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Twisted Tethered Tolanes: Unanticipated Long-Lived Phosphorescence at 77 K

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Supporting Information

ABSTRACT: Influencing the communication within a conjugated system as diphenylacetylene is a challenging subject in molecular electronics. Some examples of twisted tolanes are known, where high twists have been achieved in the solid state by steric encumbrance. The insertion of a spacer system is an alternative way to tailor rotation. Only a few examples of such tethered tolanes exist, and they all suffer from small twist angles (<35°). We report on tolanophanes containing a malonyl tether, where twist angles of almost 80° were reached. Long-lived phosphorescence (4 s at 77 K) was recorded, and quantum-chemical calculations were performed to confirm the experimental results.

Fundamental insight into the interplay of rotational conformation and optical or molecular electronic properties is attractive.[1,2] In diphenylacetylenes, the twist angle between the two benzene rings (Figure 1) determines their optical properties. When the benzene rings are coplanar (twist angle = 0°), conjugation between the rings is maximized; twisting to 90° turns the electronic interaction off, resulting in blue-shifted absorption and emission.

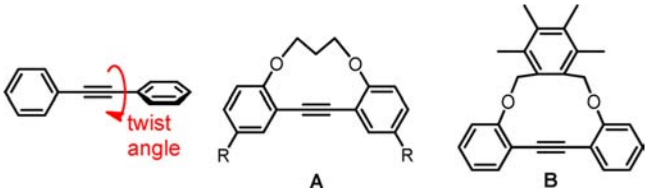

Figure 1. Definition of the twist angle and selected known tolanophanes (R = *tert*-butyl).

Torsional potential is useful for molecular electronics, where the twist angle of biphenyl derivatives modulates their performance.[3] When the biphenyl unit is "exploded" into a tolane (diphenylacetylene), the energy profile of rotation around the alkyne unit is flat in the ground state, with a barrier of rotation of less than 1 kcal mol^{-1}.[4] The planar conformation is more stable, perhaps because of increased electronic communication of the phenyl rings. However, a rational way to modulate the twist angle and therefore the twist between neighboring phenyl units in tolanes or their polymers [poly(*p*-phenylene ethynylene)s, PPEs] is not available. To hold the phenyl groups in a twisted conformation one can either impart steric bulk to the phenyl rings or use a suitable tether. The steric approach has been pursued by the groups of Yang,[5] Beeby,[6] Toyota,[7] and Vollhardt.[8]

Sterically encumbered pentiptycene oligomers[5] experience severe steric hindrance. Consequently, the phenylacetylene units are locked into a twisted conformation. Changes in the optical properties (i.e., blue shifts of the spectral features) result. The ethynylpentiptycene dimer, a tolane derivative, displays a twist angle of ca. 35° between the adjacent phenyl groups in the solid state, but its solutions in moderately apolar solvents contain a significant number of planar or nearly planar conformations at room temperature. Only upon cooling to 80 K are the absorption and emission blue-shifted.

Crisp and Bubner prepared some tethered tolane derivatives; according to their crystal structure analysis, compound **A** with the most blue-shifted absorption maximum has a twist angle of 26° (Figure 1).[9] In structure **B**, the twist angle increases to 30° according to the X-ray crystal structure.[10] No tethered tolanes with twist angles of >70° have been reported, and our own prior attempts (**B**) created structures with calculated twist angles of <60° despite a thorough computational search.

In our current approach, we treated diol **1**[11] with malonyl dichloride, and cyclophane **2** was formed in 35% yield. Reaction of **1** with other bisacid chlorides (phthaloyl, isophthaloyl, and terephthaloyl) furnished cyclophanes **3-*o***, **3-*m***, and **3-*p***, respectively, in yields of 6−33% after chromatography (Scheme 1).[12] This concept allows tailoring of the tether in the last step, starting from a single precursor and is therefore modular and efficient.

Compounds **2**, **3-*o***, and **3-*m*** gave small needlelike crystals suitable for X-ray crystal structure determination. Repeated attempts to crystallize **3-*p*** for X-ray analysis failed. The molecular structures of **2** and **3-*o*** are shown in Figures 2 and 3, respectively. The malonyl derivative **2** displays a twist angle of almost 80°; while cyclophane **3-*o*** is essentially planar (!), **3-*m*** displays a significant twist angle of 72° [see the Supporting

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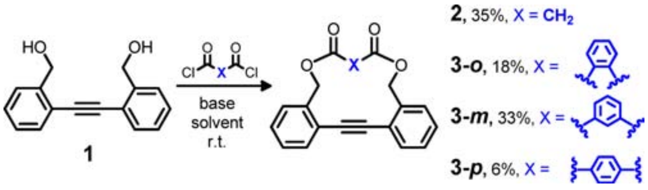
Scheme 1. Syntheses of Tethered Tolanes



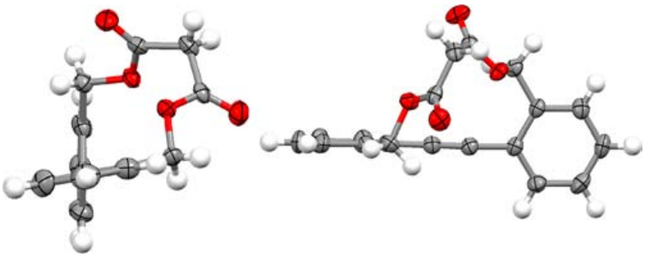


Figure 2. Crystal structure of **2** (twist angle = 79.3°).

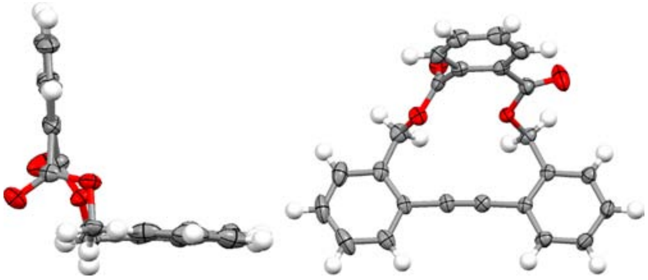


Figure 3. Crystal structure of **3-*o*** (twist angle = 6.2°).[14]

Information (SI)]. The twist angles were observed in the solid state and thus might be a consequence of crystal packing. Are the same structures assumed in solution, and how could this be proved? The absorption spectra of tolanes are sensitive to the twist angle between the neighboring benzene rings, with the absorption maxima shifting to shorter wavelengths with increasing twist angle.[13]

Figure 4 displays the absorption spectra of **1**−**3** in *n*-hexane solution. The unrestrained model compound **1** has a structured absorption at 304 nm. In the case of **3-*o***, this maximum is red-shifted to 307 nm, while cyclophanes **2** and **3-*m*** display significantly blue-shifted absorption maxima with small shoulders at 308 nm. The results of the crystal structure analyses therefore are consistent with those obtained from the absorption spectra. The emission spectra of **1**−**3** are surprisingly similar, almost superimposable to each other (Figure 5). What is the reason for this behavior and can it be understood? McFarland and Finney[11a] noticed a marked increase in fluorescence quantum yield for an oligo(ethylene glycol)-bridged tolane upon coordination of a metal cation and concomitant planarization. We did not see such an effect of planarization, as both the most twisted species **2** and the planar tolane **3-*o*** display similar emission quantum yields (Table 1). However, **3-*m*** and **3-*p*** display significantly decreased quantum yields, for unknown reasons.

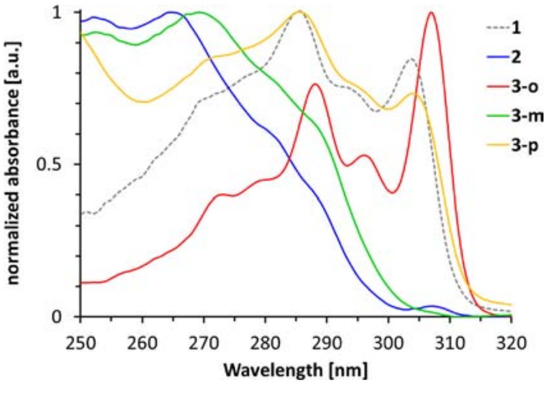


Figure 4. Absorption spectra of **1**−**3** in *n*-hexane at room temperature. The rotationally unencumbered compound **1** displays a λ_{max} of 304 nm.

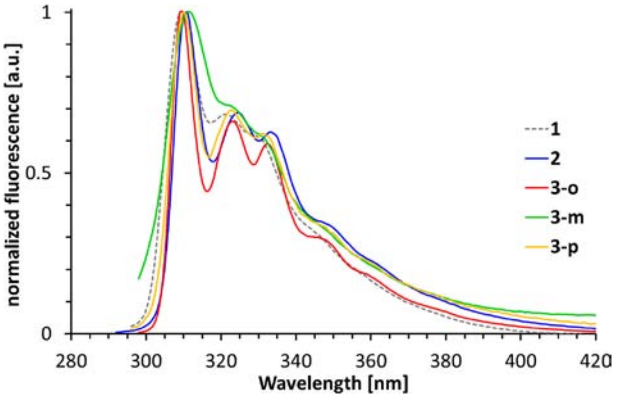


Figure 5. Emission spectra of **1**−**3** in *n*-hexane at room temperature.

Table 1. Photophysical Properties of 2, 3-*o*, 3-*m*, and 3-*p*

	2	3-*o*	3-*m*	3-*p*
λ_{max}^{abs} (nm)^a	280^d	307	288^d	304
ε (L mol^{-1} cm^{-1})^b	13224	29573	15694	14776
λ_{max}^{em} (nm)^a	311	309	311	310
Φ (%)^a	31.1	25.2	0.3	5.3
Φ (%)^b	4.4	3.9	0.1	0.1
$\tau_{298\ K}$ (ps)^b	<100	<100	<100	<100
$\tau_{77\ K}$ (ms)^c	4000	–	0.01	0.008

^{a}In *n*-hexane. ^{b}In dichloromethane. ^{c}In 5:5:2 diethyl ether/isopentane/ethanol (EPA). ^{d}Shoulder.

To investigate these issues further, we explored the optical properties of **1**−**3** at low temperature. For freely rotating ethynylene-containing systems, freezing of the sample in a rigid organic glass [5:5:2 diethyl ether/isopentane/ethanol (EPA), which is transparent at 77 K] can enable measurement of the favored planar state as the lowest-energy conformation is annealed. The rigidity of the frozen sample also serves to lower the rates of internal conversion (IC), intersystem crossing (ISC), and collisional quenching and nominally increases the rates of radiative emission and also in some cases phosphorescence.[15]

Low-temperature spectra were obtained for each of the systems in EPA (see the SI). Species **1** gives a typical response upon annealing into the lowest-energy conformation; increased vibrational fine structure in both the excitation and emission profiles was observed. Tethered **2** (Figure 6) and **3-*o***, **3-*m***, and **3-*p*** display surprisingly different responses at 77 K, exhibiting a broad emission band at lower energies than the main

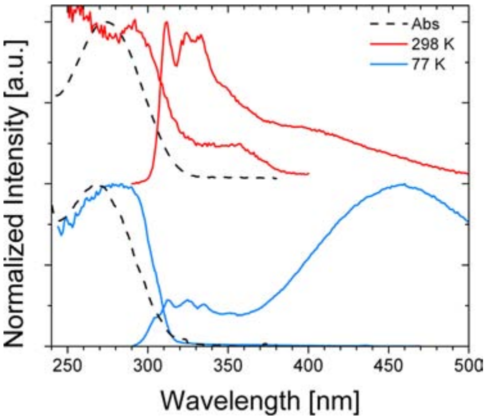


Figure 6. Variable-temperature absorption, excitation, and emission spectral profiles for **2**. Significant phosphorescence emission is observed at low temperature.

fluorescence band that was identified as phosphorescence emission.

While compounds **3-*m*** and **3-*p*** exhibited strong emission at lower energy, the phosphorescence from cyclophane **3-*o*** was very weak: a lifetime could not be recorded. The lifetimes of **3-*m*** and **3-*p*** were ca. 10 μs (see Table 1), but **2** displayed a lifetime of ca. 4 s. There appears to be a correlation between the degree of twist between the terminal phenyl rings as determined from single-crystal X-ray diffraction and the phosphorescence at low temperature.

To gain deeper insight into the different photophysical behavior of the tolanes **2** and **3-*m*** compared with **1**, **3-*o***, and **3-*p***, we performed quantum-chemical calculations on the prototypes **2** and **3-*o***. We identified three different stable ground-state conformers of **2**, which exhibit twist angles of 74.4, −17.6, and −83.5°. The first conformer corresponds to the X-ray structure and represents the thermodynamically most stable one. The second, quasi-planar conformer is 3.2 kcal/mol higher in energy, and the third conformer is even almost 4 kcal/mol less stable. According to a Boltzmann ensemble, the two latter conformers occur to less than 0.5% at room temperature.

Calculation of the vertical excited states of the conformers of **2** using time-dependent density functional theory[16] revealed a strongly optically allowed transition to the S_2 state at 243 nm for the twisted X-ray structure and an optically allowed transition to the S_1 state at 267 nm for the quasi-planar isomer. The second twisted isomer exhibits no allowed transitions to excited states in this energy regime, the first one occurring at 217 nm at this level of theory. Hence, this isomer will be ignored in the further discussion. The allowed excited states correspond to typical $\pi-\pi^*$ HOMO−LUMO excitations.

On the S_1 potential energy surface, we also found three stable minima with twist angles of 42.5, −9.8, and −91.1°. The latter, however, was discarded since it most likely corresponds to an artifact of the exchange−correlation functional. The quasi-planar isomer is 1.8 kcal/mol lower in energy than the twisted one. Since the Franck−Condon point is 15 kcal/mol above the two minima, enough excess energy is present to easily overcome the small energy barrier between the twisted and planar isomers, which originates from a slightly hindered rotation of one carbonyl group (Figure 7). These two isomers also exist on the triplet surface with only slighly smaller twist angles of 34.7 and −5.6° but overall identical structures and computed phosphorescence wavelengths of 605 and 597 nm. The same calculations performed for **3-*o*** revealed the existence of only one stable ground- and excited-state isomer, which is planar.

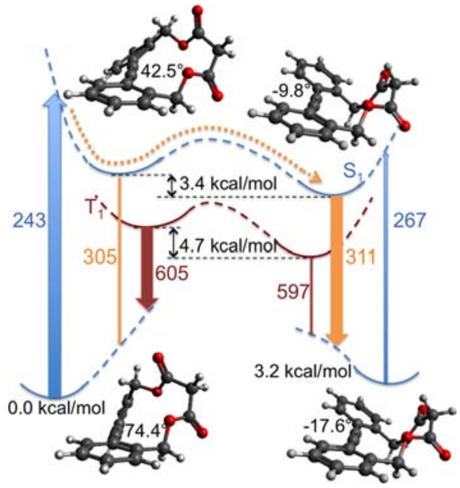


Figure 7. Sketch of the calculated energetics, equilibrium structures, and potential energy surfaces of the ground and optically allowed first excited states of **2**. Upon UV photoexcitation, the molecules planarize, and the fluorescence is red-shifted identically to the planar tolanes. At low temperature, the twisted molecules undergo ISC, and strongly red-shifted phosphorescence is observed, most likely out of the twisted minimum.

The photochemical situation is summarized in Figure 7. Initially, molecules of **2** are photoexcited, absorbing at wavelengths that are blue-shifted relative to planar tolanes such as **3-*o***. At room temperature, **2** undergoes planarization in the singlet S_1 state before it fluoresces out of a planar excited-state structure. This explains the different absorption spectra of the twisted and planarized tolanes as well as the similarity of their fluorescence spectra. At low temperatures in EPA, the detwisting motion is not possible, so the molecules undergo ISC, enabling phosphorescence from the twisted triplet structure.

The long-known tolane fluorophore surprised us with novel and unexpected properties. Upon tethering to form derivatives such as **2**, in the ground state there is an almost perpendicular arrangement of the two phenyl rings with respect to each other. Upon excitation, however, this chromophore partially planarizes, and the emission spectra of **2** and **3-*o*** (in which the phenyl groups are coplanar) are almost superimposable. This alone is surprising, as in tolanes where the twisting is suppressed by steric hindrance, both absorption *and* emission features are blue-shifted. Our attempt to enforce the nonplanarity in the excited state by cooling **2** in an organic glass to 77 K was met by yet another surprise, as the frozen system exhibited significant phosphorescence with a lifetime of ca. 4 s (!), a trait that was not previously observed in any tolane system. The observed long-lived phosphorescence opens unanticipated vistas in this chemistry. In chemical terms, the presence of the triplet state is perhaps not too surprising, as obviously in a starkly simplified picture the perpendicular phenyl rings are electronically "decoupled", therefore enabling each ring to house one electron, stabilizing the triplet state. There are a number of important questions that need to be answered, including whether the same type of behavior will be found in rotationally restricted donor−acceptor tolanes and what might be the consequences of the introduction of such an element into larger polymeric systems. We do think we have found a case where a very old dog unexpectedly has learned some new tricks; we are curious to see whether other surprises await in these fascinating tethered tolanes.

ASSOCIATED CONTENT

Ⓢ Supporting Information

Complete synthetic procedures, characterization data, X-ray crystal structures (CIF), determination of extinction coefficients and fluorescence quantum yields, low-temperature spectroscopy, lifetime measurements, and quantum-chemical calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(14) In the unit cell of **3-*o***, two independent molecules with different but very similar torsion angles were found (4.0 and 6.2°; see the SI). This article focuses on the one with the higher angle.

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