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Extremely Twisted and Bent Pyrene-Fused N-Heterocyclic Germylenes

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The first examples of pyrene-fused Janus-type N-heterocyclic germylenes (NHGe) are reported. Remarkably, the pyrene linker and the germanium containing rings are extremely twisted, with "twist angles" up to 64°. Coordination of a Lewis base modifies the twisting of pyrene to an overall bent core (141° bend angle).

Polycyclic aromatic hydrocarbons (PAHs) have gained significant attention in materials chemistry for their unique photophysical properties useful for organic light emitting diodes (OLEDs),[1] photovoltaics,[1-2] field-effect transistors,[3] organic electronics,[4] and sensors.[5] Pyrene,[6] a highly aromatic molecule comprised of four fused benzene rings, is a ubiquitous building block for synthesizing exceptionally conjugated compounds,[7] or polymeric materials.[8] While many of these fused-ring systems are planar, nonplanar or twisted conjugated molecules are rapidly emerging due to new applications in nonlinear optics,[9] semiconductors,[10] OLEDs,[11] and electronic devices.[12] Notably, twisted molecules have displayed improved stability, enhanced solubility, and provide chiroptical properties[13] deeming them versatile in new materials. A new category of distorted ribbon-like PAHs termed pyrene-fused twistacenes have recently been developed and show imminent promise towards incorporation in OLED devices.[14] Twisted pyrene-fused molecules are often characterized by the degree of their torsion angle at the carbon atoms in the K-region of pyrene.[14-15]

Until recent years, the investigation of the electronic properties, utility, and applications of nonplanar aromatic compounds have been limited due to challenging synthetic routes. Several approaches exist for twisting aromatic systems with multiple linearly fused-rings,[15-16] while methods for synthesizing nonplanar pyrene-based molecules of 2-rings or less remains sparse. Although synthetic strategies to yield twisted or bent pyrene-based molecules have been reported, all of the examples are exclusively organic.[16b, 17] By incorporating bulky phenyl rings to the silyl substituents on pyrene-fused azaacenes, Mateo-Alonso has established overall twist angles up to 24° (Figure 1a).[14, 18] Conversely, Bodwell has developed a strategy of tethering substituents at the 2- and 7-postions on pyrene to produce a negative curve in the structure with bend angles[19] up to 109° (Figure 1b).[17, 20] As the number of fused-rings increase, molecules become more flexible and acenes of 4 or more fused-rings display large twist angles up to 170°.[15-16, 21] However, promoting high degrees of structural twisting in PAHs with 3 or fewer linearly fused-rings is rare and highly challenging from a synthetic perspective.

Within the last decade, multinuclear germylenes[22] have been isolated, and all conform to a planar molecular geometry. Unlike the strongly σ-donating N-heterocyclic carbenes (NHC), N-heterocyclic germylenes (NHGe) display less nucleophilic character and perform better as electrophiles.[23] Owing to the less effective valence orbital overlap between germanium's *s* and *p* orbitals, hybridization is

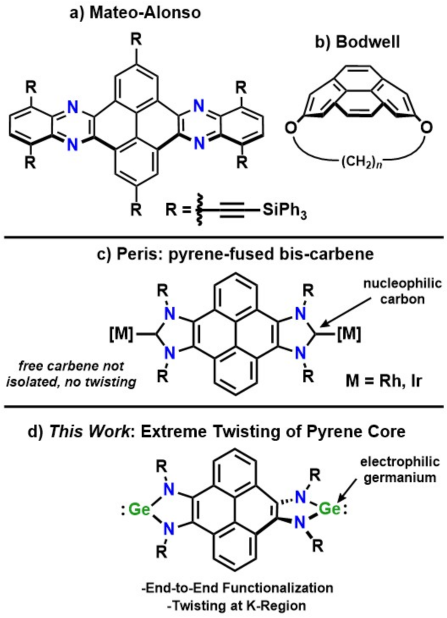

Figure 1 a) Twisted pyrene by incorporation of bulky silyl substituents; b) Tethered substituents to produce a bent pyrene; c) Planar, pyrene-fused bis-carbene; d) This work: Extremely twisted pyrene-fused germylene.

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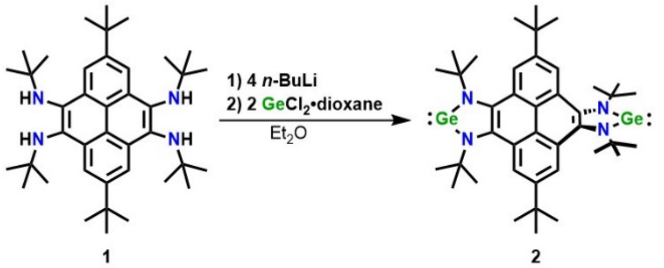
minimal,[23c, 24] and therefore the electronics at the germanium atom are vastly different from the lighter carbene analogues. Inspired by the pyrene-linked bis-carbene chemistry by Peris,[25] we initially targeted this ligand for coordination to main-group elements (Figure 1c). Unfortunately, the free bis-carbene linked by pyrene is not stable and *in situ* deprotonation was necessary for coordination to Rh and Ir. We found this method to be unsuccessful for bis-carbene coordination to a significant number of main-group Lewis acids. We then desired to isolate a stable free "heavy" bis-carbene analogue with germanium instead of carbon (Figure 1d).

Herein we report a new synthetic strategy, molecular structures, and computations of a dual-faced pyrene-fused NHGe. Remarkably, these molecules represent the first examples of highly twisted pyrene-fused germylenes, and they demonstrate the largest reported twist angles spanning only two linearly connected aromatic rings of pyrene.

The starting tetramine (**1**) was synthesized using a Buchwald-Hartwig amination.[25] Lithiation of **1** with *n*-butyllithium and subsequent salt elimination with germanium dichloride dioxane adduct gave the pyrene-fused germylene (**2**) in 75% yield (Scheme 1). The ^{1}H NMR spectrum of **2** revealed a downfield shift in resonance from 1.26 to 1.85 ppm for the protons on the *N*-(*tert*-butyl) substituents. This can be attributed to a decrease in electronic shielding by the nitrogen-based electrons that are now involved in a π-symmetric interaction with the germanium atoms.

To elucidate the structural properties of compound **2** single crystal X-ray diffraction studies were performed. Yellow rod-shaped air- and moisture-sensitive crystals of **2** were obtained from a concentrated toluene solution at −37 °C (Figure 2a). Surprisingly, both the NHGe rings and the pyrene linker display a severe distortion from planarity (Figure 2b). Significantly, twist angles of 49° and 64° were observed for C1−C2−C8−C9 and N1−N2−N3−N4, respectively (Figure 2c). The twisting of **2** at the pyrene core is completely different than that of **1**, which show 0° twist angles (SI Figure S10). Unfavorable steric interactions between the *N*-(*tert*-butyl) substituents and the hydrogen atoms on pyrene influence the twisting. Notably, the degree of twisting at the aromatic core with only two linearly fused benzene rings is substantially larger than the longer pyrene-fused azaacenes (twist angles up to 24°).[16b, 18, 26]



Scheme 1 Synthesis of highly twisted pyrene-fused N-heterocyclic germylene.

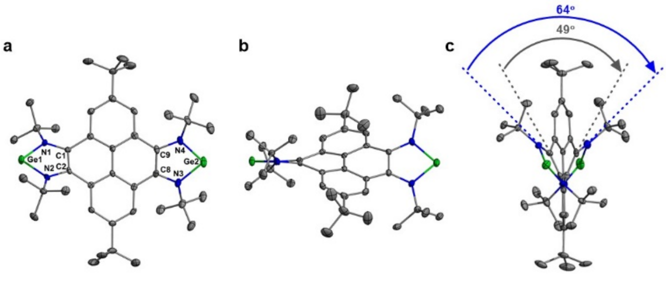
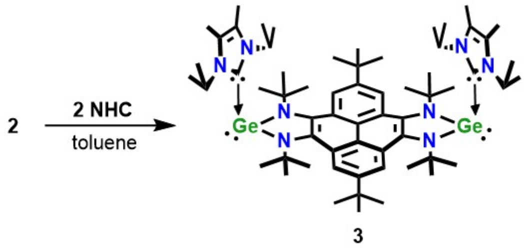


Figure 2 a) Pyrene-fused NHGe, b) view showing non-planarity of both the pyrene linker and N-heterocycle, and c) view down N atoms depicting twist angles. Thermal ellipsoids shown at 50% probability and H atoms were omitted for clarity. Selected bond lengths (Å) and angles (°): Ge1–N1: 1.871(3); Ge1–N2: 1.868(3); C1-C2-C8-C9: 49; N1-N2-N3-N4: 64.

In addition, the 64° N1-N2-N3-N4 twist angle is significantly larger than the reported 20-32° angles of phenyl-substituted heptacenes[27] and tetracene diimides.[15, 28] The severe degree of twisting in **2** is also much more substantial than the slight bow-shaped distortion observed in the bis-carbene-Ir compound with the same pyrene core.[25] The Ge1–N1 [1.871(3) Å] and Ge1–N2 [1.868(3) Å] bond lengths are within the range of reported Ge–N single bonds (1.833-2.118 Å).[22b-d]

Due to the electrophilic nature of the germanium atoms we were interested in how changes to the electronics would affect the twisting of the pyrene core. Lewis basic trimethyl phosphine (PMe$_3$), 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (IPr),[29] and (2,6-diisopropylphenyl)-4,4-diethyl-2,2-dimethyl-pyrrolidin-5-ylidene (^{Et2}CAAC)[30] were screened as possible donor ligands. However, no coordination to Ge was observed due to weak donor strength or sterics. Thus, the smaller, yet strongly σ-donating NHC, 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene (sIPr), was selected which readily coordinated to the electrophilic Ge atoms to afford compound **3** as a yellow solid in 41% yield (Scheme 2). In the ^{1}H NMR spectrum, a downfield shift in resonance from 1.85 to 1.99 ppm was observed for the protons on nitrogen bound *tert*-butyl groups. A broad singlet resonance at 6.68 ppm was attributed to the methine protons on the sIPr ligands. The significant downfield shift compared to 3.96 ppm for the free carbene supported coordination to the germylene.



Scheme 2 Synthetic route to cis-sIPr coordinated bis-germylene complex**.**

Yellow block-shaped air- and moisture-sensitive single crystals of **3** sufficient for X-ray diffraction were grown from deuterated benzene. Interestingly, the structural distortion of **3** is completely different than **2** and coordination of the carbenes flatten out the end-to-end twisting (Figure 3a). Rather than an overall twisted structure, a negatively curved pyrene core with a bend angle of 141° is observed. A bend of the pyrene core to this extent is remarkable since there are no linkers distorting the planarity as shown in the bent tied-back pyrenophanes reported by Bodwell.[17, 20, 31] Additionally, this concave shape is unique because the pyrene core is tilted out-of-plane towards the carbene ligands rather than away. Notably, the sIPr ligands add cis to each other on the same face of pyrene which induces an unusual out-of-plane distortion of the *tert*-butyl groups on the nitrogen atoms to accommodate steric repulsion. The cis-addition produces a pocket for a benzene solvent molecule and allows for interaction with the sIPr ligands in the solid-state packing diagram (Figure 3b). Twist angles are observed [C2-C1-C2′-C1′ and N2-N1-N2′-N1′ were 5° and 7° respectively] but significantly less than **2**. A torsion angle of 15° for the C21-Ge1-Ge1′-C21′ atoms indicated that the sIPr ligands are nearly parallel to each other (Figure 3c). The Ge1–N1 (1.9430(14) Å) interaction is slightly longer than **2**. This was attributed to a decreased inductive effect of the nitrogen atoms as the empty *p*-orbital on the germanium atoms is now occupied by carbenes. The Ge1–C21 (2.1321(18) Å) bond length is within the reported range for typical Ge–C single bonds (1.965-2.192 Å).[32] An intermolecular interaction between one methyl group on the sIPr ligand to the ring of a neighboring molecule's carbene ligand is observed [Me---sIPr centroid = 3.43 Å] in the crystal packing diagram (Figure 3d).

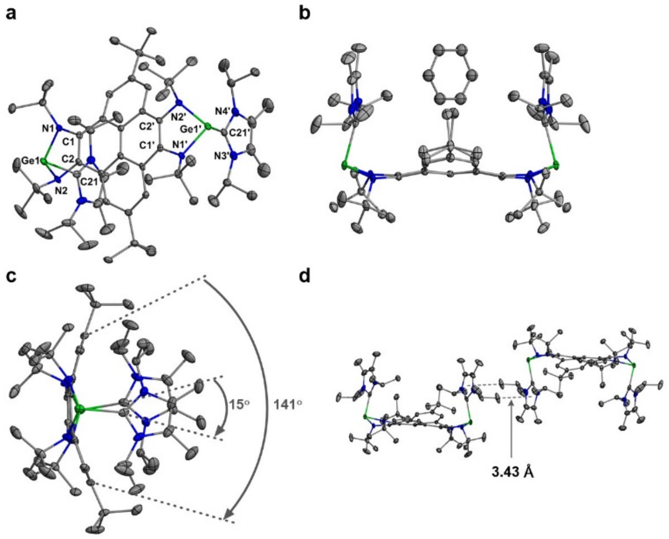


Figure 3 Molecular structure of **3**: a) cis-sIPr coordinated NHGe, b) top view with C_6D_6 molecule, c) sIPr side view, and d) crystal packing view with Me—sIPr centroid interaction. Thermal ellipsoids shown at 50% probability and H atoms were omitted for clarity. Selected bond lengths (Å) and angles (°): Ge1–N1: 1.9430(14); Ge1–N2: 1.9489(14); Ge1–C21: 2.1321(18); N4–C21: 1.359(2); N3–C21: 1.356(2); C2-C1-C2′-C1′: 5; N2-N1-N2′-N1′: 7; C21-Ge1-Ge1′-C21′: 15.

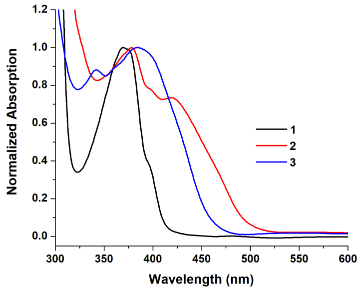


Figure 4 UV-vis absorption spectra of **1-3** in toluene at room temperature.

To gain insight into the absorption properties of **2** and **3** UV-vis studies were performed. Absorption maxima for **1-3** were exhibited at 369, 378, 384 nm respectively (Figure 4). A slight bathochromic shift in λ_{max} was observed from **1** to **3**. In order to acquire a better understanding of the electronics, computations were performed at the B3LYP/BS1 level of theory. Based on TD-DFT, the λ_{max} of **2** was assigned to the $\pi \rightarrow$Ge *p* + π^* transition, while the λ_{max} of **3** was assigned to the $\pi \rightarrow \pi^*$ transition. The broad shifts in the UV-vis spectra of **2** and **3** were attributed to fluxional behavior in solution, and the inversion barriers for twisting were further studied by computations (Figure S27-S28). Analysis of MO results indicate that the HOMO for compounds **2** and **3** is mostly delocalized across the pyrene linker, with some extension to the N atoms of the heterocycle (Figure 5). The LUMO in **2** is a Ge *p*-type orbital, while the LUMO in **3** is delocalized on pyrene. The Ge lone pair orbital of **2** is HOMO-4, which is consistent with the experimental observations. In **3**, the Ge lone pair is HOMO-2, due to enhanced nucleophilicity resulting from NHC coordination. Additional MOs and TD-DFT results are provided in the supporting information. To explore how the twisting of the structures affect the aromaticity of **2** and **3**, nucleus independent chemical shift (NICS(0)) calculations were conducted at the B3LYP/BS2 level of theory (see supporting information for details). NICS(0) values for the pyrene rings that link the NHGe heterocycles in **2** were less negative (-3.66 and -2.86) than **3** (–3.87 and –3.87) and free pyrene (-3.99 and -4.03), which supports decreased aromatic character due to twisting (Figure S23-S26).

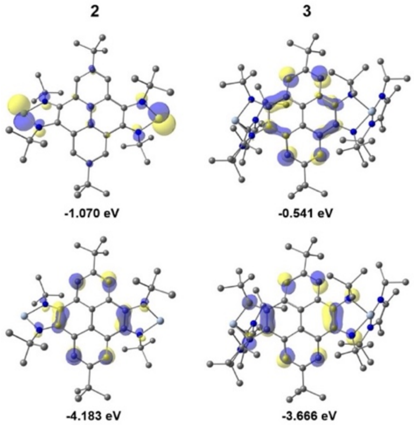


Figure 5 LUMO (top) and HOMO (bottom) orbital representations of **2** and **3** depicting the delocalization on pyrene.

In conclusion, we have prepared the first examples of pyrene-fused N-heterocyclic germylenes. Notably, compounds **2** and **3** possess exceptional twist or bend angles as a result of unfavorable steric interactions between the pyrene core and the N-(*tert*-butyl) groups. We envision that these molecules can be utilized as functional building blocks for main-group element molecular materials chemistry were the Ge atoms participate in electron transfer or bind to other metals/element centers. We also expect that this new strategy will be successful for isolating distorted PAH compounds which incorporate other main-group elements and these studies are currently underway in our laboratory.

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Conflicts of interest

There are no conflicts to declare.

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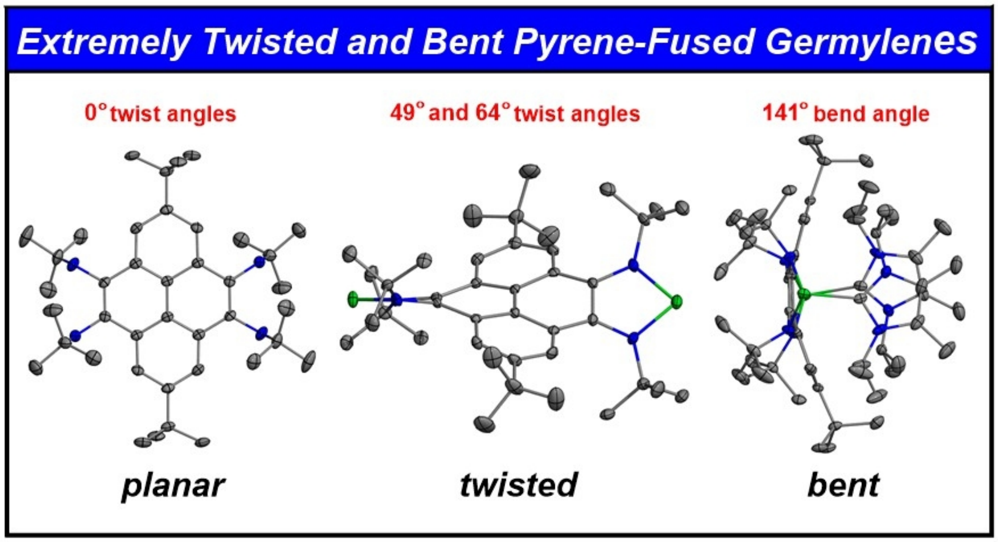

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