HETEROCYCLES, Vol. 74, 2007, pp. 763 - 769. © The Japan Institute of Heterocyclic Chemistry
Received, 31st August, 2007, Accepted, 31st October, 2007, Published online, 2nd November, 2007. COM-07-S(W)60

TWIST ANGLES AND TORSIONAL POTENTIALS OF 2,2'-BIBENZOTHIOPHENE, 2,2'-BIINDOLE, AND 2,2'-BIBENZOFURAN

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Abstract – Twist angles and torsional potentials of 2,2'-bibenzothiophene (**bi-BT**), 2,2'-biindole (**bi-BP**), and 2,2'-bibenzofuran (**bi-BF**) were obtained using HF/6-31G(d) methods. Due to the effect of fused benzene rings, both compounds were revealed to have higher rotational barriers and more planar structures at energy minima than 2,2-bithiophene (**bi-T**), 2,2'-bipyrrole (**bi-P**), and 2,2'-bifuran (**bi-F**), respectively. Calculations on 2,2'-binaphtho[2,3-*b*]thiophene (**bi-BBT**), 2,2'-bibenzo[*h*]indole (**bi-BBP**), and 2,2'-binaphtho[2,3-*b*]furan (**bi-BBF**) were also conducted to study the effect of an additional fusion of another benzene ring.

INTRODUCTION

Recently, various π oligomers with π conjugation extended throughout the whole molecule have been investigated.[1] For an efficient extension of π conjugation systems, it is necessary to arrange the π orbitals in parallel.[2] Therefore, in the case of oligo(paraphenylene), π conjugation is not expected to be extended, because the biphenyl moiety is twisted due to steric repulsion of ortho hydrogen atoms (it is known that the dihedral angle of biphenyl in the gas phase is about 45 °[3]).

There are several methods to avoid steric repulsion of ortho hydrogens and achieve increased planarity of the π conjugation system. One approach is the use of an appropriate π spacer such as in oligo(paraphenylene acetylene).[4] The acetylene groups linking the paraphenylene moieties in this structure reduce the steric repulsion of ortho hydrogen atoms while preserving π conjugation between adjacent benzene rings. As a result the structure of oligo(paraphenylene acetylene is planar and with a fully extend π conjugation. In the second strategy, the bridging by covalent bonds may lock the

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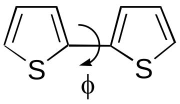
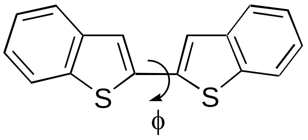
Dedicated to Professor Dr. Ekkehard Winterfeldt on the occasion of his 75th birthday molecular structure in a planar conformation. Oligo(paraphenylene) bridging imino group is well known in the literature,[5] and the electronic absorption spectra of this compound displayed a significant bathochromical shift, which is a strong indication for π conjugation. Finally, the third method employs heterocycles which possess no or only one hydrogen atom at the "ortho" position. Indeed, both theoretical[6,7] and experimental[8] studies showed that both 2,2'-bithiophene (**bi-T**), 2,2'-bipyrrole (**bi-P**), and 2,2'-bifuran (**bi-F**) have highly or considerably planar structures at energy minima.



2,2'-bithiophene (**bi-T**)



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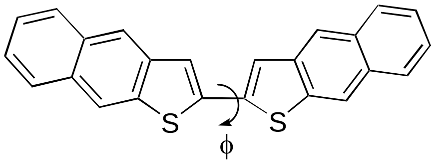
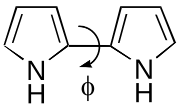
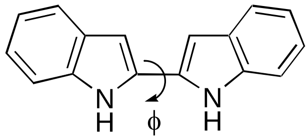


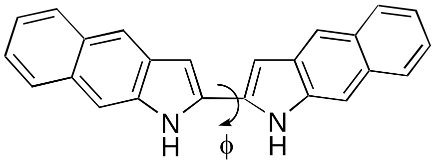
2,2'-binaphthothiophene (**bi-BBT**)



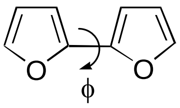
2,2'-bipyrrole (**bi-P**)



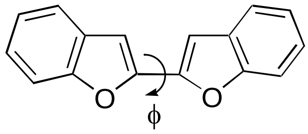
2,2'-biindole (**bi-BP**)



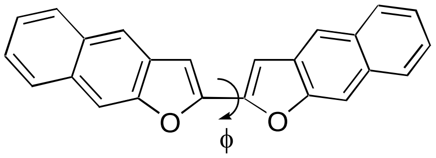
2,2'-bibenzoindole (**bi-BBP**)



2,2'-bifuran (**bi-F**)



2,2'-bibenzofuran (**bi-BF**)



2,2'-binaphthofuran (**bi-BBF**)

Prediction of twist angle at potential minima and torsional potential would be quite useful for the molecular design. However, such predictions are rather difficult even by higher-level calculations because it often fails to accurately reproduce the experimental values.[9] On the other hand, it appears to be important to compare the behavior of a series of compounds by means of the identical calculation method.[10] In this study, torsional potentials of 2,2'-bibenzothiophene (**bi-BT**), 2,2'-biindole (**bi-BP**), and 2,2'-bibenzofuran (**bi-BF**) have been calculated by HF/6-31G(d) methods and compared to those of **bi-T**, **bi-P**, and **bi-F**,[6] respectively. It is expected that energy minima of **bi-BT**, **bi-BP**, and **bi-BF** should be more planar due to enhanced electronic interaction of π conjugation systems by the fusion of additional benzene rings. In addition, calculations on 2,2'-binaphtho[2,3-*b*]thiophene (**bi-BBT**), 2,2'-bibenzo[*h*]indole (**bi-BBP**), and 2,2'-binaphtho[2,3-*b*]furan (**bi-BBF**) have also been conducted in order to predict twist angles at potential minima, which would provide further insight to the effect of a larger ring system.

RESULTS AND DISCUSSION

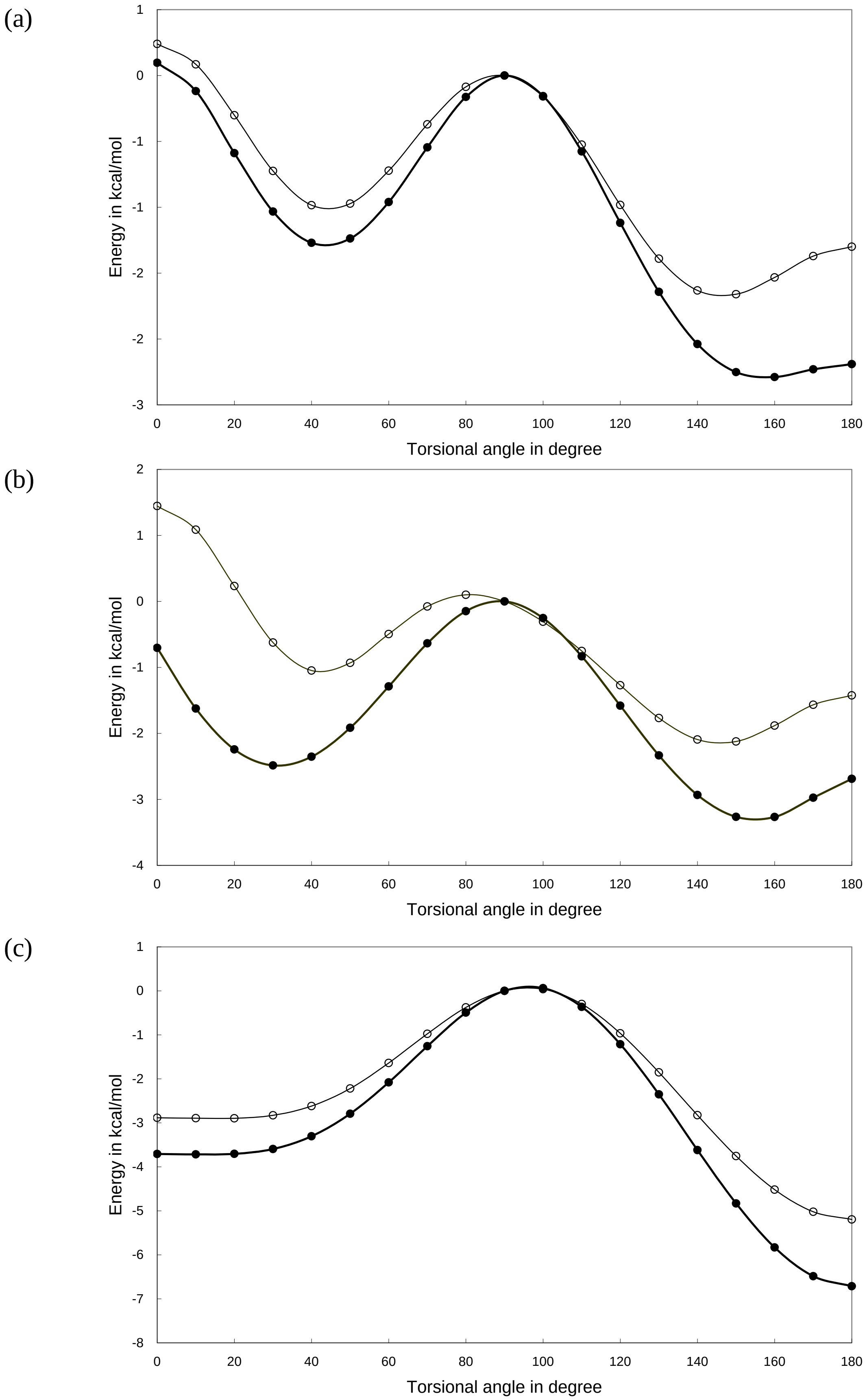


Figure 1. Torsional potential of (a) **bi-T** (open circle) and **bi-BT** (filled circle), (b) **bi-P** (open) and **bi-BP** (filled), and (c) **bi-F** (open) and **bi-BF** (filled) as obtained SCF using the 6-31G(d) basis.

Figure 1 shows torsional potentials of **bi-T**[6] and **bi-BT** (a), **bi-P**[6] and **bi-BP** (b), and **bi-F**[6] and **bi-BF** (c). The potential energy (ΔH) is defined as the difference in energy of the conformation at a given torsion angle and when ϕ = 90 °, where ϕ is the torsional angle of X-C-C-X (X = S, NH, or O), because π electronic interaction between two aromatic rings is essentially zero at ϕ = 90 °. When torsion angle is moved rotated from 90 °, the π electronic interaction is generated, and steric repulsion arises simultaneously. Although magnitude of the π electronic interaction may be dependent on the presence of a polyaromatic system, steric repulsion would have little or no effect essentially because the fused benzene rings resides far from the aryl-aryl bond. Therefore, different behavior between **bi-T** (or **bi-P**, **bi-F**) and **bi-BT** (**bi-BP**, **bi-BF**) should be explained in terms of π electronic effect of the fused benzene ring. Indeed, no significant change of structural parameters such as bond length, bond angle, and torsional angle was observed in thiophene (or pyrrole, furan) moiety between **bi-T** (**bi-P**, **bi-F**) and **bi-BT** (**bi-BP**, **bi-BF**), respectively.

With respect to all torsion angles except 90 °, ΔH of **bi-BT** is larger than that of **bi-T**. The same behavior was observed between **bi-BP** and **bi-P**, and **bi-BF** and **bi-F**. But interestingly, the magnitude of the stabilization is different. In **bi-T** and **bi-BT**, torsional potentials are rather similar in shape. Both have two energy minima at syn-gauche conformation and anti-gauche conformation, the latter being a little more (< 1 kcal/mol) stable (Figure 1a). They also have two saddle points at 0 ° and 90 ° in common, the height of which are almost the same. Notably, as the molecular structure changes from the right-angle form (ϕ = 90 °) to the anti-planar form (180 °), ΔH of **bi-BT** increase more than that of **bi-T**. This should be attributed to the great stabilization effect of benzothiophenes on π conjugation. A similar situation was observed when torsion angle moved from 90 ° to 0 °, but the maximum difference between ΔH's of **bi-T** and **bi-BT** was smaller (0.3 kcal/mol at 40 °) in this range than from the ϕ = 90 ° - 180 ° range, where it was 0.9 kcal/mol at 180 °. Figure 1 also indicates that torsional angles at syn-gauche energy minima are close between **bi-BT** and **bi-T** although those at anti-gauche minima rather are distant. Table 1 shows the ϕ's at energy minima, those being almost the same at syn-gauche minima (45 ° for **bi-T**, 44 ° for **bi-BT**), where different by 10 ° at anti-gauche minima (147 ° for **bi-T**; 157 ° for **bi-BT**). This asymmetrical behavior may be explained in terms of dipole moment. It is reported that the dipole moment of benzothiophene (0.83 Debye) is larger than that of thiophene (0.54 Debye).[11] Thus, syn or syn-gauche conformation, where dipole moments of two aryl rings lie in parallel, is energetically disadvantageous relative to anti or anti-gauche conformation, where dipole moments lie in anti-parallel.

In contrast to the small increase (< 1 kcal/mol) of ΔH in **bi-BT** relative to **bi-T**, effect of the benzene ring is larger in **bi-BP**, and the maximum difference of ΔH between **bi-BP** and **bi-P** was 2.7 kcal/mol (at ϕ = 20 °) (Figure 1b). This is probably due to the non-planar structure of the benzopyrrole and pyrrole moiety in **bi-BP** and **bi-P** respectively, which bears an N-H group contributing to either N-H/N-H or N-H/C-H (at the 3-position) repulsion in steric and/or electrostatic manner. In fact, the N-H hydrogen was found to lie out from the pyrrole ring (15 °) in **bi-P**.[6] The distortion of the molecular skeleton is likely to affect significantly on π conjugation system in **bi-P**, while rather smaller in **bi-BP** because the extended π system can disperse the disadvantage arisen from the torsional structure. As a result, the large stabilization effect of fusion of benzene ring was realized in **bi-BP**. Due to the extension of π conjugation, **bi-BP** also adopts a more planar structure at energy minima. In syn-gauche minimum, the torsional angle of **bi-BP** (31 °) was by 11 ° smaller than that of **bi-P** (42 °), and in anti-gauche minimum **bi-BP** (ϕ = 155 °) was flattened by 9 ° relative to **bi-P** (146 °).

Table 1.Torsional angles (°) at the potential minima of **bi-T**, **bi-BT, bi-BBT, bi-P**, **bi-BP, bi-BBP, bi-F**, **bi-BF, and bi-BBF**. Calculated dipole moments are in parentheses.

	opt			opt			opt	
	syn	anti		syn	anti		syn	anti
bi-T[a]	45(2.74)	146(0.51)	**bi-P**[a]	42(2.69)	146(1.14)	**bi-F**[a]	15(1.20)	180(0.00)
bi-BT	44(1.88)	157(0.48)	**bi-BP**	31(1.63)	155(1.03)	**bi-BF**	0(1.56)	180(0.00)
bi-BBT	44(1.98)	179(0.03)	**bi-BBP**	33(1.40)	160(0.65)	**bi-BBF**	0(2.36)	180(0.00)

[a] ref. 6

In contrast to **bi-F**, which has a very shallow potential minimum at ϕ = 16 °, the local potential minimum of **bi-BF** was found at ϕ = 0 ° (Figure 1c). The global potential minima was commonly observed at ϕ = 180 °. The effect of fusion of benzene ring between **bi-F** and **bi-BF** was similar to that between **bi-T** and **bi-BT** in shape: the stabilization effect was larger for anti and anti-gauche molecules than for molecules in syn and syn-gauche conformation. The difference of ΔH at ϕ = 0 ° and 180 ° between **bi-F** and **bi-BF** (0.8 kcal/mol at ϕ = 0 °, whereas 1.5 kcal/mol at ϕ = 180 °) was larger than between **bi-T** and **bi-BT** (0.3 kcal/mol at ϕ = 40 °, whereas 0.9 kcal/mol at ϕ = 180 °). Figure 1c shows that the saddle point is higher in **bi-BF** than in **bi-F**. This and the fact that two potential minima is where ϕ = 0 ° and 180 °) means the higher planarity of **bi-BF**. It is seen that the shape of torsional potentials of **bi-F** and **bi-BF** is different from those of **bi-T**, **bi-BT**, **bi-P**, and **bi-BP**. This may be explained in terms of smaller van der Waals radius of oxygen atom than that of sulfur and N-H group, by which energetic disadvantage due to interatomic steric repulsion is smaller in **bi-F** and **bi-BF** than the others around the planar conformations (ϕ = 0 ° and 180 °).

We demonstrated that the fusion of benzene ring on heterobiaryl increases π electronic interaction and enhances planarity of the molecular structure at potential minimum. Consequently, we were curious to observe if the molecular structure at potential minimum would become more planar if additional benzene rings are fused. In order to investigate this, we conducted HF/6-31G(d) geometrical optimization of **bi-BBT**, **bi-BBP**, and **bi-BBF**. As shown in Table 1, all compounds have two potential minima. The anti potential minimum of **bi-BBT** was found when ϕ = 179 °. Due to the fusion of naphthalene ring, the molecular structure of **bi-BBT** is virtually planar at potential minimum. However, the torsion angle at syn potential minimum remains to be 44 °. In contrast, the anti potential minimum of **bi-BBP** is at ϕ = 160°, which is significantly larger than the torsion angles at potential minima of **bi-P** and **bi-BP** but essentially far from 180 °. The structure of **bi-BBP** is also non-planar in the syn potential minimum (at which ϕ = 33 °). The reason of these non-planar structures is ascribable to large steric repulsion of S/S for **bi-BBT** and that of N-H/N-H and N-H/C-H (at the 3-position) for **bi-BBP**. In the furan series (**bi-F, bi-BF**, and **bi-BBF**) planar structure at potential minima was already seen in **bi-BF**, and **bi-BBF** showed planar structures at potential minima as well.

In conclusion, this paper described the effects of fusion of benzene ring on 2,2’-heterobiaryl on twist angle at potential minimum and torsional potential using HF/6-31G(d) methods. We revealed that fusion of benzene ring increases π electron interaction of adjacent aryl groups and increases the rotational barrier in the 2,2’-bithiophene, 2,2’-bipyrrole, and 2,2’-bifuran species. The magnitude of the effect varies among each molecule probably due to steric factors. The twist angle at anti potential minima was observed to approach 180 °, therefore that the molecular structure is almost planar, but the effect was relatively small at syn potential minima. The effect of fusion of naphthalene ring was larger than that of benzene and apparently more effective on the anti than the syn conformation. Although the present study employed rather lower-level calculations, the obtained results may be useful for qualitative discussion about the effect of fusion of benzene ring. In order to improve the accuracy of saddle-point energy,[12] theoretical investigations using higher-level calculation are currently in progress.

EXPERIMENTAL

MO calculations were conducted with Spartan PC ’04 software package on Microsoft Window XP. In all calculations HF/6-31G(d) level was employed and C2 molecular symmetry was postulated. For **bi-BT**, **bi-BP**, and **bi-BF**, fully relaxed single-bond torsional potentials were calculated; i.e. for each fixed torsional angle around the central single-bond, all remaining internal degrees of freedom were optimized. A 10 ° grid of points was applied. The obtained energies were least-squares-fitted to a simple analytical form, which has been used by most workers in the field:

$$V(\phi) = \frac{1}{2}\sum_{n=1}^{6} V_n (1 - \cos n\phi) \tag{1}$$

Table 2. Fitted potential parameters for the single-bond torsional potential of **bi-BT**, **bi-BP**, and **bi-BF**[a]

Compound	V_1	V_2	V_3	V_4	V_5	V_6
bi-BT	-1.53	1.09	-0.66	-1.06	-0.10	-0.07
bi-BP	-1.24	2.14	-0.49	-1.61	-0.32	-0.53
bi-BF	-1.43	5.18	-1.58	-0.43	0.01	0.02

[a] All values in kcal/mol.

The coefficients (V_n) are exhibit in Table 2.[13] For **bi-BBT**, **bi-BBP** and **bi-BBF**, fully geometrical optimizations were conducted to find energy minima (syn or syn-gauche form, and anti or anti-gauche form).

ACKNOWLEDGMENTS

Financial support by a Grant-in-Aid for Scientific and Research from the Ministry of Education, Culture, Sports, Science and Technology, is gratefully acknowledged. The authors also express their great appreciation to VBL Research Center and Center of Instrumental Analyses of University of Toyama.

REFERENCES (AND NOTES)

1. U. Bunz, *Chem. Rev.*, 2000, **100**, 1605.
2. D. K. James and J. M. Tour, *Top. Curr. Chem.*, 2005, **257**, 33.
3. A. Almenningen, O. Bastiansen, L. Fernholt, B. N. Cyvin, S. J. Cyvin, and S. Samdal, *J. Mol. Struct. (THEOCHEM),* 1985, **128**, 59.
4. (a) J. S. Moore, *Acc. Chem. Res.*, 1997, **30**, 402, (b) Y. Li, J. Zhao, X. Yin, H. Liu, and G. Yin, *Phys. Chem. Chem. Phys.*, 2007, **9**, 1186, and (c) Y. Karzazi, J. Cornil, and J.-L. Brédas, *Adv. Funct. Mater.,* 2002, **12**, 787.
5. J. M. Tour and J. J. S. Lamba, *J. Am. Chem. Soc.*, 1993, **115**, 4935.
6. A. Karpfen, C. H. Choi, and M. Kertesz, *J. Phys. Chem. A,* 1997, **101**, 7426.
7. (a) G. Raos, A. Famulani, and V. Marcon, *Chem. Phys. Lett.*, 2003, **379**, 364, and (b) G. R. Hutchison, M. A. Ratner, and T. J. Marks, *J. Am. Chem. Soc.*, 2005, **127**, 2339.
8. S. Samdeal, E. J. Samuelsen, and H. V. Volden, *Synth. Metal*, 1993, **59**, 259.
9. J. E. Chadwick and B. E. Kohler, *J. Phys. Chem.*, 1994, **98**, 3631.
10. F. Grein, *J. Phys. Chem., A*, 2002, **106**, 3823.
11. M. G. Grunfest, Y. V. Kolodyazhnyi, V. Udre, M. G. Voronkov, and O. A. Osipov, *Khim. Geterotsikl. Soedin.*, 1970, 448.
12. H. A. Duarte, H. Duani, and W. B. De Almeida, *Chem. Phys. Lett.*, 2003, **369**, 114.
13. To facilitate comparison with the coefficients in ref 6, $V(\phi)$ is defined where $V(0)$ equals to zero.