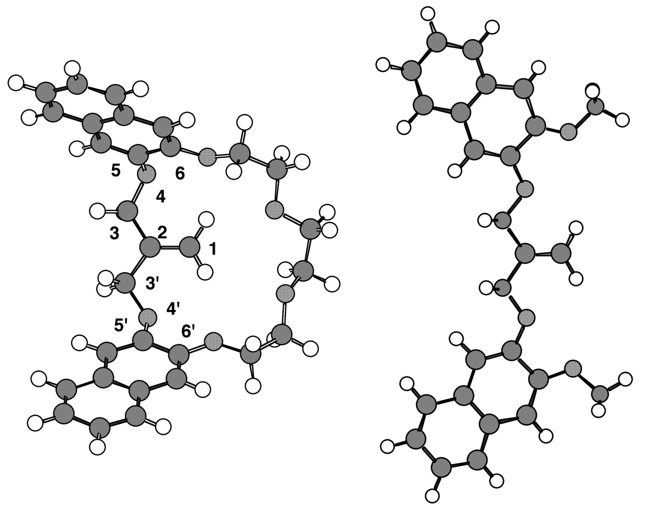
A (et)
(Crownophane 1)
B (eg)
C (st)
D (sg)
E (sg')
(Crownophane 2)

Fig. 5 The optimized geometries of five rotamers of prop-2-enyl *o*-methoxyphenyl ether **7** at the HF/6-311G** level. The conformation of rotamer **A** is the same as that of crownophane **1**. The conformation of rotamer **E** is the same as that of crownophane **2**.

The calculated relative energies of the five rotamers of 4-phenylbut-1-ene **6** are shown in Table 1. The rotamers **A** and **B** of **6** are less stable than the other rotamers in contrast to **5**, which shows that the CH–O interaction between H1 and O4 stabilizes the rotamers **A** and **B** as in the case of **3**. The phenyl ring is nearly perpendicular to the C3–C4 bond in the five rotamers of **6** as in the case of the stable conformation of ethylbenzene.[51,52]

Prop-2-enyl *o*-methoxyphenyl ether (7)

The relative energies of the five rotamers of prop-2-enyl *o*-methoxyphenyl ether **7** (Fig. 5) were calculated to evaluate the effect of the *ortho*-methoxy group of **7**. The calculated relative energies are summarized in Table 1. The calculated C1–C2–C3–O4 torsional angles are 0.0°, 3.1°, 130.9°, 128.1° and 142.0°, respectively, and the calculated C2–C3–O4–C5 torsional angles are 180.0°, 97.8°, 176.5°, 85.6° and −81.9°, respectively. The rotamer **A** is the most stable among the five rotamers. Comparison of the calculated relative energies of **7** with those of **5** shows that the *ortho*-methoxy group stabilizes the rotamer **A**. The optimized geometry of the rotamer **A** of **7** suggests the existence of an attractive CH–O interaction between the methoxy group and the terminal methylene group (C1); the H1 · · · O11 distance in rotamer **A** is 3.45 Å. The H1 · · · C6 distance in the rotamer **A** of **7** (4.10 Å) is slightly shorter than that of **5** (4.13 Å). The calculated charge distributions of **7** indicate the existence of an attractive electrostatic interaction between H1 and O11. The atomic charge distributions on H1 and O11 of this rotamer are 0.13 and −0.29 e, respectively.



2 (in-conformation) **8**

Fig. 6 The optimized geometries of the in-conformation of **2** and 1,1-bis(3-methoxy-2-naphthyloxymethyl)ethylene **8**.

Conformation of crownophanes 1 and 2

The conformational analysis of the model compounds indicates that the CH–π and CH–O interactions change the relative energies of rotamers substantially (1–2 kcal mol^{-1}), which indicates that weak interactions play important roles in the conformational preference of the crownophane core unit. Although there are many factors that may contribute to the conformations of crownophanes, the conformational preference of the core unit would be one of the important factors that determine the conformation of crownophanes.

The crystal structure of crownophane **1** (Fig. 1)[14] shows that the terminal methylene group (C1) directs toward the inside of ring cavity (in-conformation). It was reported that short C1 · · · O4 and C1 · · · O11 interatomic distances (2.73 and 3.95 Å, respectively) indicate the existence of CH–O hydrogen bonds. Our conformational analysis of the model compounds also shows that the in-conformation of crownophane **1** is stabilized by the CH–O interaction. In addition the C1 · · · O14 CH–O interaction further stabilizes this conformation. The conformational analysis indicates that the observed out-conformation of the crownophane **2**, in which the terminal methylene group directs toward the outside, is stabilized by the CH–π interaction.

The conformational analysis of **7** shows that the rotamer **A** is the most stable. The conformation of this rotamer (eclipse-*trans*) corresponds to the structure of crownophane **1** (in-conformation) in the crystal (Fig. 1). The conformation **E** of **7** (skew-*gauche'*), which corresponds to the structure of crownophane **2** (out-conformation), is slightly less stable than the conformation **A** (0.67 kcal mol^{-1}). The small energy difference suggests that other factors such as geometrical constraint may change the relative stability of conformations of crownophanes easily.

The energy difference between the in- and out-conformations of **2** (Fig. 6) was calculated by HF and DFT methods as summarized in Table 2. The calculations show that the out-conformation is about 3 kcal mol^{-1} more stable. The optimized geometry shows that the in-conformation has significant strain due to the small ring size, which is the reason for the observed out-conformation in the crystal. The optimized structure of 1,1-bis(3-methoxy-2-naphthyloxymethyl)ethylene **8** (Fig. 6) shows that this unit prefers a planar structure. Previously reported conformational analyses of anisole shows that the C–C–O–C bond prefers a planar conformation and that the internal rotational barrier height is about 3 kcal mol^{-1}.[48–50] This unit of **1** has a nearly planar structure in the crystal (Fig. 1). However this unit is highly distorted in the in-conformation of **2** (Fig. 6). The C3–O4–C5–C6 and C3′–O4′–C5′–C6′ torsional angles in the optimized geometry are 122.7° and −138.1°, respectively.

Table 2 Calculated energy difference between in- and out-conformations of **2**[a]

Basis set	HF	B3LYP	PW91
6-31G*	3.12	3.24	3.32
6-311G**	2.60	3.04	3.21

[a] Energies in kcal mol^{-1}. Calculated energies of in-conformation relative to out-conformation (Fig. 1 and 6). Geometries of two conformations were optimized at the HF/6-31G* level.

Conclusion

The conformational analysis of model compounds of the crownophane core unit (**3**–**7**) indicates that CH–O and CH–π interactions play important roles in the determination of the conformational preference of the core unit. The crownophane **1** has the in-conformation in the crystal, in which the C1=C2–C3–O4 and C2–C3–O4–C5 bonds have eclipse-*trans* conformations. The conformational analysis of model compounds indicates that the eclipse-*trans* conformation is stabilized by H1 · · · O4 and H1 · · · O11 CH–O interactions. The crownophane **2** has the out-conformation in the crystal form, in which the C1=C2–C3–O4 and C2–C3–O4–C5 bonds have the skew-*gauche'* conformation. The skew-*gauche'* conformation is stabilized by the CH–π interaction. The conformational analysis of model compound **7** shows that the eclipse-*trans* conformation is slightly more stable than the skew-*gauche'* conformation. Although these bonds have skew-*gauche'* conformation in the out-conformation of **2**, the calculated energies of the in- and out-conformations of **2** show that the out-conformation is more stable. The optimized structure of the in-conformation of **2** shows that this conformation has a large strain due to the small ring size. This strain is the cause of the observed out-conformation of **2** in the crystal.

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