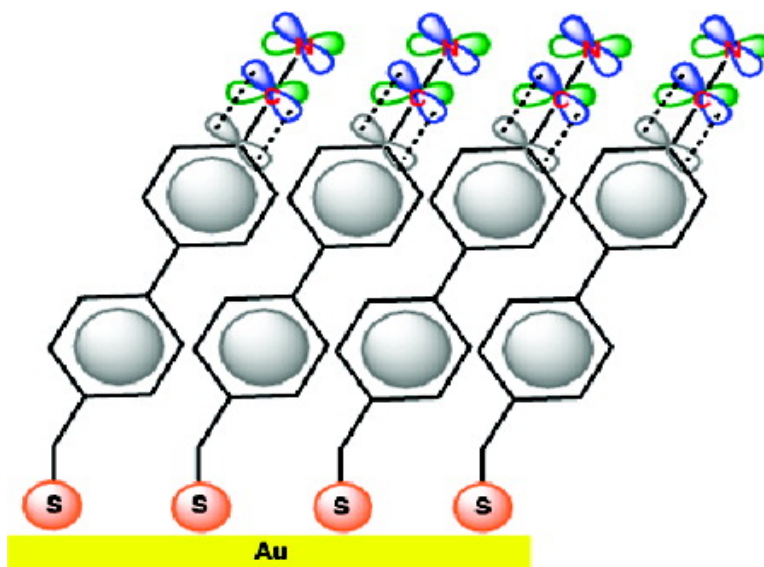


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J. Am. Chem. Soc., **2007**, 129 (50), 15416-15417 • DOI: 10.1021/ja0751882

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Direct Probing Molecular Twist and Tilt in Aromatic Self-Assembled Monolayers

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The emergence of molecular electronics¹ and other new technologies ranging from sensor fabrication² to chemical lithography³ has triggered significant interest in aromatic self-assembled monolayers (SAMs) with chalcogen headgroups.^{2,4} Both understanding the properties of these systems and their applications rely on a precise knowledge of their structure. This issue has been addressed by spectroscopy,^{4–10} X-ray scattering,¹¹ and scanning microscopy.^{6,8,12–15} According to the results of the two latter techniques, a variety of molecular arrangements is possible, depending on the exact architecture of the molecular backbone, where aromatic units are frequently combined with different tailgroups or/and aliphatic linkers.^{8,6,14} In particular, for densely packed films, $\sqrt{3} \times \sqrt{3}$ and $\sqrt{3} \times 2\sqrt{3}$ structures were observed, and herringbone packing was assumed,^{6,13,14} similar to the respective bulk materials.¹⁶ However, the proposed molecular arrangements mostly treated the SAM constituents as being oriented upright without taking into account their exact orientation, which is generally given by two angles (see Figure 1), viz. the tilt angle of the molecular axis (β) and the twist angle of the aromatic backbone with respect to the plane spanned by the surface normal and the molecular axis (γ). Unfortunately, these angles could not be determined independently by spectroscopic experiments, most of which imply that the molecules are noticeably tilted ($\beta = 16\text{--}37^\circ$)^{5–10} but fail to deliver both β and γ values. Only for a few aromatic SAMs could both tilt and twist angles be derived either from a complex analysis of Fourier transform infrared spectra (FTIR)⁸ or from a combination of FTIR and near-edge X-ray absorption fine structure (NEXAFS) data.⁷ The complexity of the above procedures and assumptions made in the course of the data evaluation affect, however, the reliability of the resulting values of β and γ .

In this communication, we present first direct measurements of both tilt and twist angles for several typical aromatic SAMs, NC-(C₆H₄)₂-(CH₂)_n-SH ($n = 0\text{--}2$) and NC-(C₆H₄)₃-CH₂-SH on Au(111), abbreviated as BPnCN and TP1CN, respectively. For this purpose, we applied NEXAFS spectroscopy. The presence of the nitrile tailgroup in the target molecules is a crucial point since this group possesses two mutually perpendicular π^* orbitals (see Figure 1), which, due to the hybridization with the π^* orbitals of the phenyl rings, are oriented either perpendicular (π_1^*) or parallel (π_3^*) to the ring plane.¹⁷ Further, the energies of these two orbitals are different,¹⁷ so that the orientation of their transition dipole moments (TDMs) can be independently derived.

Without the CN substitution, only the TDM orientation for the π^* orbitals for the phenyl rings, that is, angle α (see Figure 1), can be determined. Knowing this angle and making a realistic assump-

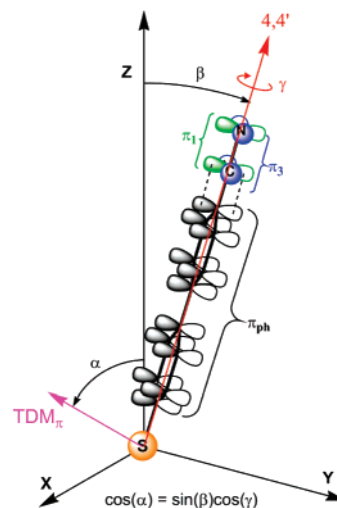


Figure 1. A schematic drawing of the orientation of the BPOCN molecule in the respective SAMs. The angles α , β , and γ describe the molecular orientation. The π_{ph}^* orbitals of the biphenyl backbone are perpendicular to the ring plane; the respective transition dipole moment TDM_{π} is shown as a magenta arrow; π_1^* (green) and π_3^* (blue) orbitals of the CN group are perpendicular and parallel to the ring plane, respectively. At $\gamma = 0$, TDM_{π} lies in the plane spanned by the z - and the $4,4'$ -axes.

tion about the twist angle (a typical value for aromatic bulk systems, 32°),¹⁶ the tilt angle β could then be calculated for a variety of aromatic SAMs^{5,9,10} according to the relation⁷

$$\cos(\alpha) = \sin(\beta)\cos(\gamma) \quad (1)$$

This simple approach relies, however, on the assumption for γ , which makes the derived tilt angles not absolutely reliable, similar to the FTIR and FTIR/NEXAFS procedures mentioned above.

In the case of CN substitution, no assumptions for γ are necessary. The C K -edge and N K -edge NEXAFS spectra of BPnCN ($n = 0\text{--}2$) and TP1CN SAMs acquired at X-ray incidence angles of 90° and 20° are presented in Figure 2a and 2b, respectively. The C K -edge spectra of all films exhibit several π^* , σ^* , and R* (Rydberg) resonances characteristic of phenyl rings;¹⁸ the most prominent absorption feature is the π_1^* resonance at ~ 285.0 eV. The N K -edge spectra are dominated by the π_1^* and π_3^* resonances related to the CN group¹⁷ at 398.7 and 399.6 eV, respectively. Both C and N K -edge spectra show noticeable linear dichroism, that is, a dependence of the absorption resonance intensity on the incidence angle of the X-ray beam. This is a clear signature of orientational order in the SAMs.¹⁸

The average tilt angles of all relevant π^* orbitals, α , could be directly obtained from a simple quantitative analysis of the entire set of the NEXAFS spectra acquired at different angles of X-ray

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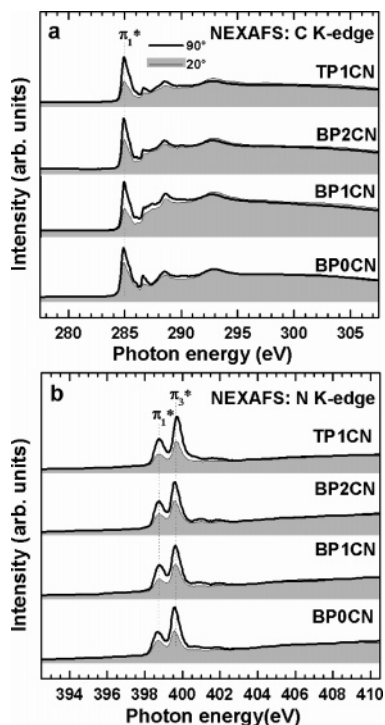


Figure 2. Carbon *K*-edge (a) and nitrogen *K*-edge (b) NEXAFS spectra of BPnCN ($n = 0-2$) and TP1CN SAMs on Au acquired at X-ray incidence angles of 90° (thick line) and 20° (thin line, shadowed). The most prominent absorption resonances are marked.

Table 1. Tilt and Twist Angles ($^\circ$) of the BPnCN ($n = 0-2$) and TP1CN SAMs Derived from the NEXAFS Data (accuracy $\pm 3-5^\circ$)

	BP0CN	BP1CN	BP2CN	TP1CN
tilt angle of the π_1^* orbital (phenyl), α_{ph}	60.6	67.3	63.0	67.3
tilt angle of the π_1^* orbital (CN), α_1	61.8	67.6	65.6	68.1
tilt angle of π_3^* orbital (CN), α_3	65.9	63.1	63.7	66.3
twist angle (γ) from α_1 and α_3	40.8	49.8	47.0	47.1
molecular tilt (β) from α_1 and α_3	38.7	36.3	37.3	33.3
molecular tilt (β) from α_{ph} and $\gamma(\alpha_1, \alpha_3)$	40.4	36.7	41.7	34.5

incidence, θ , according to the theoretical expression for a vector-type orbital¹⁸

$$I(\alpha, \theta) = A \{ P \times (1/3) [1 + (1/2)(3 \cos^2 \theta - 1)(3 \cos^2 \alpha - 1)] + (1 - P)(1/2) \sin^2 \alpha \} \quad (2)$$

where $I(\alpha, \theta)$ is the intensity of the respective resonance, A is a constant, and P is the polarization factor of the synchrotron light. The resulting values of α are given in Table 1.

Since the TDMs of the π_1^* orbitals of phenyl rings and the CN group are collinear and perpendicular to the ring plane, the average tilt angle of the aromatic chain can be calculated according to eq 1 as far as the twist angle is known. For the π_3^* orbitals of the CN group, with the TDM within the ring plane, eq 1 should be modified to

$$\cos(\alpha_3) = \sin(\beta) \cos(\pi/2 - \gamma) \quad (3)$$

which, in combination with eq 1 for α_1 , gives us a system of equations which could be easily solved with regard to both β and γ . The resulting angles are given in Table 1. Most interesting, whereas the exact values of the twist angles depend on the molecular architecture, they are around $40-50^\circ$, which is close to 32° typical of aromatic bulk systems.¹⁶ Similar to these systems, we assumed a planar conformation of the aromatic backbone;¹⁹ if the rings are

twisted differently as in the molecular state (torsion), the derived γ values represent the average over the respective values for the individual rings. Note that the results are also not affected by a presumable herringbone packing of the SAMs of this study.¹⁹

Further, the derived twist angles can be used to calculate molecular tilt β on the basis of α_{ph} , according to eq 1. The respective values in Table 1 are very close to the molecular tilt values calculated from eqs 1 and 3 on the basis of α_1 and α_3 , which is a further proof of the reliability of the results. The β values exhibit all tendencies observed previously for aromatic SAMs, viz. a decrease of molecular inclination with increasing length of the aromatic backbone⁵ and an odd–even change of the inclination as far as this backbone is combined with an aliphatic linker.^{7,9,10} There is a disturbance related to the attachment of a nitrile group,²⁰ but its extent does not exceed $8-9^\circ$ in terms of the average molecular inclination, so that the derived twist angles can be considered to be typical of non-substituted aromatic SAMs, as well, even though the exact values can be slightly different.

In summary, we have shown that aromatic molecules in the respective SAMs on Au(111) are not only tilted but also noticeably twisted ($40-50^\circ$), with the exact twist angle depending on molecular architecture. We hope that these findings help to design exact structural models for practically relevant aromatic SAMs on coinage metal substrates.

Acknowledgment. We thank M. Grunze for the support of this work, and the MAX-lab staff for the assistance. This work has been supported by DFG (ZH 63/9-2) and the EC through the IA-SFS project within the Sixth Framework Programme.

Supporting Information Available: Synthesis, SAM preparation and characterization and NEXAFS data analysis. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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JA0751882