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**Authors:** Yuri Kozhemyakin, Maximilian Krämer, Frank Rominger, Andreas Dreuw, and Uwe Heiko Bunz

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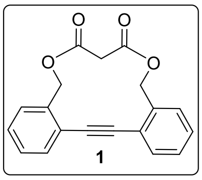
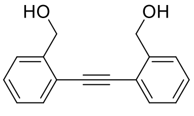
# A Tethered Tolane: Twisting the Excited State

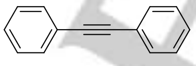
Yury Kozhemyakin,[a] Maximilian Krämer,[b] Frank Rominger,[a] Andreas Dreuw,*[b] und
Uwe H. F. Bunz*[a]

**Abstract:** We report the synthesis of a doubly bridged tolane. The target is obtained in a five-step synthesis, starting from commercially available 2-amino-*meta*-xylene by a combination of a Sandmeyer reaction, radical bromination and Stille-type coupling, followed by double ring closing. The doubly tethered tolane **7** is crystalline; the two phenyl rings are highly twisted with respect to each other both in solution and in the solid state. Optical spectroscopy and quantum chemical calculations show that doubly bridged **7** is twisted not only in the ground state but also in the excited state, leading to emission from the twisted state in solution and in the solid state. Strong phosphorescence is observed at cryogenic temperatures.

Diphenylacetylene, tolane, is an important fundamental chromophore in organic and polymer chemistry.[1] Linear and cyclic oligomers as well as tolane-based polymers display optical properties which render this class of molecules attractive, particularly in sensor-type applications.[2] The parents´ optical properties are defined by its planarity in the solid state. In solution tolane features a minute rotational barrier (<1kcal/mol). Despite this, tolane absorbs and emits only from the planar conformation, even in solution. Oligomers and polymers of tolane, optical properties strongly suggest, however, twisted phenyl rings.

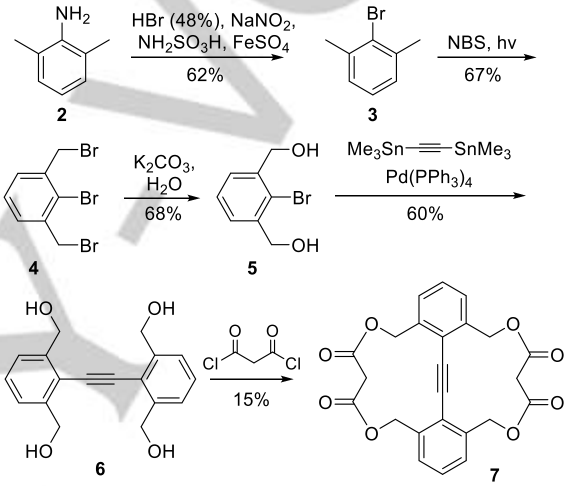

**1**


**1a**


TOLANE

One possibility to explore the photophysics of twisted tolane is to suppress planarization either through steric hindrance (difficult) or,[3] or forcing the tolane by a molecular tether into the desired twisted conformation. Tethers successfully enforce torsion angles between the two phenyl rings of tolane.[4] Length and composition of the tether are critical, or otherwise the planar form is stabilized. Since the first papers by Finney and Crisp and Bubner, tethering[5] is a tool for the engineering of the twist angle in tolanes.[6] Yet, only in 2013 we published a privileged tether structure, which sets the torsion close to 90°.[7] The tolanophane **1** is twisted in its ground state in solution, but planar in the excited state, despite tethering. This behavior is illuminated by the optical properties and quantum chemical calculations of **1**.[6] The absorption spectrum of **1** is blue-shifted in comparison to that of **1a**, while the emission spectra of **1** and **1a** are superimposable (for optical spectra of **1a** see Supporting Information). Only for samples of **1** that are cooled to 77 K one observes a blue-shifted emission and long-living phosphorescence.

Here we describe the synthesis and the properties of a doubly bridged tolanophane, **7**, twisted in its ground and excited states, due to the presence of *two* molecular tethers.



**Scheme 1.** Synthesis of a doubly bridged permanently twisted tolanophane **7**.

Starting from **2** a Sandmeyer reaction furnishes **3**.[8] Double radical bromination (via **4**[9]) and hydrolysis to **5**[10] gives the open tolane **6** after Stille coupling.[11] The last step closes both auxiliary cycles, using malonyl chloride to give the target **7** in moderate yield. **7** is crystalline so a single crystal structure analysis was performed.

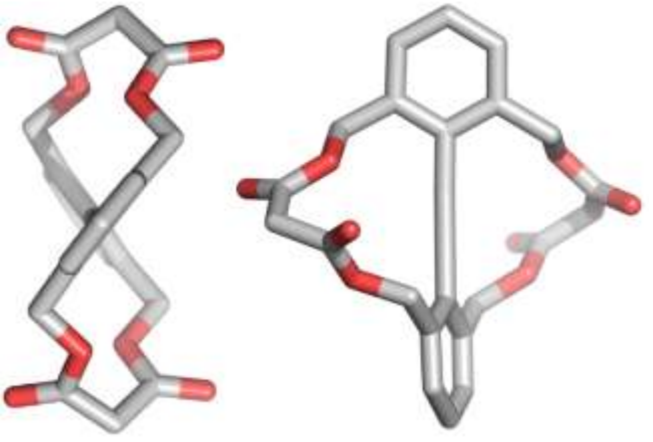


**Figure 1.** Single X-ray crystal structure of **7**. The torsion angle between both phenyl rings is $\phi$ = 74.4° in the solid state.

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[a] Prof. U. Bunz, Dr. Y. Kozhemyakin, Dr. F. Rominger,
Organisch-Chemisches Institut, Ruprecht-Karls-Universität
Heidelberg, Im Neuenheimer Feld 270, 69120 Heidelberg, FRG
E-Mail: uwe.bunz@oci.uni-heidelberg.de
[b] Prof. A. Dreuw, Dr. M. Krämer,
Interdisziplinäres Zentrum für Wissenschaftliches Rechnen,
Ruprecht-Karls-Universität Heidelberg, Im Neuenheimer Feld 205,
69120 Heidelberg, FRG

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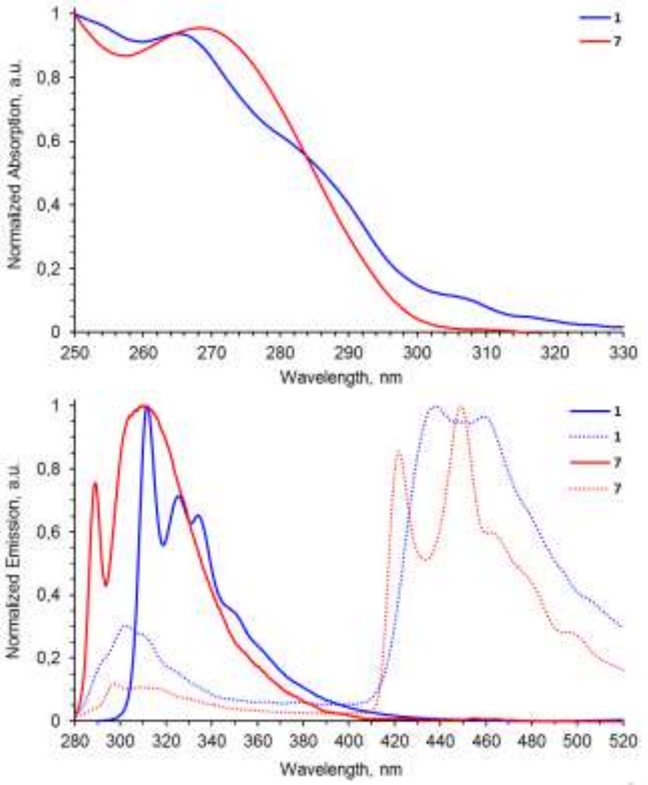

**Figure 2.** Absorption- (top) and emission spectra (bottom) of **1** and **7** in solution (*n*-hexane, solid line, excitation wavelength: **1** at 280 nm, **7** at 265 nm). Emission spectra in cryogenic matrices at 77 K in EPA (diethyl ether : isopentane : ethanol 5:5:2, dotted line, excitation wavelength: **1** at 264 nm, **7** at 265 nm).

Figure 1 displays the molecular structure of **7** in the single crystal. Bond length and bond angles are inconspicuous, the acetylene bridge linear – a consequence of the double symmetrical tethers that exact a symmetrical twisted conformation. The torsion of the phenyl rings is $\phi = 74.4°$. If one assumes that the $\pi$-overlap is proportional to $(\cos \phi)^2$ of the torsion angle, the $\pi$-overlap is only 7% of that of the planar conformation, to be neglected. The absorption and emission spectra of **7** and **1** are shown in Figure 2. The absorption spectra of **1** and **7** are similar, but the spectrum of **7** is a bit red-shifted. Significant differences, however, exist in the emission spectra. **1** shows at room temperature the typical red shift that accompanies planarization, ($\lambda_{\text{max.em}}$ at 312 nm), the emission of **7** is blue shifted but structured with a $\lambda_{\text{max.em}}$ at 289 nm (4.3 eV) and a second emission band at 310 nm (4.0 eV). The emissive quantum yield (*n*-hexane, 0.01) is low but easily measurable. The emissive life time is $\tau = 0.2$ ns fairly short; planar and singly tethered tolanes have emissive lifetimes (*n*-hexane) of 0.4 ns.[4a,b]

Upon decrease of the temperature, we find a slight blue shift of the emission of **1** and the appearance of strong phosphorescence. This behavior is also observed for **7**. The phosphorescence of **7** displays two dominant bands at 425 and 450 nm (2.75 and 2.9 eV), but the residual low temperature fluorescence is identical to the fluorescence of **7** at room temperature; **7** must be twisted in ground and excited states and does not planarize – contrary to **1** at room temperature in the excited state.
To support the interpretation of the optical spectra we performed quantum chemical calculations. The geometry of **7** was DFT-optimized, starting from the geometry of the X-ray crystal structure. DFT/CAM-B3LYP gives a torsion angle of 73.1°. Even though a search of the potential hypersurface shows the existence of further local minima, conformational isomers of **7**, all highly energetic and at least 10 kcal/mol above the energy of the twisted geometry of **7** in the crystal structure. We excluded these other conformers; the twisted one is the only one present in solution.

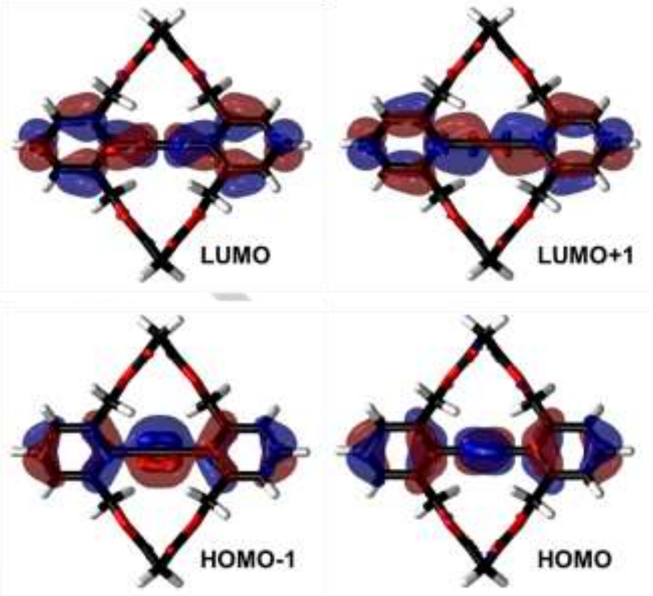

**Figure 3.** Frontier molecular orbitals of **7** (DFT/CAM-B3LYP/6-31G*) in the optimized ground state structure.

The vertical excitation energies of **7** were calculated for the optimized twisted structure (TDDFT/CAM-B3LYP, gas phase, Table 1). The $S_2$-state displays huge oscillator strength and therefore dominates the absorption spectrum. The computed vertical excitation energy is 4.92 eV, corresponding to a wavelength of 256 nm, in reasonable agreement within the expected error of the applied methodology of ±0.2 eV (*n*-hexane, Figure 2). The $S_2$ state represents the HOMO->LUMO excitation. The $S_1$ state is almost isoenergetic with excitation energy of 4.84 eV but with vanishing oscillator strength, representing an electronic excitation from HOMO-1 into LUMO. This state is not observed in the experimental spectra.

**Table 1:** Relative energies of the relevant excited states for the photochemistry of **7** at the identified local minima in the electronic ground state $S_0$ (twisted (tw), planar (pl)), in the $S_1$ state (tw), trans-bent (tb), pl) and the $T_1$ state (tw, pl), the corresponding maximum absorption/emission wavelengths ($\lambda_{max}$) as well as the twisted angle computed at TDDFT/CAM-B3LYP level of theory.

| | **$S_0$** | | **$S_1$** | | | **$T_1$** | |
|---|---|---|---|---|---|---|---|
| | tw | pl | tw | tb | pl | tw | pl |
| $E(S_0)$ [eV] | 0.0 | 0.42 | 0.45 | 1.29 | 0.74 | 0.47 | 0.83 |
| $E(S_1)$ [eV] | 4.84 (0.00) | 4.97 (0.67) | 4.39 (0.00) | 4.27 (0.01) | 4.54 (0.72) | 4.63 (0.12) | 4.57 (0.80) |
| $E(S_2)$ [eV] | 4.92 (0.27) | 5.33 (0.06) | 4.54 (0.24) | 5.42 (0.09) | 4.98 (0.09) | 4.69 (0.31) | 5.02 (0.06) |
| $E(T_1)$ [eV] | 3.45 | 3.49 | 3.22 | 3.60 | 3.13 | 3.06 | 3.11 |
| $\lambda_{max}$ [nm] | 256[a] | 273[a] | 315[b] | 416[b] | 326[b] | 479[c] | 544[c] |
| φ [deg] | 73.1 | 20.4 | 70.4 | 67.5 | -16.6 | 66.4 | -13.6 |

[a] corresponds to the maximum absorption wavelength
[b] corresponds to the maximum fluorescence wavelength
[c] corresponds to the maximum phosphorescence wavelength

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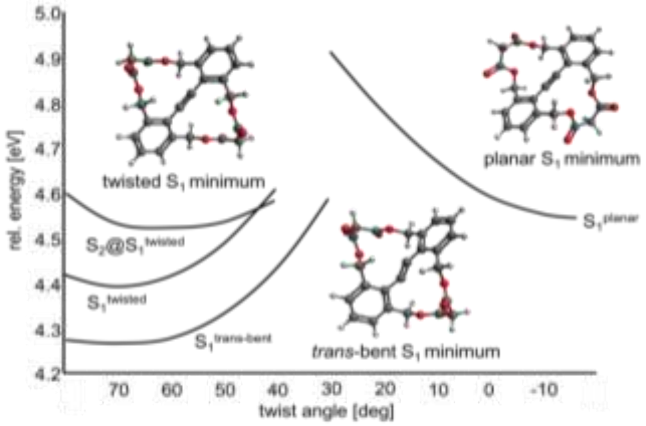

**Figure 4.** Optimized potential energy curves (TDDFT/CAM-B3LYP) of the $S_1$ state along the twist angle of the phenyl rings for the identified local minima: $S_1^{twisted}$, $S_1^{trans\text{-}bent}$ und $S_1^{planar}$. The insets show the optimized structures from above (left) and from the front (right).

The geometry optimization of the electronically excited singlet state, $S_2$, starting from the equilibrium geometry of the ground state, leads directly into a twisted minimum ($S_1^{twisted}$), structurally similar to the ground state. The twist angle decreases to 70.4°. Geometry optimization transforms the $S_2$-state into the $S_1$-state with a vertical fluorescence energy of 3.94 eV (315 nm), in excellent agreement with the fluorescence spectrum of **7**.

The $S_1$-potential surface shows further local minima corresponding to stable conformational isomers, a *trans-bent* isomer ($S_1^{trans\text{-}bent}$) and a planar isomer ($S_1^{planar}$). The planar minimum (-16.6°, 0.15 eV) is energetically localized above that of the twisted minimum (Table 1) and can only be reached via a very high energy barrier (Figure 4), so we exclude the population of the minimum after optical excitation. The twisted *trans-bent* minimum is 0.12 eV lower in energy than the twisted one and can be reached over a barrier of 0.2 eV (Figure 4). The radiationless transition of the planar *trans-bent* structure is the main deactivation channel, which leads to the fluorescence quenching of **7**; it explains the low emissive quantum yield of 0.01. Only the part of the excited molecules fluoresce that are trapped in the twisted minimum. As the oscillator strength of the twisted *trans-bent* minimum is small we find impulse deactivation leading to intersystem crossing into the triplet manifold, as shown for the unsubstituted tolane.[1a] Contrary to the unsubstituted tolane and to **1**, in case of **7** the central dihedral is still *67.5°*. Here also the double tether hinders the planarization through massive steric interactions.

To describe the phosphorescence by theory, the geometry of the lowest energy triplet, $T_1$ was optimized. As in the singlet state, the triplet is also twisted. The central dihedral displays an angle of 66.4°. For $T_1$ we found an additional, planar minimum, however, it is energetically not accessible. Both triplet structures are – by inspection – almost indistinguishable from the twisted and planar structures of the $S_1$ state, while a *trans-bent* minimum does not exist. The observed phosphorescence emanates therefore from this twisted minimum. In the twisted $T_1$ state an unpaired electron occupies the HOMO and one the LUMO of the singlet ground state. In the equilibrium geometry of $T_1$ the excitation energy is 2.59 eV, a phosphorescence wavelength of 479 nm, in good agreement with the experimental data.

In conclusion we have prepared a doubly bridged tolane **7**, and investigated its single crystal structure, spectroscopy, and quantum chemistry. We demonstrated for the first time that two tethers fixate the forcibly twisted tolane geometry in ground and excited states, with the excited state being twisted trans-bent. The blue-shifted absorption and emission of **7** fashions the doubly bridged tolane into an attractive building block, to be introduced into conjugated polymers to achieve band-gap engineering towards the blue or alternatively to achieve enforced phosphorescence.

## Experimental

All quantum chemical calculations were performed with Q-Chem 5.0, the electronic ground state was calculated with DFT and the electronically excited state was calculated using time dependent DFT (TDDFT) with CAM-B3LYP and 6-31G* basis set respectively. In earlier investigations of tolane and a bridged tolane **1** this methodology was found to be precise.

**6**: A published procedure was adapted.[11] Bis(trimethylstannyl)acetylene (1.00 g, 2.84 mmol, 0.5 eq) and $Pd(PPh_3)_4$ (0.657 g, 0.569 mmol, 0.1 eq) were added to a degassed solution of **5** (1.24 g, 5.69 mmol, 1.0 eq) in anhydrous 1,4-dioxane (140 mL) followed by stirring for 20 h at 110 °C. Upon cooling, Celite was added and volatiles were removed *in vacuo*. Chromatographic purification (silica gel; $CH_2Cl_2$/methanol 10:1, v/v) yielded a brownish solid. Yield: 509 mg (1.71 mmol, 60%). Analytical sample was prepared by recrystallization from methanol.

$R_f$=0.23 ($CH_2Cl_2$/methanol 10:1, v/v); m.p. 208°C (decomp.); $^1$H NMR (DMSO-$d_6$, 600 MHz): δ=4.77 (d; *J* 5.8 Hz; 8H; $ArCH_2$), 5.38 (t; *J* 5.8 Hz; 4H; OH), 7.41–7.48 (m; 6H, $H_{Ar}$) ppm; $^{13}$C NMR (DMSO-$d_6$, 150 MHz): δ=61.6, 94.0, 116.9, 124.3, 128.3, 143.9 ppm; IR (neat): $\tilde{v}$=3267, 2818, 1462, 1417, 1363, 1327, 1232, 1161, 1067, 1043, 780, 668 cm$^{-1}$; HRMS (DART+) m/z: $[M+NH_4]^+$ calcd for $C_{18}H_{22}NO_4$: 316.1543; found: 316.1544, correct isotope distribution; elemental analysis calcd (%) for $C_{18}H_{18}O_4$: C 72.47, H 6.08; found: C 72.07, H 6.36.

**7**: A solution of malonyl dichloride (171 μL, 1.756 mmol, 4 eq) in dry $CH_2Cl_2$ (6 mL) was added in 1.5 h to a suspension of the tetra-ol **6** (131.0 mg, 0.439 mmol, 1 eq) in dry $CH_2Cl_2$ (11 mL) under nitrogen at RT. The reaction mixture was stirred for 24 h filtered through silica gel and flushed with ethyl acetate (100 mL). Chromatography (silica gel; $CHCl_3$/petroleum ether 1:1, v/v) gives **7** as colorless material in 15% (30.0 mg, 69.1 μmol).

$R_f$=0.38 (petroleum ether/ethyl acetate 1:1, v/v); m.p. 302°C (decomp.); $^1$H NMR ($CDCl_3$, 400 MHz): δ = 3.39 (s; 4H; $COCH_2CO$), 4.91 (d; *J* 11.3 Hz; 2H; $ArCH_2$), 5.43 (d; *J* 11.3 Hz; 2H; $ArCH_2$), 7.36–7.45 (m; 6H; $H_{Ar}$) ppm; $^{13}$C NMR ($CDCl_3$, 150 MHz): δ=41.7, 67.4, 92.4, 125.3, 129.0, 131.5, 137.2, 166.1 ppm; IR: $\tilde{v}$=2954, 1724, 1472, 1373, 1274, 1211, 1138, 999, 984, 795 cm$^{-1}$; HRMS (DART+) m/z: $[M+NH_4]^+$ calcd for $C_{24}H_{22}NO_8$: 452.1340; found: 452.1334, correct isotope distribution; elemental analysis calcd (%) $C_{24}H_{18}O_8$: C 66.36, H 4.18; found C 65.90, H 4.28; X-ray analysis: $C_{24}H_{18}O_8$, $M_w$=434.40, colorless crystal was harvested after slow evaporation of a $CDCl_3$-solution of **7**. Size 0.203 × 0.097 × 0.076 mm$^3$, monoclinic, space group C2/c, *Z*=8, *a*=29.675(2) Å, *b*=10.1444(7) Å, *c* = 17.3726(12) Å, $\alpha$ = 90°, $\beta$=115.2430(19)°, $\gamma$ = 90°, *V* = 4730.3(6) Å$^3$, $\rho$ = 1.220 g/cm$^3$, *T* =200(2) K, $\Theta_{max}$ = 25.390°, Radiation $Mo_{K\alpha}$, $\lambda$=0.71073 Å, 15163 reflections measured, 4345 independent reflections, ($R_{int}$=0.0606), 2537 observed reflections ($I>2\sigma(I)$); $R_1(F)$ = 0.051, $wR(F^2)$ = 0.098 for the observed data. CCDC 1858258 contains additional crystallographic information for this publication. Data can be obtained from Cambridge Crystallographic Data Centre via https://www.ccdc.cam.ac.uk/structures/. All synthetic details and analytical data are found in the Supporting Information.

**Acknowldegement**

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**References:** Tolane • Twisting • Tolanophane • Bridged Chromophore •

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**Entry for the Table of Contents** (Please choose one layout)

Layout 1:

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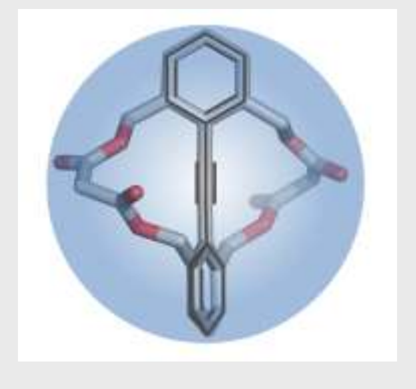
Let's twist again: Two tethers fix the two phenyl rings of the target structure, a tolane, twisted - even in the electronically excited state. The double bridging is necessary because a single linker is not sufficient for holding the two phenyl rings perpendicular to each other in the excited state.



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