EFFECT OF FUSED BENZENE RING ON ROTATIONAL BARRIERS OF 2,2'-BIFURAN, 2-PHENYLFURAN, BIPHENYL, AND THEIR BENZO ANALOGUES

Naoto Hayashi,* Yoko Saito, and Hiroyuki Higuchi*

Graduate School of Science and Engineering, University of Toyama, Gofuku, Toyama 930-8555, Japan Email: nhayashi@sci.u-toyama.ac.jp
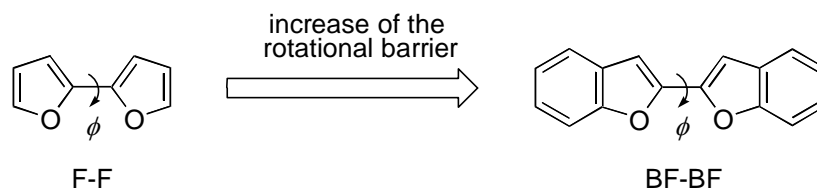
Abstract – Molecular orbital (MO) calculations of torsional potentials of 2,2'-bifuran (**F-F**), 2-(2-furyl)benzofuran (**F-BF**), 2-phenylfuran (**Ph-F**), 2-(2-naphthyl)furan (**Naph-F**), 2-phenylbenzofuran (**Ph-BF**), biphenyl (**Ph-Ph**), 2-phenylnaphthalene (**Ph-Naph**), 2-phenylbenzo[1,2-*b*:4,5-*b*']difuran (**Ph-BDF**), and 2-phenylbenzo[1,2-*b*:5,4-*b*']difuran (**Ph-BDF'**) by using HF/6-31G** and B3LYP/6-31G** methods have revealed that the rotational barriers are increased by 0.4-0.9 kcal/mol by replacement of the aryl moiety on the furan ring (furyl group of **F-F** and phenyl of **Ph-F**) with its benzo analogue. In contrast, increase of the rotational barriers is slight when the aryl moiety on the benzene ring (phenyl groups of **Ph-F** and **Ph-Ph**) is replaced with its benzo analogue and more extended π moiety.

INTRODUCTION

Planarity is one of the most important structural feature of biaryls. For example, oligoarenes comprised of planar biaryl are very frequently employed in material chemistry due to the exteneded π conjugation systems.[1] In biochemistry, the molecular planarity is relating to the cell toxicity because planar molecules can penetrate into the cell and bind to DNA more facilely than non-planar ones.[2] The planarity of biaryl is generally evaluated by energetically favorable torsional angle (minimal point of the potential curve) and the magnitude of the rotational barrier (ΔE_{rot}, which is defined as the energy difference between potential minimum and maximum). In this respect, biphenyl (**Ph-Ph**) is regarded as a non-planar molecule,[3] which bears the torsional angles (ϕ) of 42.50° at the potential minimum and the relatively large rotational barrier

Dedicated to Professor Emeritus Keiichiro Fukumoto on the occasion of his 75th birthday

of 2.17 kcal/mol ($\phi = 0$) calculated by B3LYP/6-311+G* methods[3a] due to steric repulsion of ortho hydrogen atoms. The twisted structure of **Ph-Ph** was supported by electron diffraction study, where ϕ was observed to be $44.1\pm1.2°$.[4] In contrast, 2,2'-bifuran (**F-F**) appears to be more planar because the steric repulsion of ortho hydrogens is significantly reduced therein. In fact, molecular orbital (MO) calculations predicted **F-F** to be almost planar with $\phi = 180°$ at the potential minimum.[5-7] It also bears the potential minimum at $\phi = 16°$ (HF/6-31G*)[5] ~ 37° (MP2/6-311++G**),[6] at which two furan moieties are twisted due to β-H/β-H as well as weaker O/O steric repulsions. It may be noted that molecular structure of 2,2'-bithiophene (**T-T**) is more twisted at the potential minimum than that of **F-F**.[6-8] MO calculations showed that **T-T** bears two potential minima at $\phi = 138°$ ~ 163° and 32° ~ 44°. The less planarity of **T-T** compared to **F-F** should be due to the larger atomic radius of sulfur than oxygen, which gives rise to more significant steric repulsions.

In addition to the steric factors, electronic factors can affect the molecular planarity. In this respect, we recently reported that the rotational barriers of 2,2'-bibenzofuran (**BF-BF**) is by 1~1.5 kcal/mol larger than that of **F-F**.[9] Similar effects of fused benzene moiety on the rotational barrier were found in comparison of **T-T** and 2,2'-bibenzothiophene and of 2,2'-bipyrrole and 2,2'-biindole. The increase of the rotational barriers should not be due to additional steric repulsions as seen in comparison of **F-F** ($\Delta E_{rot} = 5.72$ kcal/mol) and 2,2'-bi(isobenzofuran) (10.59 kcal/mol),[6] but to other factors.

In the present study, effects of fused benzene moiety on the torsional potentials and the rotational barriers of **Ph-Ph** and 2-phenylfuran (**Ph-F**) have been investigated by using MO calculations, and compared to that of **F-F**.

RESULTS AND DISCUSSION

Torsional potentials (Figure 1) of **F-F**, 2-(2-furyl)benzofuran (**F-BF**), **Ph-F**, 2-(2-naphthyl)furan (**Naph-F**), 2-phenylbenzofuran (**Ph-BF**), 2-phenylbenzo[1,2-*b*:4,5-*b*']difuran (**Ph-BDF**), 2-phenylbenzo[1,2-*b*:5,4-*b*']difuran (**Ph-BDF'**), **Ph-Ph**, and 2-phenylnaphthalene (**Ph-Naph**) were calculated by HF/6-31G** and B3LYP/6-31G** methods. The potential energy, ΔE_x, is defined as the energy gap of the conformer whose geometrical parameters are fully optimized and that with fixed ϕ (to be x°). The energies at the global minimum (ΔE_{min}), local minimum ($\Delta E_{min'}$), and maxima (ΔE_{max}) are shown in Table 1.

F-F F-BF Ph-BDF

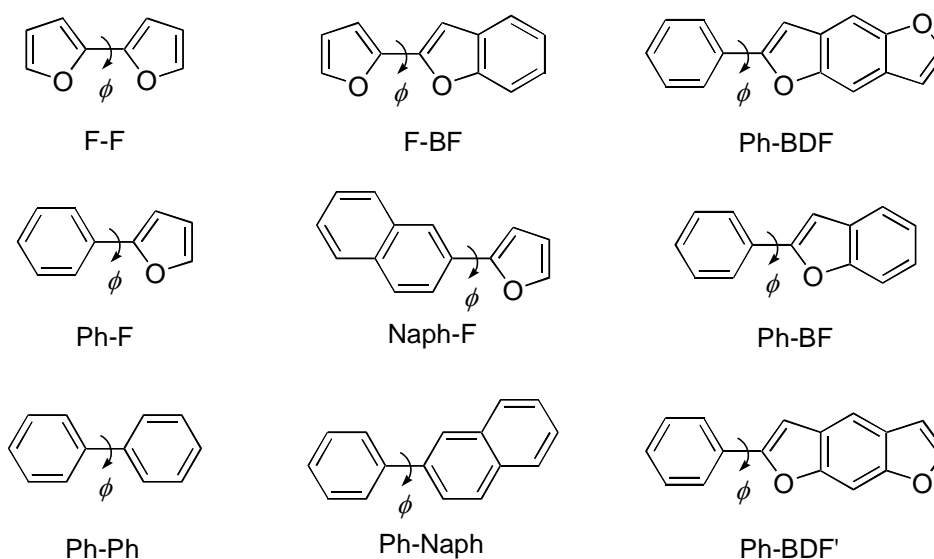Ph-F Naph-F Ph-BF

Ph-Ph Ph-Naph Ph-BDF'

Table 1. Energies (kcal/mol) at the potential mimima and maxima of **F-F**, **F-BF**, **Ph-F**, **Naph-F**, **Ph-BF**, **Ph-BDF**, **Ph-BDF'**, **Ph-Ph**, and **Ph-Naph**. Torsional angles (°) are in parentheses.

Compd	HF/6-31G**				B3LYP/6-31G**			
	ΔE_{min}	$\Delta E_{min'}$	ΔE_{max}		ΔE_{min}	$\Delta E_{min'}$	ΔE_{max}	
F-F	0 (179.96)	2.28 (15.84)	5.26 (100)[a]		0 (179.79)	1.78 (0.24)	5.36 (90)[a]	
F-BF	0 (179.98)	2.61 (11.81)	6.15 (100)[a]		0 (179.94)	2.00 (0.08)	6.28 (90)[a]	
Ph-F	0 (0.00)		4.04 (90)[a]		0 (0.00)		5.41 (90)[a]	
Naph-F	0 (179.95)	0.43 (15.84)	4.46 (90)[a]		0 (179.96)	0.34 (0.85)	5.83 (90)[a]	
Ph-BF	0 (1.63)		4.19 (90)[a]		0 (0.08)		5.45 (90)[a]	
Ph-BDF	0 (3.43)		4.27 (90)[a]		0 (0.13)		5.58 (90)[a]	
Ph-BDF'	0 (2.94)		4.19 (90)[a]		0 (0.17)		5.42 (90)[a]	
Ph-Ph	0 (45.61)		3.52 (0)[a]	1.57 (90)[a]	0 (38.33)		2.07 (0)[a]	2.47 (90)[a]
Ph-Naph	0 (45.34)		3.39 (0)[a]	1.60 (90)[a]	0 (36.78)		2.05 (0)[a]	2.58 (90)[a]

[a]Not optimized.

The calculated torsional potential of **Ph-Ph** was identical to the reported ones in principle[3]: the potential minima are at $\phi \sim 40°$, and by HF calculations the rotational barrier at $\phi = 0°$ (that is, ΔE_0) is larger than that at $\phi = 90°$ (ΔE_{90}), whereas ΔE_0 to be smaller than ΔE_{90} in B3LYP calculations. The reported torsional potential of **F-F**[5-7] was also reproduced by the HF and B3LYP calculations, where in contrast to **Ph-Ph**, the molecular structure of **F-F** was almost planar at the potential minima.

In both HF and B3LYP calculations the rotational barriers of **Ph-Ph** and **Ph-Naph** are very close, the deviations of which are less than 0.13 (HF) and 0.11 kcal/mol (B3LYP). Small effects of fused benzene ring on the torsional potential were reported in comparison of **Ph-Naph** and 2-(2-naphthyl)naphthalene,[10] **Ph-Ph** and **Ph-Naph**,[11] and **Ph-Ph** and 2-(2-naphthyl)naphthalene.[12] In contrast, the torsional potential curves of **F-F** and **F-BF** are significantly different. The rotational barriers of **F-BF** are larger than those

of **F-F** by 0.89 (ΔE_{100} - ΔE_{min}) and 0.56 kcal/mol (ΔE_{100} - $\Delta E_{min'}$) for HF, and by 0.92 (ΔE_{90} - ΔE_{min}) and 0.70 kcal/mol (ΔE_{90} - $\Delta E_{min'}$) for B3LYP calculations. These results are similar to our previous report[9] describing increased rotational barrier of **BF-BF** compared to that of **F-F**.
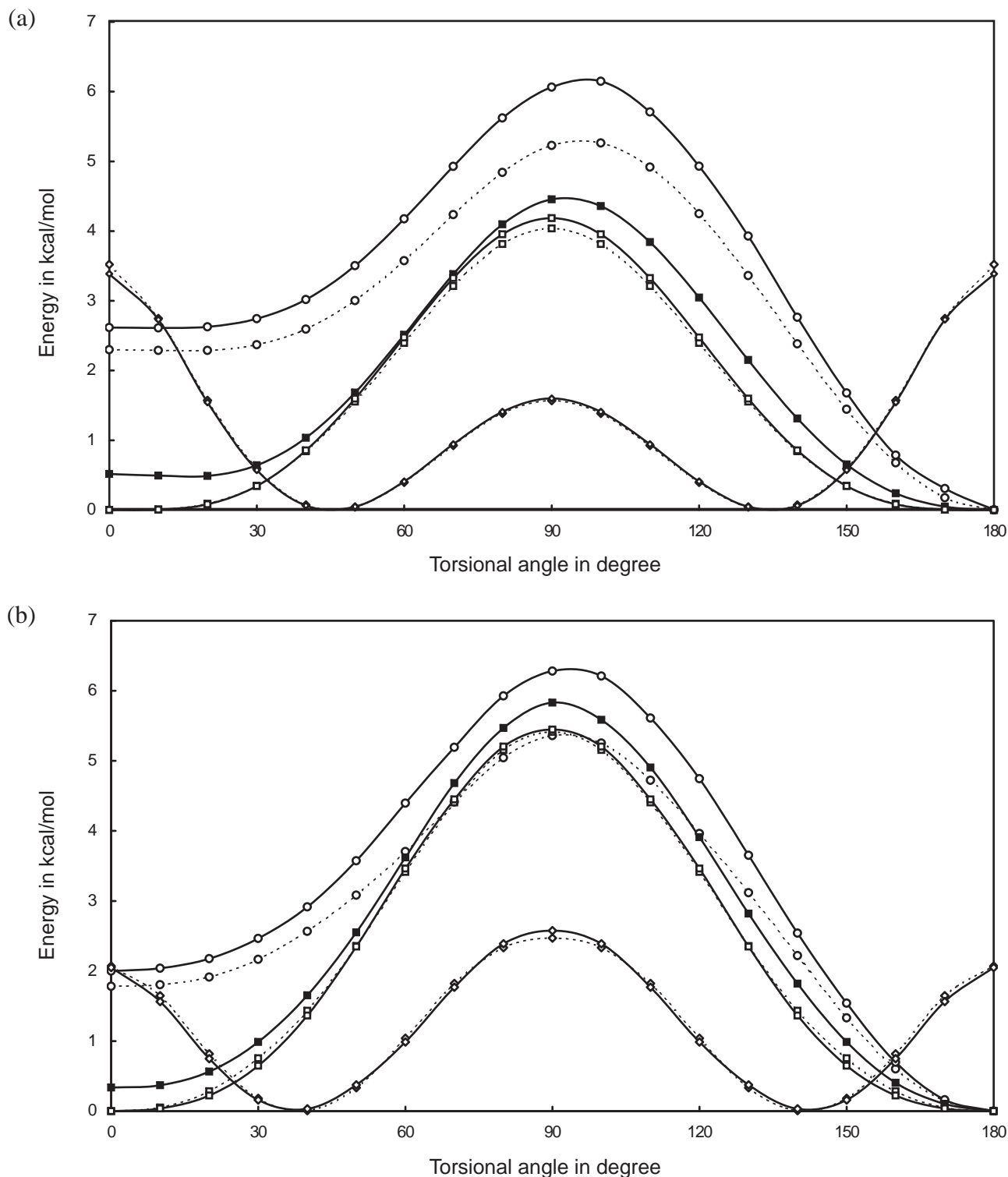

Figure 1. Torsional potentials of **F-F** (open circle/dotted line), **F-BF** (open circle/solid line), **Ph-F** (open square/dotted line), **Naph-F** (filled square/solid line), **Ph-BF** (open square/solid line), **Ph-Ph** (open rhombus/dotted line), and **Ph-Naph** (open rhombus/solid line) as obtained by (a) HF/6-31G** and (b) B3LYP/6-31G** methods.

Noteworthily, the torsional potentials of **Ph-F** and **Ph-BF** are very close with slightly different rotational barriers by 0.05 (HF) and 0.04 kcal/mol (B3LYP), while that of **Naph-F** is considerably different. Comparing to that of **Ph-F**, one rotational barrier (ΔE_{90} - ΔE_{min}) of **Naph-F** is much larger (by 0.42 kcal/mol for HF and B3LYP calculations), whereas the other one (ΔE_{90° - $\Delta E_{min'}$) is comparable with the difference of -0.01 (HF) and -0.02 kcal/mol (B3LYP).

The aforementioned results may be summarized as follows. When the aryl substituent on the furan ring is replaced with its benzo analogue, the rotational barrier increases significantly. This will give rise to the coplanar conformer to be more favorable. In contrast, replacement of the aryl substituent on the benzene ring with its benzo analogue affects the rotational barrier slightly. The latter effect is small, but not zero. Table 2 shows that the rotation barriers of **Ph-F**, **Ph-BF**, **Ph-BDF'**, and **Ph-BDF** become larger in this order (**Ph-F** < **Ph-BF** ~ **Ph-BDF'** < **Ph-BDF**) albeit slightly, indicating large π group may increase the rotational barrier even if it is substituted on the benzene ring.

Obviously, the increased rotational barrier should not be due to additional steric repulsions but to electronic factors. It, however, is not meant to be enhanced double bond character of aryl-aryl bond because as shown in Figure 2 aryl-aryl bond length (d_{Ar-Ar}) is intact on substitution of aryl group with its benzo analogue in **Ph-Ph**, **Ph-F**, and **F-F**. The effect of fused benzene ring on the rotational potentials is presumably ascribable to dipole-dipole and/or dipole-induced dipole interactions of the aryl moieties. The existence of those interactions is suggested by the fact that ΔE_0 and ΔE_{180} of **Naph-F** differ by 0.43 (HF/6-31G**) and 0.34 kcal/mol (B3LYP/6-31G**). The dipole-induced dipole interaction appears to be more important because, although the magnitude of dipole moment differs less significantly between phenyl and naphthyl groups than between 2-furyl and 2-benzofuryl groups, deviation of the torsional potentials is larger in **Ph-F** and **Naph-F** than in **Ph-F** and **Ph-BF**.

Table 2. Potential energies (kcal/mol) of **Ph-F**, **Ph-BF**, **Ph-BDF**, and **Ph-BDF'** calculated by using HF/6-31G** and B3LYP/6-31G** methods.

| ϕ (°)	HF/6-31G**				B3LYP/6-31G**			
	Ph-F	**Ph-BF**	**Ph-BDF**	**Ph-BDF'**	**Ph-F**	**Ph-BF**	**Ph-BDF**	**Ph-BDF'**
0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	-0.08
10	0.01	0.00	0.02	0.01	0.05	0.04	0.05	-0.04
20	0.09	0.08	0.09	0.08	0.28	0.22	0.23	0.15
30	0.35	0.34	0.36	0.35	0.75	0.65	0.65	0.58
40	0.84	0.85	0.88	0.86	1.43	1.36	1.38	1.30
50	1.55	1.60	1.63	1.61	2.36	2.35	2.41	2.31
60	2.40	2.47	2.53	2.48	3.41	3.46	3.54	3.43
70	3.21	3.33	3.39	3.33	4.41	4.45	4.55	4.40
80	3.82	3.95	4.03	3.96	5.16	5.20	5.35	5.21
90	4.04	4.19	4.27	4.19	5.41	5.45	5.58	5.42
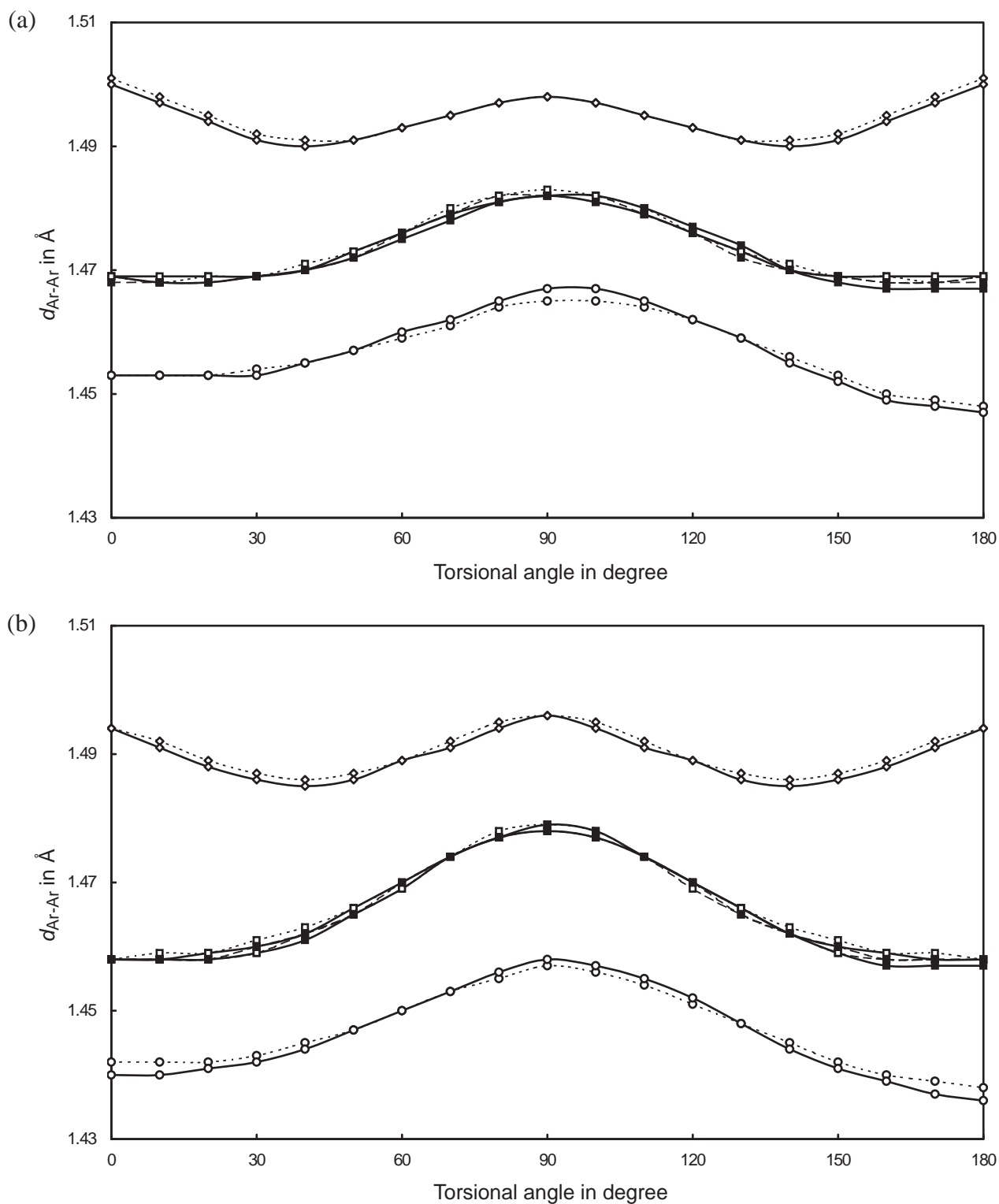
Figure 2. Ar-Ar bond lengthes ($d_{\text{Ar-Ar}}$) of **F-F** (open circle/dotted line), **F-BF** (open circle/solid line), **Ph-F** (open square/dotted line), **Naph-F** (filled square/solid line), **Ph-BF** (open square/solid line), **Ph-Ph** (open rhombus/dotted line), and **Ph-Naph** (open rhombus/solid line) as obtained (a) HF/6-31G** and (b) B3LYP/6-31G** methods.

In conclusion, this paper described the effects of fused benzene ring on heterobiaryl stabilizing planar conformations based on HF/6-31G** and B3LYP/6-31G** calculations. The stabilization effect is larger when aryl moiety substituted on furan ring is replaced with its benzo analogue than when aryl substituent on benzene ring is replaced. The origin of this is not yet clear, albeit the dipole moments of aromatic moiety are likely concerned. The present results will provide a guideline to design oligo(heteroarene)s as a π linker or a molecular wire and useful information to understand structure-properties relationship between heterobiaryls and bioorganism.

EXPERIMENTAL

MO calculations were conducted with Spartan PC '04 software package on Microsoft Window XP . In all calculations HF/6-31G** and B3LYP/6-31G** levels were employed and for **F-F** and **Ph-Ph** C2 molecular symmetry was postulated. For all compounds, fully relaxed single-bond torsional potentials were calculated; i.e. for each fixed torsional angle (ϕ) around the central single-bond, all remaining internal degrees of freedom were optimized. A 10° grid of points was applied. Fully geometrical optimizations were also conducted to find global and local potential minima.

ACKNOWLEDGMENTS

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