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Nitrogen-Centered Concave Molecules with Double Fused Pentagons

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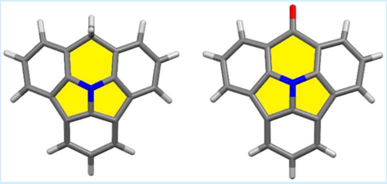
Supporting Information

ABSTRACT: Distinctive concave compounds bearing a nitrogen core and double fused pentagons were synthesized with a palladium-catalyzed intramolecular coupling of 1-chloro-8*H*-indolo[3,2,1-*de*]acridine as the key step. Structural analysis confirmed the formation of bowl-shaped molecules. Experimental characterizations and theoretical calculations reveal the incorporation of nitrogen is crucial to alleviate the pentagon fusing strain, as well as in property regulation.



Polycyclic aromatic concave molecules, the so-called buckybowls, are partial structures of fullerenes and tips of carbon nanotubes.[1] They have attracted considerable attention not only for the structure-related properties but also for the synthetic challenges due to the high strain originated from the curved structure.[2] One way to form bowl-shaped molecules is to reduce the size of the central rings of polycyclic compounds by the introduction of smaller rings, such as a pentagon and tetragon, with corannulene, sumanene, and quadrannulene as representatives.[3] Another way is to use multiple heteroatoms to cause different bond lengths and as a concave vertex for the favored tetrahedron geometry deriving from the lone pair electrons.[4] The heteroatoms can modulate the properties of the buckybowls, some of which are unreachable by pure carbon ones.[5]

Most of the reported bowl-shaped molecules have one thing in common: the pentagon is isolated from each other by hexagons. The synthesis of concave molecules with fused pentagons is quite limited. Inspired by the structure of *N*-heterotriangulene **1**,[6] herein we report the synthesis of nitrogen-centered bowl-shaped molecules with double fused pentagons by a strategy of introducing a pentagon and heteroatom. Compound **1** is a typical structure of nitrogen-centered polycyclic compounds, which can be viewed as a triphenylamine that is bridged with three carbonyl moieties at the rim to form a planar conformation (Figure 1). Once a carbonyl in **1** is replaced by a C−C single bond, the resulted ketone **2** is still in planarity, as confirmed by the density functional theory (DFT) calculation. However, switching another carbonyl in **2** to a C−C single bond will generate the ketone **3**, which possesses two fused pentagons with higher strain, thus leading to the formation of a curved shape. If the carbonyl was reduced to methylene, the gained compound **4** is still bowl-shaped in principle. Considering the nitrogen-centered tricyclic moiety, compounds **1**−**4** also can be viewed as a π-extended cyclazine, and the latter, as chromophores have shown interesting photoelectronic properties.[7]

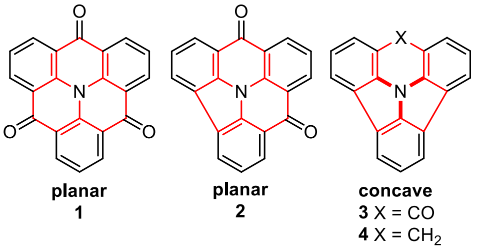


Figure 1. Structures of nitrogen-centered planar and concave molecules with different types of rings.

The synthetic route started with 2-chlorocarbazole **5**, which reacted with methyl 2-iodobenzoate via copper-catalyzed Ullmann amination to give compound **6** in 82% yield (Scheme 1). The ester was then hydrolyzed to generate the carboxylic acid, which was directly cyclized in polyphosphoric acid to afford the acridone−carbazole hybrid **7** in 73% yield in two steps. Attempts to close the fjord in compound **7** via palladium-catalyzed C−C bond formation was not successful; only a dechlorinated compound was obtained. The difficulty in the formation of a concave structure is to overcome the stiffness of the coplanar acridone and carbazole backbone. To lessen the rigidity, the carbonyl in compound **7** was reduced to methylene by borane nearly quantitatively. Indeed, the slightly flexible compound **8** could undergo the intramolecular cyclization readily. The bowl-shaped amine **4** was acquired in 72% yield via the palladium-catalyzed C−Cl/C−H coupling reaction when 4 equiv of potassium carbonate was used. To render the conjugation at the rim, the oxidation of methylene to carbonyl by sodium dichromate supplied compound **3** in 95% yield.

Compounds **3** and **4** are stable at ambient condition and show good solubility in common solvents, similar to the stable indolo[3,2,1-*jk*]carbazole if the carbonyl or methylene is

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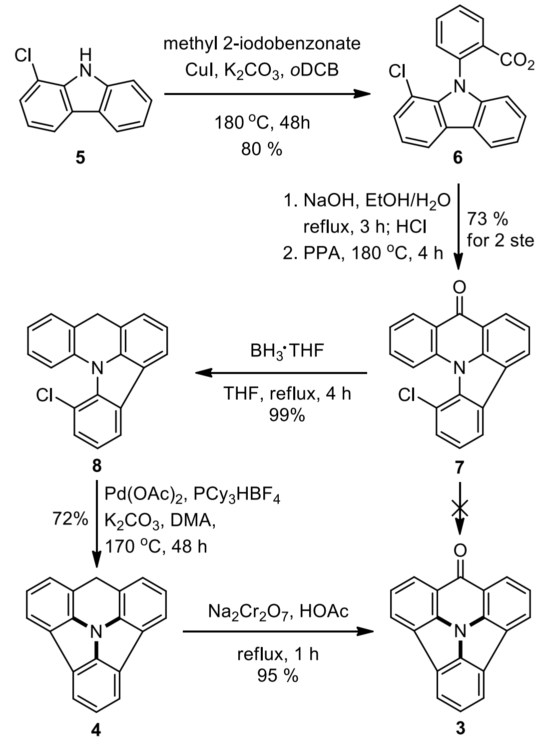
Scheme 1. Synthetic Route to Bowl-Shaped Molecules 3 and 4



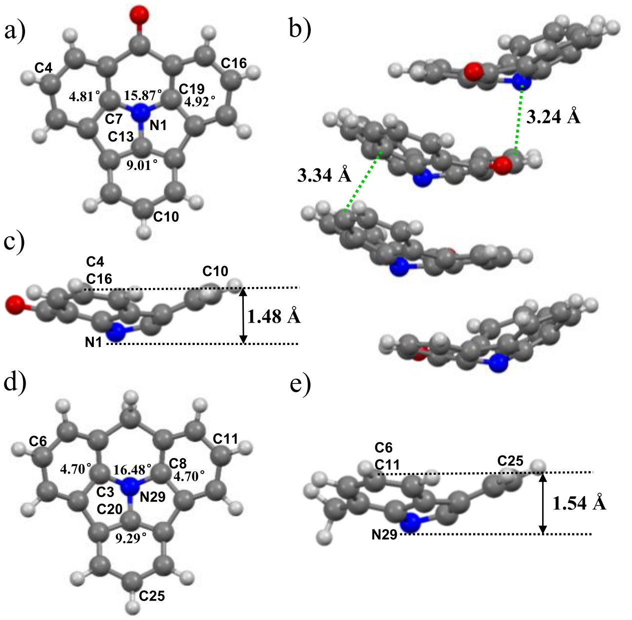


Figure 2. Structural information on **3** and **4**. (a) Top view of the crystal structure of **3** and POAV angles; (b) molecular stacking in crystalline state and the distances of intermolecular interactions; (c) side view of the crystal structure of **3** and bowl depth; (d) top view of the optimized structure of **4** and POAV angles; (e) side view of the optimized structure of **4** and bowl depth.

removed.[8] The structures of **3** and **4** were confirmed by NMR, IR, and HRMS. The ^{1}H NMR spectrum of **4** shows simple three doublet, two triplet peaks and a methylene peak at δ = 4.33 ppm due to the presence of a symmetry plane in the molecule. After the oxidation, the methylene peak disappears and the protons of the benzene rings shift to low field in the spectrum of **3** as a result of the electron-withdrawing carbonyl group. The molecular structure of **3** was further confirmed by the X-ray diffraction analysis of single crystals grown by slow evaporation of the dichloromethane/isopropanol solution. Compound **3** crystallized in the $P2_1/c$ group with eight molecules in the unit cell. The crystal structure reveals that **3** is a bowl-shaped molecule and forms a concave−convex dimer by $\pi-\pi$ interaction with the shortest distance of 3.24 Å, which is shorter than that of the classical buckybowls sumanene (3.86 Å)[9] and corannulene (3.32 Å),[10] a hint of strong $\pi-\pi$ interactions between the bowls (Figure 2). Referring to the distance of the central nitrogen atom and the plane of the outer three carbon atoms on the rim, the bowl depth is 1.48 Å, which is deeper than that of corannulene (0.87 Å) and sumanene (1.11 Å). Due to the compression from the outer rings, the three N−C bond lengths are in the range 1.36−1.37 Å, which are slightly shorter than those in the analogous structures, such as *N*-phenylcarbazole (1.39 Å)[11] and *N*-phenylacridone (1.39 Å).[12] The three C−N−C bond angles are 121.6°, 107.8°, and 108.7°, respectively, which are quite close to that at the corresponding positions in *N*-phenylcarbazole (108.3°) and *N*-phenylacridone (121.5°). The molecules are stacked in the slipped concave−convex manner with the bowls aligned in one direction to form a column. The arrangement of neighboring columns is oriented as opposed to each other.

Although single crystals of **4** were obtained, the collected data were too bad to be used for the structural analysis. DFT calculation was carried out to optimize its structure at the B3LYP/6-31G(d,p) level of theory, which has been proved to match well with the crystal data of bowl-shaped molecules,[13] as well as in the case of **3**. The calculated structure of **4** is also bowl-shaped with a depth of 1.54 Å, a little deeper than **3**. The more flexible methylene group sinks a little bit toward the bottom direction, which in turn tilts the vicinal benzene rings, thus making the bowl deeper.

The difference in bowl depth can also be evaluated by the π-orbital axis vector (POAV) angle, which is a meaningful index for nonplanar conjugated molecules.[14] In bowl **3**, the POAV angles are 4.8°−9.0° for the inner carbon atoms and 15.9° for the nitrogen atom. For compound **4**, the POAV angles are 4.7°−9.3° for the inner carbon atoms and 16.5° for the nitrogen atom, which are larger than those of bowl **3**, reflecting a more curved structure. The carbon POAV angles are smaller than that of corannulene (8.4°)[15] and sumanene (8.7°)[16] with the exemption of C20 (9.3°) in **3** and C13 (9.0°) in **4**. The nitrogen POAV angles in **3** and **4** are much larger than those of single nitrogen-centered buckybowls (7.55°−9.23°),[5e,f,i] indicating further deviation of the nitrogen atom from the planes of pyrrole and pyridone in **3** and **4**.

An interesting feature of the bowl-shaped molecule is the bowl-to-bowl inversion. DFT calculations of the single-point energy at the B3LYP/6-311+G(2d,p) level of theory was performed to determine the inversion barrier.[16] The calculated bowl inversion energy of compounds **3** and **4** are 8.1 and 11.6 kcal/mol, respectively. These values are lower than that of sumanene (19 kcal/mol),[16] but quite close to corannulene (10.6 kcal/mol) calculated at the same level.

DFT calculations in vacuo revealed the π-delocalization of the concave molecules **3** and **4** (Figure 3). Due to the bowl-shaped structure, the orbital coefficients were not symmetric at the concave and convex sides. LUMOs are mainly located on the acridone moiety in **3**, but are distributed over the whole

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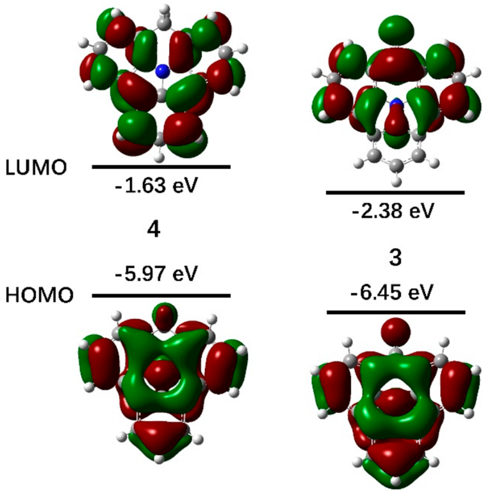


Figure 3. DFT calculations of molecular orbitals viewed at the concave side and energy levels at the B3LYP/6-311+G(d,p) level of theory.

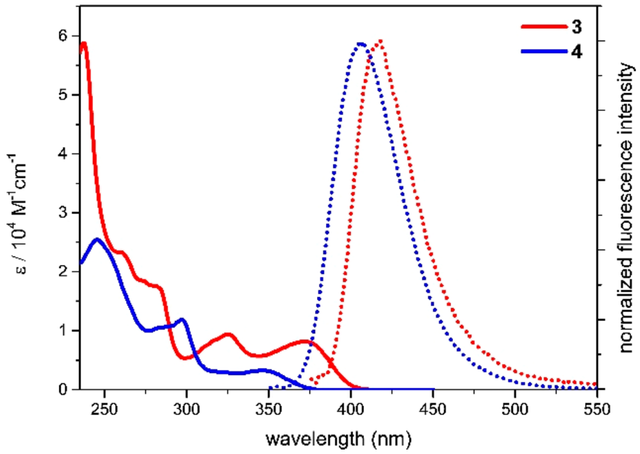


Figure 4. UV/vis absorption (solid line) and emission (dot line) spectra of **3** and **4** in dichloromethane.

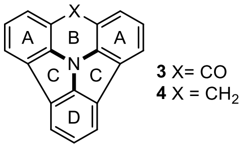
molecule in **4**. The lone pair electrons of the nitrogen atom contributed to the HOMOs, and the latter delocalized over the whole backbones of **3** and **4**. The distributions of the HOMO and LUMO orbitals in **3** revealed an intramolecular charge transfer process between the nitrogen atom and carbonyl group. The HOMO and LUMO energy levels of **4** are −5.97 eV and −1.63 eV (Table 1), respectively, which decline to −6.45 eV and −2.38 eV in **3** ascribed to the π-extension and the influence of the electron-withdrawing carbonyl group.

The photophysical properties of **3** and **4** in dichloromethane are evaluated by UV/vis absorption and emission spectroscopies (Figure 4). The UV/vis spectrum of **4** shows three absorption bands at 246, 297, and 346 nm. These bands are red-shifted in the spectrum of **3** due to the intramolecular charge transfer, which is consistent with the theoretical calculations. The optical energy gaps of **3** and **4** are 3.10 and 3.29 eV, respectively, estimated from the onset of absorption. Both **3** and **4** demonstrate weak blue fluorescence in dichloromethane with the emission maxima at 417 nm ($\Phi_F = 0.02$, $\tau = 1.98$ ns) and 405 nm ($\Phi_F = 0.08$, $\tau = 1.04$ ns), respectively.

The redox properties of **3** and **4** were studied by cyclic voltammetry (CV) and differential pulse voltammetry (DPV) measurements in dichloromethane. Both **3** and **4** showed irreversible redox waves in the CV spectra due to the interference of electrochemical polymerization at the *para*-position of amine. The DPV measurements clarified a further redox property. **3** exhibits an oxidation wave at 1.34 V and a reduction wave at −2.05 V. The HOMO and LUMO energy levels calculated from the oxidation and reduction waves are −6.14 eV and −2.75 eV, respectively, with an energy gap of 3.39 eV, close to the optical energy gap. Meanwhile, **4** affords two oxidation waves at 1.07 and 1.45 V and the calculated HOMO and LUMO energy levels are −5.87 eV and −2.58 eV, respectively, considering the optical energy gap. The variation trends of energy levels are in good agreement with the DFT calculations. In comparison to **3**, amine **4** is more likely to be oxidized, attributable to the absence of the electron-withdrawing carbonyl group.

The aromaticity of **3** and **4** was studied by nucleus-independent chemical shift (NICS) calculations (Table 2).[17]

Table 2. NICS$_{zz}$ Values of 3 and 4



compd	NICS$_{zz}$^{a,b}	A	B	C	D
3	NICS(1)$_{zz}$	−22.1	5.2	−1.5	−19.0
	NICS(−1)$_{zz}$	−26.1	5.3	−4.2	−27.3
4	NICS(1)$_{zz}$	−22.3	4.9	−5.6	−22.1
	NICS(−1)$_{zz}$	−27.5	0.9	−8.5	−29.8

[a]Calculated at the GIAO/DFT/B3LYP/6-311+G(d) level of theory of the DFT/B3LYP/6-31G(d,p) optimized geometries. [b]1 and −1 denote the points at convex and concave side, respectively.

The NICS$_{zz}$ values at the same positions are always larger in **3** than those in **4** owing to the influence of the electron-withdrawing carbonyl group. Due to the curved structures, the NICS$_{zz}$ values of the peripheral benzene rings at the concave side are smaller than those at the convex side. Compared to **3**, the values of pyrrole ring in **4** are smaller, indicating more aromatic character. The NICS values of pyrrole moieties in **3** and **4** are larger than those of the other azabuckybowls

Table 1. Photophysical and Electrochemical Properties of 3 and 4

compd	λ_{ab}^{a,b} (nm)	λ_{em}^{a} (nm)	Φ_F^{a} (%)	τ^{a} (ns)	E_{ox1}^{a,c} (V)	E_{red1}^{a,c} (V)	E_g^{d} (eV)	E_{HOMO}^{e} (eV)	E_{LUMO}^{e} (eV)	E_{HOMO}^{f} (eV)	E_{LUMO}^{f} (eV)
3	371	417	2	1.98	1.34	−2.05	3.10 (3.39)^{h}	−6.14	−2.75	−6.45	−2.38
4	346	405	8	1.04	1.07	–^{g}	3.29	−5.87	−2.58^{i}	−5.97	−1.63

[a]Measured in dichloromethane at room temperature. [b]The absorption maxima at the longest wavelength. [c]Bu_4NPF_6 (0.1 M) as the supporting electrolyte and ferrocene as internal reference. [d]Estimated from the onset of absorption. [e]$E_{HOMO/LUMO} = -(4.8 + E_{(ox1/red1)})$ eV. [f]Calculated at the B3LYP/6-311+G(d,p) level of theory. [g]Not observed. [h]Estimated from the electrochemical analysis. [i]$E_{LUMO} = E_{HOMO} + E_g$.

containing a single pyrrole ring in the center (−16.6, −17.6).[5f,i] The reduced aromaticity of the pyrrole rings in **3** and **4** is ascribed to the nonplanarity of the pyrrole rings caused by the trigonal nitrogen atom, which is verified by the analysis of nitrogen POAV angles. The pyridone ring is slightly antiaromatic, while the dihydropyridine ring is nonaromatic.

In summary, we have developed a synthetic protocol for the preparation of nitrogen-centered bowl-shaped compounds with two fused pentagons. The centric nitrogen atom plays a significant role not only in releasing the strain of double fused pentagons but also in the modulation of the molecular property in combination with the carbonyl group. These bowl-shaped molecules provide novel insight into heteroatom concave compounds. Efforts to further derivatize the nitrogen-centered bowl-shaped compounds and synthesize such pentagon-fused all-carbon concave molecules are underway in our laboratory.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.9b01861.

> Experimental details, NMR spectra, X-ray crystal data of compound **3**, photophysical and electrochemical measurements, DFT calculations (PDF)

Accession Codes

CCDC 1908481 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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