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Twisting and bending photo-excited phenylethynylbenzenes – a theoretical analysis†

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Oligo(phenylethynyl)benzenes are a family of compounds that exhibit a rich photochemistry changing dramatically with different orientation of a phenyl group in the molecule. Quantum-chemical calculations have been performed to investigate different members of this family of compounds and compared to previous experimental and theoretical studies. 1,4-Bis(phenylethynyl)benzene (BPEB) has different optical properties than its smaller relative diphenylacetylene; however, upon twisting an outer phenyl ring of BPEB, its photochemistry becomes very similar. Fluorine substituents at the central benzene ring are shown to have only small effects on the optical properties of BPEB.

1 Introduction

Phenylethynylbenzenes are important building blocks for electroluminescent, semiconductor, and nonlinear optical materials,[1–5] mostly because of their rigid molecular structure[2] and extended delocalized π-electron system.[3,4,6] From a more theoretical point of view, they caught the interest of many researchers due to their absorption/emission and nonlinear optical properties,[7] as well as hole-transport properties in molecular wires[8] that are related to changes in electron correlation and self-interaction energy.

The smallest member of this family is diphenylacetylene (tolan), which, of course, has been studied most intensely both experimentally and theoretically.[9–14] The single dominating degree of freedom is the torsion of the phenyl rings around the acetylene axis, that largely controls its electronic structure and thus many of its optoelectronic properties.[14] Both planar and twisted tolanes with torsion angles $>0^\circ$ show fluorescence from a planar S_1 minimum, which means that twisted tolanes planarize before emission.[14] However, a *trans*-bent configuration of tolan was found to drastically alter the emission properties as it possesses a relatively stable minimum in the 1 ^1A_u state.[13,14]

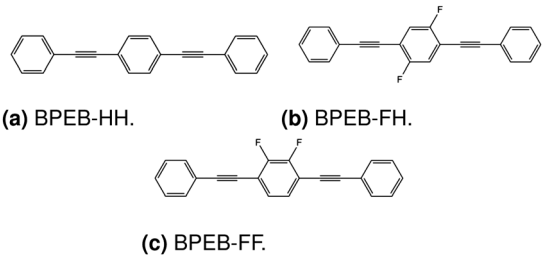

Fig. 1 Structures of three bis(phenylethynyl)benzenes according to their short names investigated in this work.

In this study, the second largest member of this family is investigated, namely 1,4-bis(phenylethynyl)benzene (BPEB-HH), as well as its derivatives with two fluorine substituents at the middle ring, one in the *para* position (BPEB-FH) and one in the *ortho* position (BPEB-FF), as shown in Fig. 1.

In previous studies of these systems[5,6,15] it was argued that tolan and BPEB-HH display very different optical properties despite their similar structure,[5] based mainly on the large difference of the fluorescence quantum yield measured in solution.[16,17] It is the purpose of this study to re-investigate the photophysical and photochemical properties of BPEB-HH and to compare them to those of tolan. Similarities and differences between the two related systems are pointed out, particularly with respect to their reactivities along the twisting and bending motions of the phenyl units or triple bonds, respectively. Furthermore, the influence of fluorine substituents at the middle phenyl unit on its optical properties is discussed. We predict that when one of the triple bonds is bent, BPEB-HH will display very similar emission properties as tolan.

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† Electronic supplementary information (ESI) available: Geometrical parameters, attachment/detachment density and molecular orbital plots, torsional and bending scans, vibrationally-resolved electronic spectra, spin–orbit coupling elements. See DOI: 10.1039/d0cp01662d

2 Computational methodology

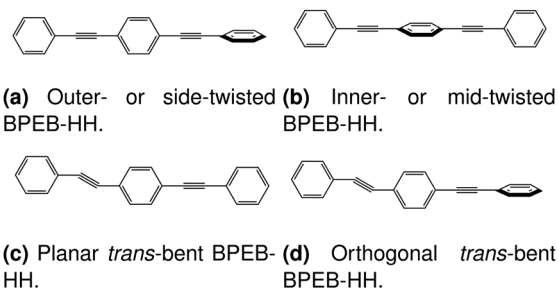
All quantum-chemical calculations were carried out with density functional theory (DFT) and linear-response time-dependent DFT (TDDFT).[18–20] The Gaussian 16 program package[21] was used throughout, except for calculations of spin–orbit coupling (SOC) constants,[22–24] transition moments between excited states, spin–flip (SF) DFT,[25] and attachment and detachment densities[26–28] for which the Q-Chem 5.2 program package was used.[29] Previous benchmark calculations against the algebraic-diagrammatic construction (ADC) scheme for the polarization propagator of second order[30–32] have shown the CAM-B3LYP functional[33] to yield accurate results for excitation energies of tolan.[34] It is thus also chosen for the bis(phenylethynyl)benzene systems. Furthermore, a recent study on similar aromatic systems[35] showed basis set convergence for excitation energies calculated in the TDDFT framework to be achieved at the triple-zeta level with no additional sets of polarization functions required.[36] Thus, the def2-TZVP basis set[37] is chosen for this study. Diffuse functions are not expected to play an important role since Rydberg or similarly diffuse states are not investigated in this work. When studying these molecules, specific atoms, bonds, angles, and dihedral angles are investigated, with labels according to Fig. S1 in the ESI.† Different geometrical configurations are also investigated, along torsional and *trans*-bent motions as demonstrated in Fig. 2, with the nomenclature for these motions used in the remainder of this work.

3 Results and discussion

In the following, effects of torsion and bending of BPEB-HH, as well as introduction of fluorine substituents on its excited states and photochemical properties, are investigated, and differences to tolan discussed.

3.1 Planar and twisted BPEB-HH

In the electronic ground state, BPEB-HH adopts a linear and planar equilibrium structure with D_{2h} point-group symmetry. Two eminent degrees of freedom are the torsion, or twisting, motion of one of the terminal phenyl units and of the middle phenyl unit. The corresponding energy profiles in the electronic ground state calculated at the DFT/CAM-B3LYP/def2-TZVP level of theory are shown in Fig. 3 (bottom), in which the angles have been scanned from the planar (Fig. 1a) to the orthogonal (Fig. 2a and b) configuration in 10° steps while all other geometrical parameters were reoptimized. The energy barrier for torsion of the outer ring is about 0.032 eV (256 cm^{-1}), which agrees very nicely with the experimental value of 220–235 cm^{-1},[6] while that of the inner ring was calculated to be about twice as large with 0.068 eV (548 cm^{-1}), which is closer to the experimental value than previous DFT-based calculations,[5] but still significantly larger.



(a) Outer- or side-twisted BPEB-HH. **(b)** Inner- or mid-twisted BPEB-HH.

(c) Planar *trans*-bent BPEB-HH. **(d)** Orthogonal *trans*-bent BPEB-HH.

Fig. 2 Visualization of twisted and *trans*-bent BPEB-HH.

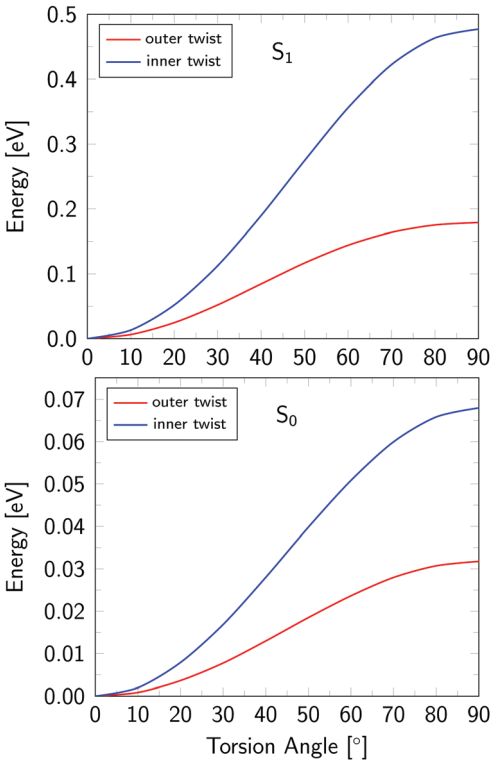


Fig. 3 Energy profile of outer- and mid-twisted BPEB-HH in the S_0 and S_1 states calculated at the CAM-B3LYP/def2-TZVP level of theory.

An analogous scan has been conducted in the first excited S_1 state, using linear-response TDDFT with the same functional and basis set. The results are shown in Fig. 3. The outer-twist barrier was found to be about 0.18 eV (1443 cm^{-1}), which again is in fairly good agreement with the experimental value of about 1840 cm^{-1} and in significantly better agreement than previous DFT calculations.[5] An energy barrier of about 0.48 eV (3847 cm^{-1}) was found for torsion of the middle ring, which again is closer to the experimental value than the previous TDDFT result of 7500 cm^{-1}.[5] Rotation of a single outer ring is thus more likely to occur. And in contrast to what has been stated earlier,[6] DFT-derived potentials can indeed be used to describe torsional motions of BPEB-HH when the exchange–correlation functional[34] and basis set are carefully chosen.[36]

The effects of torsion on geometrical parameters has been investigated as well, the results of which are shown in Table S1 in the ESI.† Twisting the inner or outer ring of BPEB-HH has little or no effect on the triple bond lengths of 1.20 Å, which is already 0.04 Å shorter than that of tolan in the electronic ground state.[14]

Table 1 Vertical excitation energies ω (in eV) and oscillator strengths f as well as their irreducible representation ("Irrep") in the respective point group of the six energetically lowest singlet and triplet excited states of planar, side- and mid-twisted BPEB-HH calculated at the CAM-B3LYP/def2-TZVP level

	Planar			Side-twisted			Mid-twisted		
State	Irrep	ω	f	Irrep	ω	f	Irrep	ω	f
S_1	B_{1u}	3.92	1.931	A_1	4.22	1.643	B_{3u}	4.80	1.242
S_2	B_{2u}	4.83	0.000	A_2	4.88	0.000	B_{3g}	4.92	0.000
S_3	B_{3g}	5.09	0.000	B_2	4.91	0.000	A_u	4.97	0.000
S_4	B_{2u}	5.09	0.000	A_2	5.07	0.000	B_{1u}	5.00	0.000
S_5	B_{1g}	5.13	0.000	B_2	5.10	0.000	B_{3g}	5.09	0.000
S_6	A_u	5.16	0.000	A_2	5.17	0.000	A_u	5.15	0.000
T_1	B_{1u}	2.38	—	A_1	2.54	—	B_{3u}	2.82	—
T_2	A_g	3.08	—	A_1	3.22	—	A_g	3.22	—
T_3	B_{1u}	3.56	—	A_1	3.39	—	B_{3u}	3.24	—
T_4	B_{2u}	4.30	—	B_2	4.35	—	B_{1u}	4.42	—
T_5	B_{1u}	4.40	—	A_1	4.38	—	B_{3u}	4.46	—
T_6	B_{2u}	4.48	—	A_1	4.47	—	A_g	4.48	—

Vertical excitation energies and oscillator strengths of the six energetically lowest singlet and triplet excited states at the planar and the twisted configurations have been calculated in the gas phase to investigate the influence of the orientation of the phenyl groups on the absorption spectrum. The results are shown in Table 1. At the planar configuration of BPEB-HH, the first excited singlet state has B_{1u} symmetry and an excitation energy of 3.92 eV and is the only one with a nonvanishing oscillator strength among the six lowest states. By twisting one outer ring to 90°, the excitation energy of the S_1 state increases by 0.3 eV, but it remains bright with a substantial oscillator strength and is about 0.5 eV lower than that of planar tolan calculated at the ADC(2)/cc-pVDZ level.[14] For the configuration with twisted inner-ring, the S_1 state is also a bright one with an excitation energy of 4.80 eV, *i.e.*, almost 0.9 eV higher than that for the planar configuration due to the reduced size of the π system, and comparable to the $S_0 \rightarrow S_1$ excitation energy of 4.99 eV for twisted tolan, which does not possess oscillator strength at the ADC(2)/cc-pVDZ level, however.[14] In the molecular orbital (MO) picture, the bright S_1 states of planar and twisted BPEB-HH can be understood as a single electron transition from the highest occupied MO (HOMO) to the lowest unoccupied one (LUMO) as shown in Fig. 4 together with the amplitude of the corresponding excitation vector for the examples of planar and outer-twisted BPEB-HH. They correspond to typical π–π* excited states. Attachment and detachment densities[26–28] were also calculated and confirmed the bright S_1 states as π–π* transitions, which can be found in Fig. S2 in the ESI.† Thus, in comparison to tolan, BPEB-HH is similar in that it has only one low-lying excited state with nonvanishing oscillator strength for both the planar and twisted configurations of the molecule. However, the S_6 excited state is the first bright state for twisted tolan,[14] while it is the S_1 for inner- and outer-twisted BPEB-HH.

In the experimental absorption spectrum, tolan has two very prominent peaks at 4.20 and 4.46 eV,[14] while the spectrum of BPEB-HH is dominated by one broad peak around 3.85 eV. Vibrationally-resolved electronic absorption and emission

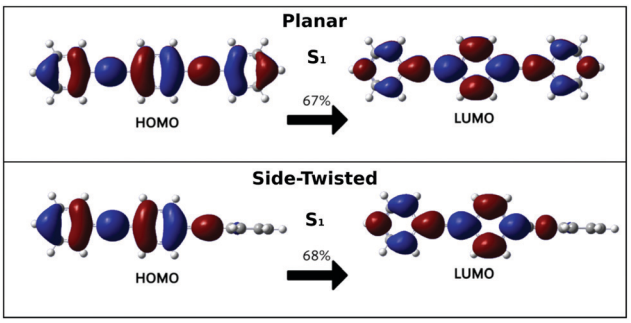


Fig. 4 Molecular orbitals of planar (top) and side-twisted (bottom) BPEB-HH with significant contributions to the respective bright S_1 state calculated at the CAM-B3LYP/def2-TZVP level of theory.

spectra were computed in the gas phase considering only the S_1 excited state and compared to the experimental spectra that were measured in chloroform. The adiabatic Hessian (AH) model[38–41] in combination with the Franck–Condon approximation[42–44] for the electronic transition dipole moment was chosen for the vibronic transition, the harmonic oscillator approximation was assumed valid and temperature effects have been neglected throughout. The results are shown in Fig. 5. For both the absorption and emission spectra, it can be seen that the position of the peaks is quite well reproduced, but their relative intensities differ slightly between experiment and

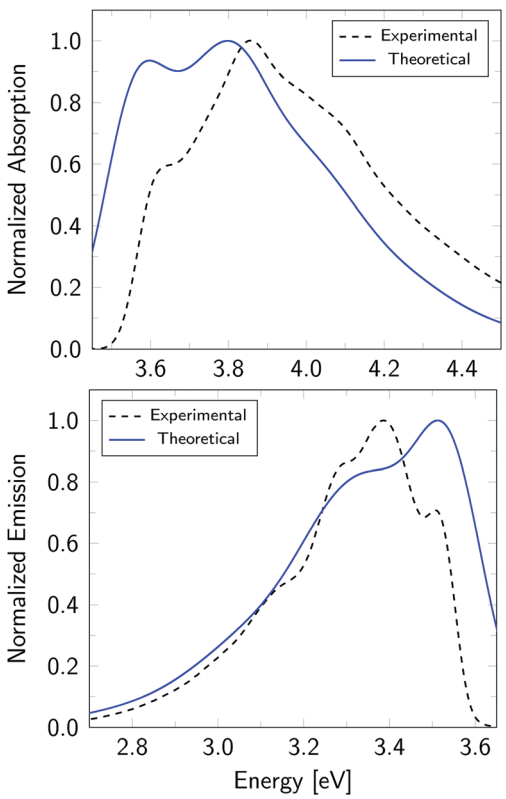


Fig. 5 Vibrationally-resolved electronic absorption (top) and emission spectrum (bottom) of planar BPEB-HH calculated using the AH model compared to the experimental spectra. Lorentzian functions with a half-width of 0.09 eV were used to convolute the calculated stick spectrum.

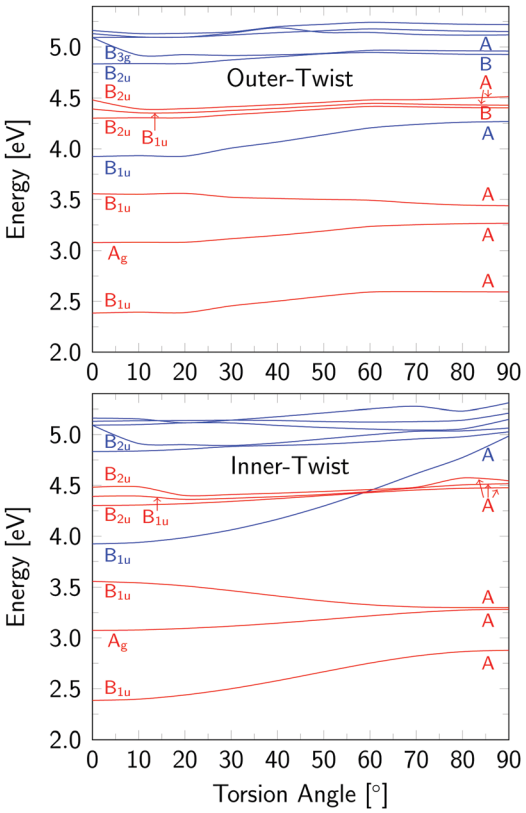


Fig. 6 Potential energy surfaces of excited singlet (blue) and triplet (red) states along the relaxed ground-state scan of side-twisted (top) and mid-twisted (bottom) BPEB-HH at the TDDFT/CAM-B3LYP/def2-TZVP level. The energy is given relative to the ground state in its planar equilibrium geometry, respectively. The states are labeled according to the D_{2h} point group on the left, and according to the C_2 point group on the right.

simulation. The deviation of the most intense peaks between experimental and theoretical absorption spectra is 0.05 eV while it is 0.12 eV for the emission spectra. These spectra were also computed using the conductor-like polarizable continuum model (C-PCM)[45–47] to account for solvation effects in chloroform, but it was found not to improve the results.

To gain more insight into the role of the twisting motion for the fluorescence and phosphorescence properties of BPEB-HH, the potential energy surfaces of the excited states have been investigated along two relaxed and unrelaxed scans in the electronic ground state (Fig. 6). The unrelaxed scans along the torsion of these two phenyl rings were determined to be extremely similar to the relaxed scans, as shown in Fig. S8 in the ESI.† For the complete scan, C_2 point-group symmetry has been adopted. As can be seen in Fig. 6 (top), no singlet/triplet crossings occur when twisting an outer ring. However, there are three singlet/triplet crossings that occur when the middle ring is twisted (Fig. 6 (bottom)). In order to check for possible intersystem crossing (ISC), spin–orbit coupling (SOC) constants[22–24] between singlet and triplet states were calculated using the one-electron Breit–Pauli Hamiltonian[48] as implemented in Q-Chem 5.2 and are shown in Table 2. The SOC constants at all crossings are very small (<2.1 cm^{-1}) and there is no twisted

Table 2 Computed SOC constants between the S_1 and T_n states that are crossed when twisting the middle ring of BPEB-HH at the TDDFT/CAM-B3LYP/def2-TZVP level of theory

Crossing	Angle [°]	SOC [cm^{-1}]
S_1/T_4	60	1.24
S_1/T_5	60	0.03
S_1/T_6	60	2.03

minimum in the S_1 state. Thus, it appears unlikely that ISC occurs and that significant phosphorescence is observable. We would like to remark that the small values of the SOC constants can also be understood by means of El-Sayed's rule.[49–51]

Twisting the inner ring of BPEB-HH is more similar to twisting tolan, according to corresponding relaxed scans.[14] Twisting tolan involves five singlet/triplet crossings of the S_1 singlet state, while twisting only one outer ring of BPEB-HH involves none and twisting the inner ring of BPEB-HH involves three crossings at the CAM-B3LYP/def2-TZVP level of theory. The SOC constants are similar in magnitude for BPEB-HH and tolan, however, they occur at higher angles of torsion in tolan than in BPEB-HH. They occur only when tolan is twisted by at least 70°, but occur at 60 in BPEB-HH.

3.2 Effects of fluorine substituents

The effects of substituting two hydrogen by two fluorine atoms at the inner ring of BPEB-HH in both the *para* (BPEB-FH) and *ortho* (BPEB-FF) positions (see Fig. 1) have been investigated in order to study the influence of moieties with strong inductive effects on the photophysical properties. Accordingly the point-group symmetry is decreased from D_{2h} to C_{2h} for BPEB-FH and to C_{2v} for BPEB-FF. The two torsional degrees of freedom of the outer and inner phenyl rings remain the same. The effects on the central internal coordinates and orientation can be seen in Table S2 in the ESI.†

As for BPEB-HH, vertical excitation energies as well as oscillator strengths of the energetically lowest singlet and triplet excited states of the planar and twisted configurations have been calculated for BPEB-FH and BPEB-FF in the gas phase to investigate the influence of the fluorine atoms on orientation of the phenyl groups and thus on the absorption spectrum (Table 3). The most important MO contributions to the bright states of the two molecules are shown in Fig. S3 and S4 in the ESI.† The S_1 state is still the brightest one for both planar, outer- and inner-twisted BPEB-FH and BPEB-FF, but unlike in BPEB-HH, there are also other low-lying excited states with nonvanishing oscillator strength, especially for BPEB-FH. Furthermore, the fluorine substituents cause a slight decrease in the excitation energies by less than 0.1 eV on average. Vibrationally-resolved absorption and emission spectra have been computed at the same level of theory as for BPEB-HH and compared to experimental ones as well. The results shown in Fig. S11–S13 in the ESI† show a remarkably good agreement with experiment, but the effect of the fluorine substituents on the spectra is in general rather negligible.

Relaxed and unrelaxed scans along torsion of both the inner and outer rings for BPEB-FH and BPEB-FF have also been

Table 3 Vertical excitation energies ω (in eV) and oscillator strengths f of the six energetically lowest singlet and triplet excited states of planar, side-twisted, and mid-twisted BPEB-FH and BPEB-FF calculated at the CAM-B3LYP/def2-TZVP level of theory

	BPEB-FH							BPEB-FF						
	Planar			Side-twisted		Mid-twisted		Planar			Side-twisted		Mid-twisted	
State	Irrep	ω	f	ω	f	ω	f	Irrep	ω	f	ω	f	ω	f
S_1	B_u	3.85	1.868	4.13	1.552	4.57	0.931	B_2	3.91	2.000	4.20	1.636	4.78	1.248
S_2	B_u	4.74	0.074	4.74	0.000	4.79	0.000	A_1	4.74	0.000	4.78	0.000	4.83	0.008
S_3	A_g	4.88	0.000	4.81	0.078	4.80	0.000	A_1	4.92	0.002	4.83	0.015	4.85	0.005
S_4	A_g	5.09	0.000	5.14	0.000	5.03	0.242	B_2	5.09	0.000	5.14	0.000	4.92	0.015
S_5	B_u	5.09	0.001	5.14	0.000	5.18	0.000	A_1	5.09	0.001	5.17	0.000	5.19	0.000
S_6	B_g	5.12	0.000	5.26	0.001	5.20	0.000	B_1	5.14	0.000	5.26	0.001	5.19	0.000
T_1	B_u	2.34	—	2.49	—	2.76	—	B_2	2.37	—	2.53	—	2.80	—
T_2	A_g	3.07	—	3.22	—	3.22	—	A_1	3.07	—	3.22	—	3.22	—
T_3	B_u	3.55	—	3.38	—	3.24	—	B_2	3.56	—	3.39	—	3.24	—
T_4	B_u	3.91	—	3.92	—	3.94	—	A_1	4.05	—	4.08	—	4.11	—
T_5	B_u	4.30	—	4.33	—	4.39	—	B_2	4.34	—	4.35	—	4.39	—
T_6	A_g	4.34	—	4.40	—	4.51	—	A_1	4.35	—	4.43	—	4.48	—

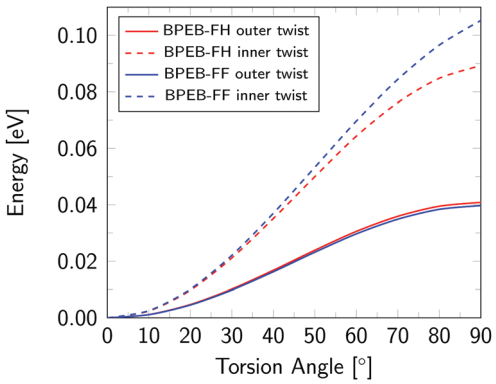


Fig. 7 Torsion profile of side- and mid-twisted BPEB-FH and BPEB-FF in the ground state at the CAM-B3LYP/def2-TZVP level of theory.

calculated in the ground state analogous to BPEB-HH. As can be seen in Fig. 7, the ground-state energy barriers are 0.04 eV for both outer-twisted molecules, 0.09 eV for inner-twisted BPEB-FH and about 0.1 eV for inner-twisted BPEB-FF, all slightly larger than those of the unsubstituted system. Results of the scans in the excited states can be found in Fig. S6 and S7 in the ESI.† Rigid scans were again found to be extremely similar to the relaxed ones and can be found in Fig. S9 and S10 in the ESI.†

In contrast to BPEB-HH, there is one singlet/triplet crossing when twisting an outer ring, and three singlet/triplet crossings along twisting of the inner ring. The SOC constants have been calculated and are shown in Tables S3 and S4 in the ESI.† For both molecules the SOC constants at all crossings are again very small (<1 cm^{-1}), in fact even smaller than for BPEB-HH, and thus, it appears unlikely that ISC occurs. In general, fluorine substituents do not significantly influence the emission properties of BPEB-HH.

3.3 Effects of *trans*-bending

To gain insight into the role of the *trans*-bending motion for the fluorescence and phosphorescence properties of BPEB-HH analogous to tolan,[14] two further relaxed scans have been performed in the ground state at the CAM-B3LYP/def2-TZVP level of theory. The *trans*-bent angle was investigated from the linear (180°) to the bent (115°) configuration, once with the third phenyl ring in plane with the others (Fig. 2c) and once with the third phenyl ring orthogonal to the other two (Fig. 2d).

As can be seen in Fig. S14 in the ESI,† the energy penalty of bending a triple bond in BPEB-HH to an angle of 115° is about 3.8 eV with a planar outer ring, while it is about 3.3 eV with an orthogonal outer ring. The corresponding potential energy curves of the excited states are shown in Fig. 8, where the S_1 state can be seen to have a minimum for the planar and orthogonal configuration at angles of 130° and 128°, respectively, as confirmed by harmonic frequency calculations in the excited state. Unconstrained geometry optimizations in the S_1 state from both initial planar and orthogonal configurations revealed an elongation of the original central triple bond from 1.20 Å to 1.34 Å, similar to the 1.38 Å in tolan,[14] revealing mostly double-bond character. Inspection of the orbitals involved in the $S_0 \rightarrow S_1$ transition (see Fig. S5 in the ESI†) confirms that an azobenzene-like structure is obtained at the S_1 minimum, analogous to tolan.[14] In order to check the validity of taking a closed-shell reference when bending a triple bond towards a double bond with biradical character, spin–flip (SF) TDDFT calculations[25] within the Tamm–Dancoff approximation[52] were performed along the *trans*-bent scan (see also Fig. S14 in the ESI†). Since the expectation value of the total spin operator $\hat{S}^2$ at an angle of 120° in the singlet ground state at the SF-DFT level is merely $\langle \hat{S}^2 \rangle = 0.06$, spin contamination seems not to play an important role along the *trans*-bending mode.

With either a planar or an orthogonal outer ring, there are five crossings between the S_1 and triplet states. The SOC constants were calculated at the *trans*-bent angles at which these crossings occurs, but all other geometrical parameter were kept from the nearest constraint optimization (Table 4). For both of these configurations of the molecule, there is one crossing with T_3 and two with each T_4 and T_5 (Fig. 8). Both configurations have at least one crossing with substantial spin–orbit coupling (>10 cm^{-1}). Tolan also exhibits five S_1/T_n crossings with the largest coupling occurring at 151°, similar to the planar

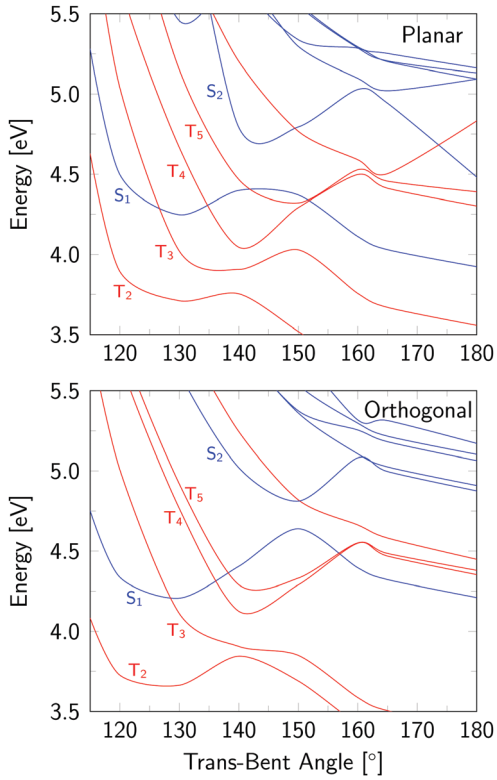


Fig. 8 Potential energy surfaces of excited singlet (blue) and triplet (red) states along the relaxed ground-state scan of planar (top) and orthogonal (bottom) *trans*-bent BPEB-HH at the TDDFT/CAM-B3LYP/def2-TZVP level of theory. The energy is given relative to the ground state in its linear equilibrium geometry, respectively.

Table 4 Computed SOC constants between the S_1 and T_n states that are crossed when bending BPEB-HH at the TDDFT/CAM-B3LYP/def2-TZVP level of theory

Conformation	Crossing	Angle [°]	SOC [cm^{-1}]
Planar	S_1/T_3	127	11.49
Planar	S_1/T_4	135	10.16
Planar	S_1/T_5	142	0.56
Planar	S_1/T_4	152	0.24
Planar	S_1/T_5	152	13.51
Orthogonal	S_1/T_3	128	13.49
Orthogonal	S_1/T_4	136	2.40
Orthogonal	S_1/T_5	138	5.25
Orthogonal	S_1/T_4	157	0.16
Orthogonal	S_1/T_5	157	0.53

configuration of BPEB-HH,[14] with a value of only 7.5 cm^{-1}. However, ISC is still likely for tolan in this state.

The S_1 state of linear, planar and outer-twisted BPEB-HH is a bright state (see Table 1). However, the S_1 state is dark ($f < 0.005$) in the region of its *trans*-bent minimum, at 127° and 135° for planar BPEB-HH and at 128° for orthogonal BPEB-HH, where the SOC constants are larger than 10 cm^{-1}. Since fluorescence is thus slow at the minima, the S_1 lifetime may be long enough for ISC to occur *via* this path, especially since the crossing is very close to the S_1 minimum. Excited BPEB-HH molecules can reach a triplet *trans*-bent minimum and phosphoresce, which is very similar to the results of bending tolan,[14] for which experiments have proved that phosphorescence does occur. We thus predict phosphorescence to occur for both planar and orthogonal *trans*-bent BPEB-HH as well, especially since the SOC constants are significantly larger than those for tolan.

4 Conclusions

The excited states of 1,4-bis(phenylethynyl)benzene ("BPEB-HH") and two of its derivatives with fluorine atoms have been investigated using a time-dependent density functional theory methodology and compared to experimental results as well as to the related tolan molecule.[14,34] The optical properties of BPEB-HH and its derivatives are strongly dependent on the twisting angles, which determine the relative orientation of an outer or the central phenyl ring and thus the degree of π-electron delocalization, similar to tolan.[14] Relaxed scans have been performed along these twisting modes as well as along the *trans*-bent motion, where equilibrium structures on the potential energy curve of the S_1 state were found for both the planar system and for an orthogonal third phenyl ring. The electronic structure of the *trans*-bent S_1 minimum is very similar to that of tolan,[14] which is isoelectronic to the azobenzene dication and corresponds to an unusual π–n* excited state. While twisted BPEB-HH is expected to planarize in the excited state and show the same fluorescence behavior as planar BPEB-HH, *trans*-bent BPEB-HH can be populated along a similar pathway as for tolan,[14] which is then expected to undergo efficient intersystem crossing and phosphoresce since the spin–orbit coupling elements are significantly larger than those for tolan. The effect of fluorine substituition at the central phenyl ring were shown to be of minor importance for the optical properties and thus the same absorption and emission behavior as for unsubstituted BPEB-HH is expected.

Hence, planar BPEB-HH is different from tolan, but outer-twisted BPEB-HH is expected to behave very similar to planar tolan, whereas inner-twisted BPEB-HH should be similar to twisted tolan. In the future, inner- and outer-twisted 1,4-bis(phenylethynyl)benzenes with appropriate linkers should be synthesized in order to verify our theoretical findings.

Conflicts of interest

There are no conflicts to declare.

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