J. Phys. Chem. A **2002,** *106,* 3823−3827

Twist Angles and Rotational Energy Barriers of Biphenyl and Substituted Biphenyls

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Received: June 12, 2001; In Final Form: January 29, 2002

Using B3LYP/6-311+G* and other methods, twist angles and torsional energies were obtained for biphenyl (BP), 2-halogen BPs, 2,2′-dihalogen BPs, and 3,3′-dihalogen BPs, the halogens ranging from F to I. The results were compared with available gas phase and X-ray data. 2,2′-difluoro BP has a rotational double minimum, at 57.9 and 128.9°, whereas the other 2,2′-dihalogen BPs have a single minimum at dihedral angles ranging from 84.9 to 94.8°. All 3,3′-dihalogen BPs have a double minimum at about 45 and 135°. Optimized twist angles and energy barriers were also calculated for 2,2′-dimethyl BP and for perfluoro as well as perchloro BP. Most structures are accounted for by steric effects. For 2,2′-dihalogen BPs, however, attractive forces also appear to play a role, as evidenced by the dihedral angle of 2,2′-dichloro BP lying well below 90°.

Introduction

It is well-known that in the gas-phase biphenyl (BP) is twisted, with a dihedral (or twist) angle (ϕ) of about 45° (the most recent electron diffraction value is 44.4 ± 1.2° [1]). In the crystalline state at room temperature (and still at 110° K), biphenyl appears to be planar, which however has been shown to be a statistically centered arrangement, caused by rotation of the two rings in a double minimum potential.[2] As the temperature is lowered, a phase transition occurs (around 40° K), leading to twisted biphenyl with a dihedral angle of about 10°.[3]

The near 45° twist angle in gaseous BP is usually explained as arising from competition between the repulsion of the ortho hydrogens, favoring a 90° twist angle, and the π-electron delocalization effect, preferring a coplanar arrangement.

For steric reasons, it is expected that, both in gas phase and in crystalline form, substitution of two ortho hydrogens by larger atoms or groups leads to a double minimum potential, with the dihedral angle of the syndiagonal form ($30° \leq \phi \leq 60°$) being larger than the BP value of 45°, and ϕ of the antidiagonal form ($120° \leq \phi \leq 150°$) being smaller than 135°, with the antidiagonal structure being lower in energy. Substitution of one ortho hydrogen should lead to an increase of ϕ over the BP value.

According to X-ray data, the twist angle is 57.6° for 2,2′-difluoro BP,[4] 66.5° for 2,2′-dichloro BP,[5] 85.4° for 2,2′-dibromo BP,[6] and 85.3° for 2,2′-diiodo BP.[7] Older electron diffraction (gas-phase) studies gave twist angles of 60,[8] 74, 75, and 79°[9] for the four 2,2′-dihalogen BPs. As one expects, substitution by heavier halogen atoms increases the (syndiagonal) twist angle, with X-ray data ranging from 57.6° for 2,2′-difluoro BP to 85.3° for 2,2′-diiodo BP (practically the same as for 2,2′-dibromo BP) and electron diffraction data ranging from 60 to 79°.

It appears that because of the strong X,X repulsion (X = halogen atom) the twist angle for the heavier halogen atoms approaches 90° in the crystal, and the question arises whether the expected double minimum in such case collapses into a single one, with an orthogonal structure ($60 \leq \phi \leq 120°$) for the 2,2′-diX BP. Also, all observed dihedral angles are smaller than 90°, although steric arguments predict them to be larger than 90°.

Questions about the structure of substituted biphenyls and the reason for such apparent inconsistencies gave rise to the theoretical investigations presented in this paper.

Numerous theoretical studies have been performed on biphenyl. References to work done prior to 1991 are given by Tsuzuki and Tanabe.[10] These authors found, at the HF/6-31G** level, a twist angle of 46.26° and barrier heights of 3.33 kcal/mol at 0° and 1.51 kcal/mol at 90°. (Barrier heights are given with respect to the energy of the most stable conformation. The barrier height at 0° will be denoted as ΔE_0, and that at 90° as ΔE_{90}.)

A complete list of theoretical references for BP is not intended. However, several more recent studies might be mentioned. Rubio et al. [11] found, at the CASSCF/DZP level, a twist angle of 44.3° and, from CASPT2 calculations, barrier heights of 12.93 kJ/mol (3.09 kcal/mol) at 0° and 6.40 kJ/mol (1.53 kcal/mol) at 90°, using a 4s3p1d/2s1p basis set (their highest level). Karpfen et al.,[12] in 1997, studied torsional potentials in conjugated systems, among them BP, comparing ab initio with density functional theory (DFT) results. They found that, in general, DFT methods give too high barriers at 90° and too low ones at 0°, compared to SCF or MP2 results using the same basis set. For BP, always using a 6-31G* basis set, ΔE_0 is 3.3 (46), 3.9 (46), and 2.0 (39) kcal/mol for SCF, MP2, and B3LYP methods, respectively, whereas ΔE_{90} is 1.5, 1.8, and 2.4 kcal/mol. The optimized ϕ's are given in parentheses. Using the 6-311++G(d,p) basis set, ΔE_0 is 3.1 (48) and 2.0 (42) and ΔE_{90} is 1.2 and 1.8 kcal/mol for SCF and B3LYP, respectively. The differences between SCF and B3LYP results decrease with improved basis set.

According to Tsuzuki et al.,[13] ΔE_0 is 2.28 kcal/mol, whereas ΔE_{90} is 2.13 kcal/mol, as obtained by MP2/cc-pVQZ//MP2/6-31G* calculations. Using such a large basis set, ΔE_0 and ΔE_{90} are close in energy and closer to the B3LYP than the MP2 results of Karpfen et al.[12] The optimized dihedral angle is 45.7°.

There is also some theoretical work on substituted BPs. Cioslowski and Mixon[14] obtained, at the HF/6-31G** level, a double minimum with twist angles of 54.7 and 128.7° for 2,2′-

10.1021/jp0122124 CCC: $22.00 © 2002 American Chemical Society
Published on Web 03/19/2002

TABLE 1: Energy Differences (in kcal/mol) for Biphenyl and Ortho Substituted Biphenyls, at Dihedral Angles of 0 (coplanar), 45, and 90° (perpendicular), Relative to the Energy at the Optimal Dihedral Angle ϕ_{Opt}, Given at Bottom[a]

ϕ	biphenyl	2-fluoro	2-chloro	2-bromo	2-iodo[b]
0	2.17	3.04	7.57	8.55	8.31
	3.28	4.36	10.40	11.08	
45	0.02	0.00	0.65	0.93	0.79
	0.00	0.05	1.22	1.26	
90	1.79	1.20	0.39	0.23	0.41
	1.48	1.09	0.18	0.27	
ϕ_{opt}	42.50	45.13	59.87	63.62	60.40
	46.31	49.22	66.54	65.41	

[a] First line, B3LYP/6-311+G*; second line, HF/6-31G*. The total energies at ϕ_{opt} are (in a.u.) −463.405223/−460.253849 for biphenyl, −562.673524/−559.103176 for F, −923.025505/−919.148634 for Cl, −3036.944506/−3029.556615 for Br, and −474.003148 for I. [b] B3LYP/LanL2DZ results.

TABLE 2: Energy Differences (in kcal/mol) for 2,2′-disubstituted Biphenyls, at Dihedral Angles ϕ of 0 (coplanar cis), 45, 90, 135, and 180° (coplanar trans), Relative to the Energy at the Optimal Dihedral Angle ϕ_{opt}, Given at Bottom[a]

ϕ	F,F	Cl,Cl	Br,Br	I,I[b]	M,M
0	10.82	30.11	36.54	43.56	168.77
	12.64	36.36	42.15	53.31	219.27
45	0.79	7.54	10.70	14.75	5.37
	0.90	9.75	11.88	19.26	7.38
90	0.72	0.01	0.00	0.03	0.00
	1.03	0.00	0.30	0.02	0.01
135	0.19	3.38	4.42	4.98	2.82
	0.31	4.64	5.26	7.97	4.52
180	4.79	17.61	19.98	21.74	16.72
	6.12	22.74	24.91	29.37	21.79
ϕ_{opt}	57.87/128.90[c]	84.86	91.54	94.77	90.69
	57.13/128.82	89.66	77.89	92.68	92.16

[a] M,M stands for 2,2′-dimethylbiphenyl. First Line, B3LYP/6-311+G*; second line, HF/6-31G*. The total energies at ϕ_{opt} are (in a.u.) −661.942127/−657.953909 for F, −1382.647634/−1378.045569 for Cl, −5610.485851/−5598.862250 for Br, −484.775191/−481.244416 for I, and −541.935930/−538.322520 for M. [b] LanL2DZ results. [c] For F,F, the 128.90° minimum is 0.09 kcal/mol higher than the 57.87° global minimum. In HF/6-31G*, the 128.82° minimum is 0.19 kcal/mol higher than the 57.13° global minimum.

difluoro BP, with the energy at 128.7° being 0.24 kcal/mol higher than at 54.7°. The energy at 180° (anti) is 6.07 kcal/mol higher than at the global minimum. Pan et al. obtained, at the B3LYP/6-31G** level, a twist angle of 55.89° for 2-chloro BP[15] and of 71.83° for 2,2′-dichloro BP.[16] Bock et al.[7] found for 2,2′-diiodo BP a minimum close to 90°.

In this paper, geometry optimizations will be described for biphenyl, for monosubstituted ortho-halogen BPs, and for the ortho- and meta-dihalogen BPs. For comparison, similar calculations have been performed on 2,2′-dimethyl BP and on perfluoro as well as perchloro BP.

Results and Discussion

Results for Biphenyl and Mono- and Dihalogen Biphenyls. The geometries of BP and the ortho and meta substituted BPs were optimized using the HF/6-31G* and B3LYP/6-311+G* methods, as implemented in Gaussian 98.[17] For iodine, these basis sets are not available and were replaced by LanL2DZ, the Los Alamos effective core potential plus double-ζ. On occasion, other methods and basis sets will be used. Because according to the literature review B3LYP methods led to too low ΔE_0 and too high ΔE_{90}, and too low twist angles for BP, whereas HF methods fared somewhat better, in the following, both B3LYP/6-311+G* and HF/6-31G* results will be given, in this order.

Optimized twist angles and energies at 0°, 45°, and 90°, relative to the global minimum, for biphenyl (D_{2h}, D_2, and D_{2d} symmetries, respectively) and the ortho (mono) substituted halogen BPs (C_s at 0° and C_1 at other angles) are shown in Table 1. (In these and all following cases, the phenyl rings were kept planar.) At this level of theory, the twist angle in biphenyl is 42.5° (46.3), to be compared with an experimental value of 44.4 ± 1.2°.[1] The barrier at 0° is 2.17 (3.28), and at 90°, it is 1.79 (1.48) kcal/mol. The HF/6-31G* results are in full agreement with those of Karpfen et al.[12]

From electron diffraction studies, Almenningen et al.[1] estimated the barrier heights of biphenyl to be 1.4 ± 0.5 kcal/mol for 0° and 1.6 ± 0.5 kcal/mol for 90°. Our 90° values lie in the range of experimental results, as do those obtained by other authors. The problem all along has been the barrier at 0°, being the subject of several discussions in the literature.[10−13] HF, MP2, and CASPT2 methods give a 0° barrier between 3.1 and 3.9 kcal/mol, our HF result included. The exception is the more recent MP2/cc-pVQZ value of 2.28 kcal/mol.[13] Similarly low 0° barriers have been found by B3LYP methods, with values of 2.0 kcal/mol using the 6-31G* or 6-311++G(d,p) basis sets[12] and 2.17 kcal/mol using 6-311+G* (this work). These low barriers lie closer to the experimental result but are still outside the error limits.

As expected, the optimized twist angle increases when replacing an ortho hydrogen by a halogen atom, from the biphenyl angle of 42.5° (46.3) to 45.1° (49.2) for F, 59.9° (66.5) for Cl, 63.6° (65.4) for Br, and 60.4° for I (no HF result). The twist angle for iodine has not increased over that of bromine and actually is close to that of Cl. Such a result is likely in error, because of the change from the 6-311+G* basis set to LanL2DZ for iodine. When performing HF/3-21G* calculations, where the 3-21G* basis set can be maintained throughout the whole series, the optimized twist angles are 45.1° for F, 74.5° for Cl, 70.6° for Br, and 90.1° for I, numbers that decline between Cl and Br but show a large increase for iodine. Obviously, these HF/3-21G* optimized twist angles lack the accuracy achieved in the high-level calculations but may nevertheless indicate a trend toward a larger twist angle for iodine.

The increase in twist angle is particularly pronounced in going from F to Cl (by about 20°). The energies required to force the molecule into a coplanar conformation ($\phi = 0°$) increase from 2.2 (3.3) for BP to 8.5 (11.1) kcal/mol for Br. Again, the lower value for iodine is considered to be in error.

A search for X-ray diffraction data on 2-halogen BP molecules gave twist angles of 55.39 and 52.78° (distorted structure) for 2-fluoro BP, with an average of 54.08°,[18] about 9° (5) higher than calculated.

In Table 2, energies and optimized twist angles are shown for the 2,2′-disubstituted biphenyls. The twist angles present quite an interesting situation. For difluoro BP, there are two minima, at 57.9 (57.1) and 128.9° (128.8), as one would expect for small substituents. Compared with the twist angle of 42.5° (46.3; and 137.5°/133.7) for biphenyl, the increased repulsion between F atoms compared to H atoms causes shifts of 15.4° (10.8) and 8.6° (4.9), respectively, toward 90°. The larger shift on the syn side is caused by the F−F repulsion being stronger than the F−H repulsion. Yet the energy calculated for the 57.9° (57.1) minimum is 0.09 (0.19) kcal/mol lower than for the

128.9° (128.8) minimum, contrary to expectations. Energy differences so small may not be reliable. Another possible reason for such anomaly is the basis set superposition error (BSSE). Because of basis set superposition, the energy at 0° is calculated to be too low (the F atoms are very close) compared to the energy at 180°, where the F atoms are maximally separated. For the BSSE calculations, one fluorine was removed from 2,2′-difluoro BP. The BSSE given is the energy difference between this radical and the radical having the full basis set of the removed F restored, with a nuclear charge zero on F. In ROHF/6-311+G* calculations, the BSSE was found to be about the same over the range of dihedral angles from 0° to 180° (changing by about 0.1 kcal/mol in an irregular pattern. With the 6-31G* basis set, the BSSE is about 0.25 kcal/mol larger at 0° than at 180°). Therefore, the BSSE cannot be used to rationalize the preference of the syn over the anti minimum.

Moving to dichloro BP and the heavier halogens, only a single minimum, around 90°, is found. Interestingly, for dichloro BP, this minimum lies below 90°, at 84.9° (89.7). (Using B3LYP/STO-3G, two minima, at 79.3° and 120.3°, are obtained.) Assuming that the Cl−Cl repulsion is stronger than the Cl−H repulsion, a minimum above 90° would have been expected. For the bromide and iodide compounds, such predictions are borne out, with the dibromo BP minimum at 91.5° (77.9) and the diiodo BP one at 94.8° (92.7). Again, it was investigated whether the BSSE might be able to shift the optimum twist angle of dichloro BP to a value higher than 90°. Here, ROHF/6-311+G* calculations gave a BSSE that is small and again roughly constant over the whole range of ϕ values, and no preference of smaller dihedral angles over larger ones could be seen. On the other hand, the torsional potential around the minimum is extremely shallow, with a calculated energy difference between 85° (close to the minimum) and 95° being only 0.05 kcal/mol (B3LYP/6-311+G*; geometry optimized for each angle). This value is so small that BSSE or other corrections could easily shift the minimum by a few degrees. More on this will be said in the last section.

For all compounds in Table 2, the energy difference relative to the global minimum at 0° (syn) is about twice as large as at 180° (anti). Considering 180° to be the energy barrier for internal rotation, such a barrier is quite small for F (4.8 (6.1) kcal/mol), but much larger for the heavier halogens (17.6 (22.7) to 21.7 (29.4) kcal/mol).

The calculated twist angle for 2,2′-difluoro BP is close to the older experimental gas-phase value of 60°. However, for the heavier halogens, calculated values are 10−15° higher than the experimental ones.

When comparing the optimized twist angles of Table 2 with those in the corresponding crystals, as given in the Introduction, it is seen that ϕ_{opt} for difluoro BP (57.9°/57.1) is very close to the crystal value (57.6°). For the heavier halogens, however, the twist angles in the crystal are below those calculated. The largest discrepancy, of about 20°, is seen for dichloro BP and smaller ones, 6 to 10°, for dibromo and diiodo BP.

In Table 3, 3,3′-disubstituted biphenyls are considered. For each compound, a double minimum occurs, and in each case, the minium around 135° is lower in energy than that around 45°, although by extremely small amounts (less than 0.1 kcal/mol). All energy differences given in Table 3 are small, because the two halogen substituents interact little with each other, even at 0°. Relative to the minimal energy, for all systems in Table 3, the barriers at 0° and 180° (about 2 kcal/mol with B3LYP and about 3 kcal/mol with HF) are virtually the same, whereas the 90° energies are about 1.7 (1.5) kcal/mol. (As before, the iodine compound is an exception.) For 3,3′-dibromo BP, electron diffraction measurements in the gas phase gave a dihedral angle of 43.8° (1.3°)[19] to be compared with our syn value of 43.1° (or 46.8 in HF). (No X-ray data could be found for other 3,3′-dihalogen BP compounds.)

TABLE 3: Energy Differences (in kcal/mol) for 3,3′-disubstituted Biphenyls, at Dihedral Angles of 0 (cis), 45, 90, 135, and 180° (trans), Relative to the Energy at the Optimal Dihedral Angle ϕ_{Opt}, Given at Bottom[a]

ϕ	F,F	Cl,Cl	Br,Br	I,I[b]
0	2.07	2.26	2.29	1.34
	3.05	3.37	3.23	
45	0.04	0.06	0.06	0.29
	0.04	0.07	0.09	
90	1.78	1.72	1.69	3.02
	1.53	1.42	1.44	
135	0.03	0.01	0.00	0.23
	0.00	0.01	0.01	
180	2.01	2.17	2.19	1.24
	2.99	3.25	3.11	
ϕ'_{opt}	0.02	0.05	0.05	0.08
	0.04	0.06	0.08	
ϕ_{opt}	138.32	137.23	136.46	144.30
	134.43	133.39	133.56	
ϕ'_{opt}	42.00	42.89	43.15	35.82
	45.73	46.91	46.77	

[a] ϕ'_{opt} corresponds to a secondary minimum. First line, B3LYP/6-311+G*; second line, HF/6-31G*. The total energies at ϕ_{opt} are (in a.u.) −661.946042/−657.956626 for F, −1382.654119/−1378.053476 for Cl, −5610.493431/−5598.867569 for Br and −484.785527 for I. [b] B3LYP/LanL2DZ results.

The 6-311+G* basis set used in conjunction with the B3LYP method does not have diffuse and polarization functions on the hydrogens (but on all non-hydrogens) and may therefore not correctly represent the torsional potential, especially for the 2,2′-dihalogen series. Test calculations have been performed on 2,2′-difluoro BP and 2,2′-dichloro BP, comparing 6-311+G* with 6-311++G** results. For 2,2′-difluoro BP, B3LYP/6-311++G** gives ΔE values (in kcal/mol) of 10.66 (10.82) at 0°, 0.79 (0.79) at 45°, 0.72 (0.72) at 90°, 0.15 (0.19) at 135°, 4.63 (4.79) at 180°, and 0.07 (0.09) at the secondary minimum (the B3LYP/6-311+G* values of Table 2 are given in parentheses). The optimized dihedral angles are 57.03° (57.87) and 129.01° (128.90). It is seen that all deviations are very small. Similarly small are those for 2,2′-dichloro BP. The ΔE's (in kcal/mol) are 29.87 (30.11) at 0°, 0.01 (0.01) at 90°, and 17.03 (17.61) at 180°, with an optimized dihedral angle of 84.97° (84.86).

Another possible source of error is the forced planarity of the individual rings in BP. Relaxing the planarity constraint should lead to somewhat lower energies for all dihedral angles except 0° and 180° and should therefore also influence the optimized twist angles. Comparing B3LYP/6-311+G* results for nonplanar rings with those for planar rings (as given in Table 2), the ΔE's (in kcal/mol) for 2,2′-difluoro BP are 10.91 (10.82) at 0°, 0.47 (0.79) at 45°, 0.80 (0.72) at 90°, 0.20 (0.19) at 135°, 4.88 (4.79) at 180°, and 0.15 (0.09) at the secondary minimum. The optimized dihedral angles are 57.25° (57.87) and 130.42° (128.90). For 2,2′-dichloro BP, the ΔE's (in kcal/mol) are 30.13 (30.11) at 0°, 0.04 (0.01) at 90°, and 17.63 (17.61) at 180°, with an optimized dihedral angle of 82.14 (84.86)°. Again, the changes in energy and dihedral angle because of the nonplanarity of the rings are very small, much smaller than changes caused by using different basis sets and methods, and do in no way influence the interpretation of the results.

Results for 2,2′-Dimethylbiphenyl, Perfluorobiphenyl, and Perchlorobiphenyl. For these systems, geometry optimizations

TABLE 4: Energy Differences Δ*E* (in kcal/mol) for Perfluoro- and Perchlorobiphenyl at Dihedral Angles 0, 45, and 90°, Relative to the Energy at the Optimal Dihedral Angle ϕ_{opt}, Given at Bottom[a]

ϕ	perfluoro BP, Δ*E*	perchloro BP, Δ*E*
0	24.54	134.96
	30.15	161.38
45	1.23	38.89
	2.36	49.16
90	1.56	0.00
	0.80	0.00
ϕ_{opt}	55.01	90.00
	59.91	90.01

[a] First line, B3LYP/6-311+G*; second line, HF/6-31G*. The total energies at ϕ_{opt} are (in a.u.) −1455.564965/−1448.683060 for perfluoro BP and −5059.193293/−5048.164261 for perchloro BP.

were performed with B3LYP/6-31G*, compared to the higher-level B3LYP/6-311+G* calculations used in the previous section.

2,2′-dimethyl BP (calculated in the C_2 symmetry group) may be compared with the 2,2′-dihalogen BPs discussed before. It is seen (Table 2) that the energy at 0° is very high (169/219 kcal/mol), much higher than even for 2,2′-diiodine BP, because of the bulkiness of the methyl groups. The minimum occurs at a twist angle slightly above 90°, which compares best with that of 2,2′-dibromo BP.

An optically active form of 2,2′-dimethyl BP had been obtained at low temperature. The half-life at −32 °C is 7 min and estimated to be 1.1 s at 25 °C. From these data, an activation energy for racemization of 15.1 kcal/mol has been determined,[20] to be compared with our energy difference at 180° of 16.7 kcal/mol (B3LYP result).

In Table 4, results for perfluoro BP and perchloro BP are shown. Perfluoro BP has a minimum at 55.0°, slightly below that of 2,2′-difluoro BP (57.9°). Perchloro BP, on the other hand, optimizes at $\phi = 90.0°$ (higher than 2,2′-dichloro BP), which is the best choice in light of the strong repulsion between the Cl atoms. The energy differences relative to the minimal energy are quite high at 0°, and still relatively high at 45° for perchloro BP (39/49 kcal/mol), but quite low for perfluoro BP.

X-ray structures for perfluoro BP give a twist angle of 59.7°,[21] compared with 55.0° calculated, and of 86.9° for perchloro BP,[22] compared with 90.0° calculated. For both compounds, the torsional angle in the crystal is close to that calculated for the gas phase. The extremely high barrier toward planarity calculated for perchloro BP (135 kcal/mol, compared to 30 kcal/mol for 2,2′-dichloro BP) is certainly a factor in keeping the twist angle in the crystal close to that in the gas phase.

Summary and Conclusion

Using high-level Hartree−Fock and density functional calculations, the dihedral (or twist) angles and energies of ortho and meta substituted biphenyls, with one or two halogen atoms, as well as perfluoro BP, perchloro BP, and dimethyl BP, were investigated and compared with corresponding data for biphenyl.

For mono substituted biphenyls, the twist angle increases with a heavier halogen atom, from 42.5° for biphenyl to 45.1° for 2-fluoro BP (54.1° expt in solid), 59.9° for 2-chloro BP, and 63.6° for 2-bromo BP (B3LYP/6-311+G* values). (The calculated numbers for iodine substituents are often out of line, which is most likely because of the use of an effective core potential, and will in the following be ignored.) The energy barrier (energy at 0°) increases from 2.2 kcal/mol for BP to 3.0, 7.6, and 8.6 kcal/mol, respectively.

Of the 2,2-disubstituted BPs, difluoro BP has two torsional minima, one below (57.9°) and the other above (128.9°) 90°. The other 2,2′-disubstituted BPs have only one minimum, close to 90°. For 2,2′-dichloro BP it is calculated at 84.9°.

Reliable gas-phase measurements for the 2,2′-disubstituted BPs could not be found. Older values give dihedrals ranging from 60 to 79°. On the other hand, crystal structures are known for all 2,2′-dihalogen BPs. The twist angle of difluoro BP equals the calculated value (57.6° measured, 57.9 calculated). For dichloro BP, the measured value of 66.5° is well below the calculated one (84.9°), and for dibromo BP as well as diiodo BP, the twist angles are shifted below 90° (to about 85°). The energy required to twist dichloro BP from the optimal dihedral angle of 84.9° to that found in the crystal, 66.5°, is calculated to be only 0.9 kcal/mol (B3LYP/6-311+G*).

All 3,3′-disubstituted BPs have a double minimum in the torsional potential, as expected, with the anti minimum at slightly lower energy than the syn minimum. The optimal twist angles are close to the biphenyl value of 42.5° (or 137.5°). For 3,3′-dibromo BP, a measured gas-phase twist angle of 43.8° is to be compared with the calculated syn value of 43.1°.

For comparison with the 2,2′-dihalogen BPs, the geometry of 2,2′-dimethyl BP was also optimized. The twist angle is 90.7°, and the 180° barrier is calculated to be 16.7 kcal/mol, in good agreement with an experimental activation energy for racemization of 15.1 kcal/mol.

Perfluoro BP has a calculated twist angle of 55.0°, compared with a crystal value of 59.7°. The calculated twist angle of perchloro BP, 90.0°, is to be compared with 86.9° in the crystal.

Our best calculations place ϕ_{opt} for 2,2′-dichloro BP at about 85°, whereas steric arguments would suggest such angle to lie above 90°. In calculations with the 6-311+G* basis set, the BSSE at 0° was found to be about the same as that at 180°, although the accuracy is not better than 0.1 kcal/mol. Because the energy at 95° is calculated to lie only 0.05 kcal/mol higher than at the minimum of 85°, basis set superposition cannot completely be ruled out. Nevertheless, it appears that attractive forces are active in overcoming the steric effect, and van der Waals interactions between the two chlorine atoms are to be considered. Using a commonly accepted van der Waals radius for Cl of 1.8 Å, the corresponding dihedral angle is about 60−65°. An estimate of the energy lowering is 0.2 kcal/mol at a Cl−Cl distance of 3.6 Å (the Ar−Ar value at R_e is 0.25 kcal/mol) and about 0.1 kcal/mol at 3.9 Å (the Cl−Cl distance at the minimum).

For 2,2′-difluoro BP, the syndiagonal minimum is calculated to be about 0.1 kcal/mol lower than the anti minimum, contrary to steric arguments. At a dihedral angle of about 50°, the two F atoms are separated by 2.7 Å, which is twice the van der Waals radius of 1.35 Å. The attractive forces between the two fluorine atoms would therefore favor the syn over the anti minimum. (As for 2,2′-dichloro BP, the BSSE is very small and inconlcusive.) In this connection, it is interesting that in the liquid-crystalline phase of 2,2′-difluoro BP a double minimum has been found by Aldridge et al.,[4] with twist angles of 51° and 130° and with the syn and anti forms being present in the approximate ratio 0.58:0.42, indicating the syn form to be slightly more stable. Solid-state and gas-phase measurements for 2,2′-dihalogen BPs only show dihedral angles below 90°.

For 2,2′-dibromo BP, the twist angle is calculated to lie above 90°. Here, a van der Waals radius of 1.95 Å corresponds to a dihedral angle of about 65°, but the van der Waals attraction appears to be overshadowed by the strong Br−Br repulsion.

TABLE 5: Optimized Dihedral Angles (in Degrees) for Biphenyl (BP) and 2,2′-Dihalogen Biphenyls, Using Different Basis Sets and Methods

	6-31G*			6-311+G*	
	HF	MP2	B3LYP	HF	B3LYP
BP	46.31	45.72	39.33	48.00	42.50
F,F	57.13	55.43	52.03	61.65	57.87
	128.82	131.01	137.24	122.87	128.90
Cl,Cl	89.66	80.42	86.18	87.76	84.86
Br,Br	77.89	74.50	73.58	90.52	91.54

In summary, the structures of mono substituted and 3,3′-disubstituted biphenyls can be rationalized by using steric arguments only. For the 2,2′-dihalogen BPs, however, an attractive force between the two halogen atoms may need to be included. This is indicated by the optimized dihedral angle of 2,2′-dichloro BP lying well below 90°.

The optimized twist angles are very sensitive to the employed method and basis set. For BP and the 2,2′-dihalogen BPs, this is demonstrated in Table 5, for 6-31G* (HF, MP2, and B3LYP) and 6-311+G* (HF, B3LYP) basis sets, and for the methods given in parentheses. Additional examples can be found in the literature review.

For BP, ϕ_{opt} ranges from 39.3 to 48.0°. For 2,2′-difluoro BP, it ranges from 52.0 to 61.6° for the syn minimum, and from 122.9 to 137.2° for anti. For 2,2′-dichloro BP, it ranges from 80.4 to 89.7°, and for 2,2′-dibromo BP, it ranges from 73.6 to 91.5°. Deviations in the latter case are extreme. For 2,2′-dibromo BP, all 6-31G* calculations give ϕ’s in the 70−80° range, whereas 6-311+G* ones give 90−91°. It appears that for the Br−Br interactions, the 6-31G* basis set is too compact and that additional less compact functions are needed to correct for this error.

Table 5 shows that a good choice of basis set is more important than the choice of method, and HF/6-311+G* values are overall quite acceptable for the dihedral angles. For a given basis set, the B3LYP method gives the lowest twist angle (or equivalently the highest for the anti minimum of 2,2′-difluoro BP), with the exception of the dichloro 6-31G* result, where MP2 gives the lowest ϕ and dibromo 6-311+G*, where the B3LYP angle is slightly higher than the HF one.

To verify the quality of the predictions made in this paper, gas-phase measurements of dihedral angles and rotational barriers would be most useful. It is encouraging to see that ab initio/crystal field calculations done on biphenyl were successful in reproducing diffraction data for the various solid-state phases, over a wide range of temperatures, thereby explaining experimentally observed facts.[23] There is a need to perform such calculations also on substituted biphenyls.

Acknowledgment. Many thanks to Dr. Andreas Decken for suggesting calculations on substituted biphenyls and for help in finding crystallographic references. Both he and Dr. Scott Brownridge read the manuscript and made helpful comments. Financial support by NSERC (Canada) is gratefully acknowledged.

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