

Chemically Controlled Conductivity: Torsion-Angle Dependence in a Single-Molecule Biphenyldithiol Junction**

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Dedication to Professor Hans Kuhn on the occasion of his 90th birthday

Electron transport through molecules has received great attention since organic structures have been considered as the active elements in electronic nanoscale devices.^[1–5] In various experimental setups it is possible to integrate single molecules in electronic circuits and to measure their conductance. Examples include mechanically controlled break junctions (MCBJ)^[6,7] and break junctions based on scanning tunneling microscopy (STM),^[8,9] which enabled basic investigations of correlations between molecular structures and transport properties on a single-molecule level.^[10–14] However, these studies depend on several parameters: 1) the formation of a reproducible and stable contact between the molecule and both metal electrodes, 2) the structure and the conformation of the bridging molecule, and 3) the algorithms used for the subsequent processing of the obtained raw data. Since parameters (1) and (2) can be controlled by synthetic chemistry to a large extent, synthesis currently plays a major role in the study of structure–transport correlations and the design of functional molecules as active components in electronic circuits.

Biphenyl derivatives, which consist of two aromatic rings connected by a single C–C bond, have attracted considerable interest as model compounds because of their size and ready availability.^[15–17] Furthermore this type of unit has been considered as a potential conductance switch as the two

π systems can be either in the same plane or perpendicular to each other representing the “on” and “off” states of a molecular switch, respectively.^[18–20] In a recent study, Venkataraman^[10] and co-workers reported the interdependence between the calculated molecular conformation and the single-molecule conductance of a series of various substituted biphenyls having terminal amino groups.^[10] Despite several varying parameters such as electron density on the phenyl rings and steric repulsion of the substituents, a linear correlation was found between the conductance and the square of the cosine of the calculated torsion angle between the planes of the two rings. While these transiently immobilized diamines contribute to understanding the structure–property relationship, sulfur-functionalized structures form considerably more stable single-molecule junctions between gold electrodes.^[21] Furthermore, theoretical studies on sulfur-functionalized biphenyls have gained considerable attention^[19,20] and even molecular junctions comprising biphenyldithiols (BPDT) have been reported.^[18] Despite the strong interest in the correlation between the torsion angle and transport properties, suitable model compounds enabling the systematic variation of the torsion angle in biphenyl systems have not been realized so far. Here we report our new approach towards biphenyl systems with controlled torsion angles.

As displayed in Figure 1, an alkyl chain of varying length connected at the 2,2'-positions of the biphenyl system in compounds **1–5** can be used to adjust the torsion angle Φ . In this series of compounds the length of this alkyl chain is the

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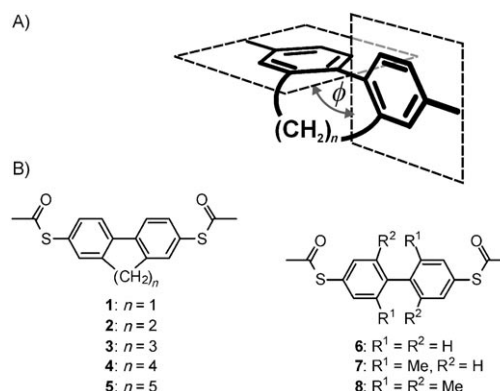
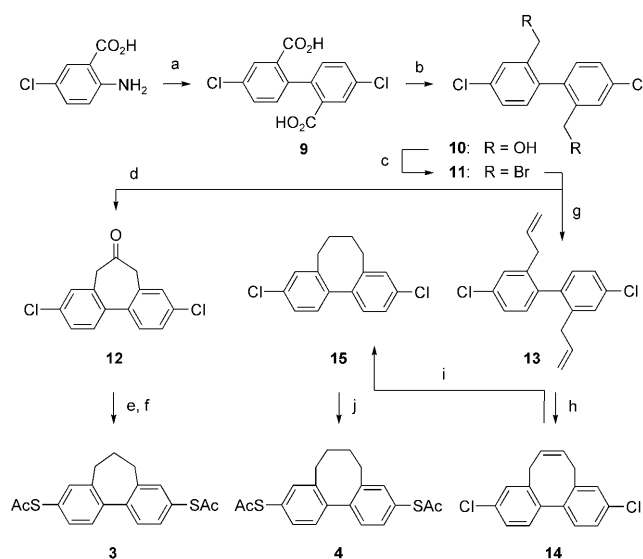


Figure 1. A) The torsion angle Φ formed by the planes of the phenyl rings is adjusted by the length of the bridging chain. B) Compounds **1–8**.

only structural variation; the electronic structure of the biphenyl systems in this family of compounds is kept as uniform as possible. We note that considerable effects of the electron-donating character of substituents on the transport properties of immobilized single molecules have been reported.^[22] Furthermore, the biphenyl conformation is locked by the intramolecular bridge; the number of CH₂ units dictates the torsion angle Φ and decreases the expected motion and conformational variation of each molecule immobilized in the junction considerably. The individual compounds of this series form stable molecular junctions through their terminal sulfur anchor groups. Finally, single crystals of these compounds can be grown and X-ray structure analyses can be used to determine the torsion angle Φ .

To follow this strategy we focused on the biphenyls **1–5** with $n = 1–5$ in which the length of the alkyl bridge and thus also the torsion angle Φ increases. In addition, this series of terminally acetylsulfanyl-functionalized biphenyl systems was complemented by compounds **6–8**, in which the torsion angle was expected to depend on the substitution pattern.

The synthesis of the biphenyldithiols (BPDTs) **1, 2, 6**, and **7** has already been published,^[23] and the synthetic route to the tricyclic BPDTs **3** and **4** is displayed in Scheme 1. The key building block **11** was obtained in three steps. An oxidative coupling provided the doubly chlorine and carboxylic acid functionalized biphenyl **9**. Its reduction gave diol **10**, which was subsequently transformed to the benzylic dibromide **11** in a yield of 41 % over the three steps.

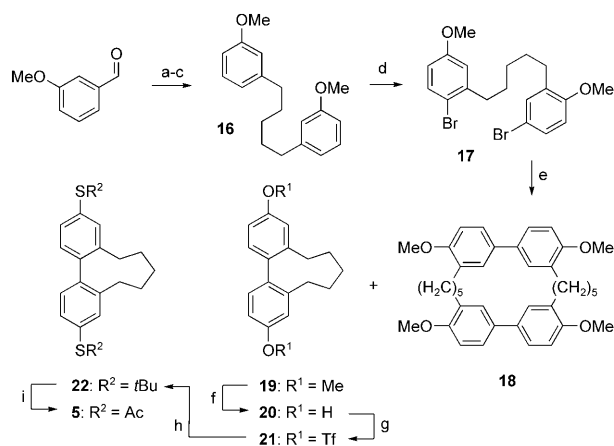


Scheme 1. Reagents and conditions: a) NaNO₂, HCl, 0 °C, then CuSO₄, HO-NH₂, NH₄OH, H₂O, 0 to 70 °C, 84 %; b) NaBH₄, BF₃·Et₂O, THF; c) PBr₃, CH₂Cl₂, 0 °C, 49 % (over 2 steps); d) TosMIC, NaOH, TBAB, CH₂Cl₂/H₂O; then HCl, *t*BME/H₂O, 77 %. e) PMHS, (C₆F₅)₃B, CH₂Cl₂, RT, 61 %. f) NaSCH₃, DMI; then AcCl, 110 °C, 49 %. g) CH₂CHMgBr, CuI, CH₂Cl₂, –40 °C to RT, 58 %. h) Grubbs' first generation catalyst, CH₂Cl₂, reflux, 88 %. i) H₂, Pd/C 10 %, RT, EtOAc, 95 %. j) NaSCH₃, DMI; then AcCl, 110 °C, 32 %. DMI = 1,3-dimethyl-2-imidazolidinone, PMHS = poly(methylhydrosiloxane), TBAB = tetrabutylammonium bromide, *t*BME = *tert*-butylmethyl ether, TosMIC = *p*-toluenesulfonylmethyl isocyanide.

To obtain a compound with a bridging alkyl chain containing three carbon atoms, an additional carbon atom was introduced by the intramolecular cyclization of **11** with the masked formaldehyde equivalent TosMIC.^[24] The resulting ketone **12** was obtained in 77 % yield. After the Lewis acid catalyzed reduction of the keto group,^[25] the substitution of both chlorines with methylthiolates followed. The resulting methylsulfanyl derivative was converted in situ into the acetylsulfanyl-functionalized target structure **3**.^[23,26]

Again starting from **11**, a copper-mediated Grignard addition gave the diallylic biphenyl **13**. Although the formation of eight-membered rings by ring-closing metathesis (RCM) was reported to be difficult,^[27,28] the cyclization of **13** to give **14** proceeded smoothly, probably because the allyl chains in **13** are conformationally predisposed. Subsequent hydrogenation and reaction sequence similar to that described for **3** resulted in the replacement of the chlorines by acetylsulfanyl groups to provide the butylene-bridged BPDT derivative **4**.

The cyclononane structure in **5** was assembled by an alternative strategy. As shown in Scheme 2, the inter-ring pentyl chain was established prior to the formation of the



Scheme 2. Reagents and conditions: a) Acetone, NaOH, EtOH. b) H₂, Pd/C (10 %), EtOAc, 1 atm, 52 % (over 2 steps).^[29] c) Hydrazine (85 %), KOH, triethylene glycol, 190–200 °C, 72 %.^[30] d) Br₂, pyridine, –10 °C to RT, 42 % (after recrystallization).^[31] e) *t*BuLi, CuCN, LiBr, methyl-THF, –60 °C, then 1,3-dinitrobenzene, 23 % for **19**. f) BBr₃, CH₂Cl₂, RT. g) Tf₂O, pyridine, 4 °C to RT. h) *t*BuSNa, [Pd₂(dba)₃], xantphos, *p*-xylene, 140 °C, 52 % (over 3 steps). i) BBr₃, AcCl, toluene, 61 %. dba = dibenzylideneacetone, Tf₂O = trifluoromethanesulfonic anhydride, xantphos = 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene.

biphenyl core. The terminal methoxyphenyl-functionalized pentane derivative **16** was obtained following an established protocol.^[29,30] Subsequent bromination^[31] gave the building block **17**, which was purified by several recrystallizations. Implementation of the Lipshutz methodology^[32] gave the unwanted dimer **18** as the main product (27 %) together with almost comparable amounts (23 %) of the desired pentylene-bridged biphenyl system **19**. In subsequent functional group transformations the terminal methoxy groups in **19** were replaced with triflate groups (→**21**). The *tert*-butyl-protected

terminal sulfur groups in **22** were introduced in good yields by a palladium-catalyzed cross-coupling reaction. A final adjustment of the protecting groups^[33,34] gave the target structure **5**, as acetyl-protected pentylene-bridged BPDT.

All new compounds and intermediates were fully characterized by ¹H and ¹³C NMR spectroscopy, mass spectrometry, and elemental analysis. A comprehensive description of the syntheses of the target structures will be published elsewhere.^[35]

Of particular interest was the X-ray crystal structure analysis of the new BPDT structures **1–8** not only to confirm the identity of the compounds, but also to investigate the correlation between the length of the bridging alkyl chain and the resulting torsion angle Φ . While attempts to crystallize the fluorene derivative **1** and the unsubstituted BPDT compound **6** failed, we were able to obtain single crystals of the bridged BPDTs **2–4** from hot cyclohexane and, in the case of **5**, from hot pentane, after storing at 4 °C.^[36] In addition, the solid-state structure of the dimethylated BPDT **7** has already been reported, and suitable single crystals from the tetramethyl-substituted BPDT **8** were also obtained from hot cyclohexane.^[35]

The solid-state structures of the BPDTs **2–5** in order of the increasing length of the bridging alkyl group are shown in Figure 2. The intramolecular sulfur–sulfur distances and the torsion angles Φ are listed in Table 1. Within the series of compounds the sulfur–sulfur distances are very comparable; the values between 1.059 nm for **5** and 1.062 nm for **7** indicate that the alkyl chain length has hardly any effect on the BPDT backbone. Apparently, steric repulsion arising from the various alkyl substituents is compensated by adjustment of

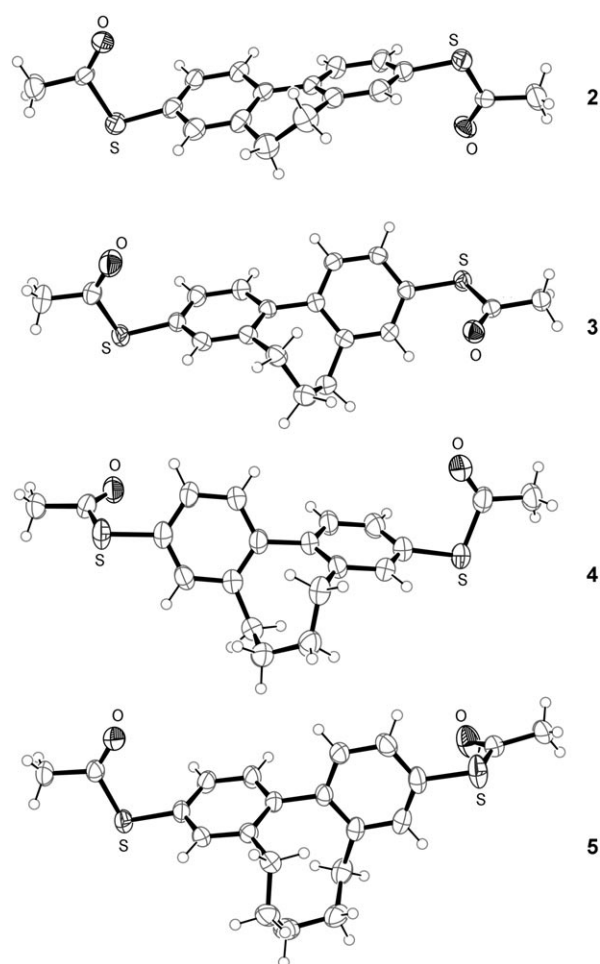


Figure 2. X-ray structures of the bridged BPDTs **2**, **3**, **4**, and **5** (from top to bottom).

Table 1: Molecular structures and measured properties.

	Structure ^[a]	Φ [°] ^[b]	d [nm] ^[c]	G/G_0
1		1.1 ^[38]	–	$1.45 \pm 0.1 \times 10^{-4}$
2		16.8	1.061 (2)	$2.19 \pm 0.2 \times 10^{-4}$
3		44.7	1.060 (9)	$1.30 \pm 0.2 \times 10^{-4}$
4		57.8	1.060 (5)	$6.97 \pm 1.7 \times 10^{-5}$
5		71.5	1.059 (4)	$1.68 \pm 0.3 \times 10^{-5}$
6		36.4 ^[19]	–	$1.72 \pm 0.2 \times 10^{-4}$
7		79.7 ^[23]	1.06 (2) ^[23]	$1.29 \pm 0.2 \times 10^{-5}$
8		89.0	1.061 (2)	$9.03 \pm 1.7 \times 10^{-6}$

[a] Synthesized with R = Ac; immobilized with R = Au electrodes. [b] Φ is the torsion angle between the planes of the phenyl rings. [c] d is the distance between the sulfur atoms.

the inter-ring torsion angle Φ . This torsion angle was measured between the planes of the two phenyl rings of the biphenyl system which were obtained by considering all six carbon atom positions of the solid-state structure for the least squares minimization procedure. The obtained torsion angles Φ (Table 1) increase continuously with the increasing length of the alkyl bridge. While the elongation by one CH₂ unit on going from fluorene **1** to dihydrophenanthrene **2** increases the torsion angle by 15.7°, the largest increase in the torsion angle, almost 28°, is observed on going from dihydrophenanthrene **2** to the C₃-bridged BPDT system **3**. Further extension to the C₄- and C₅-bridged derivatives **4** and **5** result in additional expansions of the angle Φ by 13.1° and 13.7°, respectively.

An almost perpendicular arrangement of the two phenyl rings was found in the solid-state structures of the dimethyl and tetramethyl derivatives **7** and **8** (Φ = 79.7° and 89°, respectively). The rotational barriers of the methyl-substituted compounds **7** and **8**, and in particular of the alkyl-bridged derivatives **2–5**, are expected to be considerably higher than that of the unsubstituted BPDT **6** (2–3 kcal mol^{−1}).^[37] Thus, in spite of the increased structural flexibility of these compounds in solution, the Φ values obtained by

solid-state structure analysis remain the best approximation of the values in solution.

Of particular interest is the conductance through these BPDT structures, which vary mainly in the inter-ring torsion angle Φ . The BPDT structures **1–8** were investigated between the gold tip and the gold substrate at the solid–liquid interface of a scanning tunneling microscope (STM) break junction setup^[9] protected by an argon gas atmosphere. A 250 μm solution of the BPDT under investigation in mesitylene/tetrahydrofuran (4:1) was treated with a 125 μm solution of tetrabutylammonium hydroxide to remove the acetyl protection groups. The resulting free thiols form covalent gold–sulfur bonds thus immobilizing the rod-shaped molecule inside the junction. To distinguish the molecular junctions from the synthesized molecules **1–8**, they will be denoted as **1'–8'**. Three different voltages (65, 100, and 180 mV) were applied between tip and substrate while the junction was repeatedly opened and closed to establish transient single-molecule contacts. Several thousand junctions were created, and the current was recorded as a function of tip distance. Only current traces displaying typical single-molecule current plateaus were selected by an automated algorithm and considered ($20 \pm 10\%$) for the conductance analysis. The extracted conductance histograms revealed characteristic peaks corresponding to the conductance of the single BPDT junction. A comprehensive technical description of the single-molecule investigation and the analysis algorithm will be published elsewhere.^[39]

According to theory, the orbital overlap of adjacent π systems correlates linearly with $\cos \Phi$ and the electron transmission is proportional to $\cos^2 \Phi$, where Φ is the torsion angle.^[40] Figure 3 displays the plot of the junction conduc-

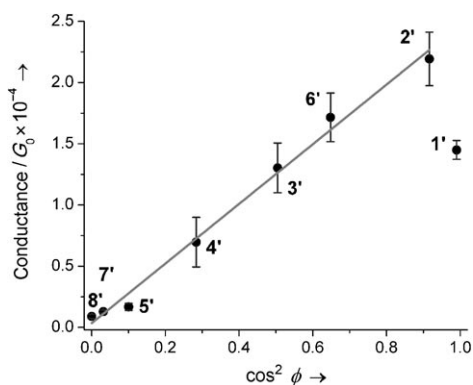


Figure 3. Conductance peaks of the molecular junctions **1'–8'** plotted against $\cos^2 \Phi$, with Φ as the measured torsion angle obtained from the X-ray structure analysis.

tance (G/G_0) against $\cos^2 \Phi$ for each BPDT derivative investigated. The data represent averages of the three bias voltages applied as extracted from the corresponding conductance histograms.

With the exception of the fluorene structure **1**, the series of BPDTs displays a linear correlation between the conductance of their single-molecule junction and the value of $\cos^2 \Phi$ obtained from the X-ray data. Interestingly, the

conductance values observed for **1** are considerably lower than expected. Theoretical calculations did not support an additional stabilization of the HOMO resulting from the extended delocalization of the fluorene π system.^[41] Therefore, only the single bridging methylene unit in **1** and the resulting bend of its biphenyl axis remain as distinctive structural features which may cause the observed decrease in conductance.

In conclusion, we have described the synthesis and the structural analysis of a family of BPDTs in which the torsion angle Φ is fixed by a bridging alkyl chain. The series is complemented by three derivatives with various numbers of methyl substituents in the 2,2',6,6'-positions to vary Φ by steric repulsion. Investigation of the single-molecule conductance of the series displays a linear correlation with $\cos^2 \Phi$ of the inter-ring torsion angle for BPDTs with a divided π system. A similar trend in increased conductance values has been reported for various substituted amino-terminated biphenyls.^[10] In contrast to these findings, the planar fluorene derivative **1** displays reduced conductivity in our case, pointing at additional, equally important parameters governing the transport efficiency besides the planarity of the π system. During the preparation of this manuscript, Haiss and co-workers reported transport investigations through several BPDTs.^[18] While the reported current values are surprisingly low, a clear relationship between conductance and conformation relationship was not found.

The biphenyl unit **7** has already been used as π -system-dividing subunit in a single-molecule rectifier.^[42] Currently we are integrating the series of biphenyl building blocks with fixed torsion angles into model compounds to study the relationship between the structure and nonlinear optical properties.^[43] Furthermore, we are working on potential switching systems based on the changes of conductivity with changes in torsion angle.

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