

First Isocyanoazulene and Its Homoleptic Complexes

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Azulene is a nonbenzenoid aromatic hydrocarbon, which has a dipole moment of 1.08 D (Figure 1).¹ Many natural and synthetic derivatives of azulene find applications in synthetic chemistry, medicine, and pharmacology, as well as in the design of nonlinear optical materials and liquid crystals.^{1,2}

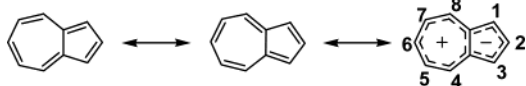
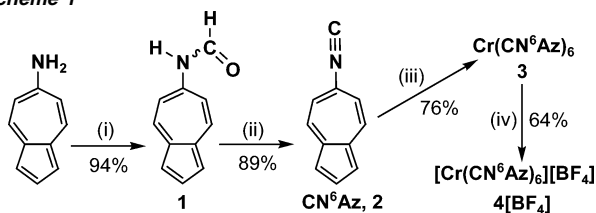


Figure 1. Resonance structures of azulene and its atom labeling scheme.

Transition metal complexes of organic isocyanides are of long-standing importance in organic and organometallic synthesis, catalysis, materials science, and diagnostic medicine.³ Given the unique nature of the azulenic moiety, hitherto unknown isocyanoazulenes would constitute an intriguing class of compounds of multidisciplinary interest. In principle, *five* isomeric isocyanoazulene molecules can be envisioned. Depending on the mode of attachment of the azulenyl group, these would exhibit different dipole moments, optical properties, and steric and donor/acceptor characteristics as ligands. Herein, we report on the initial member of the isocyanoazulene family, 6-isocyanoazulene (CN⁶Az, **2**), and its binary complexes [Cr(CN⁶Az)₆]^{0/1+} (Scheme 1). Notably, CN⁶Az represents the first example of an *organic* nonbenzenoid isocyanide.⁴

Scheme 1^a



^a (i) ex. H(O)COC(O)CH₃, 20 °C; (ii) POCl₃, ex. ⁱPr₂NEt, 20 °C; (iii) 1/6 Cr(η⁶-naphthalene)₂, -60 to 20 °C; (iv) AgBF₄, 20 °C.

A highly efficient synthesis of teal-blue **2** involved treating a red-maroon solution of 6-aminoazulene⁵ in CH₂Cl₂ with excess acetic-formic anhydride followed by dehydration of the resulting dark lavender formamide (**1**) with POCl₃ in the presence of Hünig's base. Combining 6 equiv of **2** with Cr(η⁶-naphthalene)₂⁶ in THF afforded a royal blue solution/slurry, from which lustrous, indigo-black microcrystals of Cr(CN⁶Az)₆ (**3**) were isolated. Addition of CH₂Cl₂ to a solid mixture of **3** and 1 equiv of AgBF₄ produced a purple solution. This was separated from the Ag metal, concentrated, and diluted with pentane to provide air-stable, deep purple leaflets of [Cr(CN⁶Az)₆][BF₄] (**4[BF₄]**).

The isocyanide **2** has a melting point identical to that of 6-cyanoazulene⁷ (~52 °C) and can be easily distinguished from the latter species on the basis of the characteristic features in its IR (ν_{CN} = 2111 cm⁻¹), ¹³C NMR (δ{CN⁶Az} = 165 ppm), and ¹⁴N NMR (δ{CN⁶Az} = 187 ppm) spectra. Compound **2** is almost

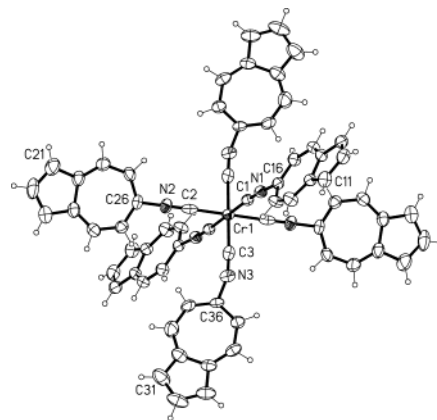


Figure 2. ORTEP diagram of **4[BF₄]**. The [BF₄]⁻ anion is omitted for clarity. Selected bond distances (Å) and angles (deg): Cr–C1 1.946(7), Cr–C2 1.985(7), Cr–C3 1.974(7), C1–N1 1.188(7), C2–N2 1.176(7), C3–N3 1.175(7), av. *cis*-C–Cr–C 87.9(2), *trans*-C–Cr–C 180, av. C–N–C 171.0(6).

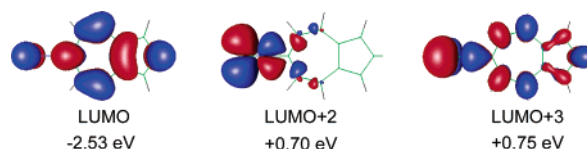


Figure 3. The virtual molecular orbitals of **2** capable of back-bonding and their corresponding energies calculated at the B3-LYP/6-31G (D, F) level.

odorless and only slightly air-sensitive. It does not rearrange into 6-cyanoazulene upon moderate heating and remains pristine for months if stored under argon. This is in sharp contrast to the properties of many CNPh derivatives, which have a pungent odor, deteriorate rapidly upon exposure to air, and isomerize into the corresponding cyanides at 40–50 °C.⁸ The stability of **2** is particularly remarkable in view of its relationship to the elusive isoelectronic 6-azulenyl diazonium cation⁵ and hypothetical isocyanotropylium.

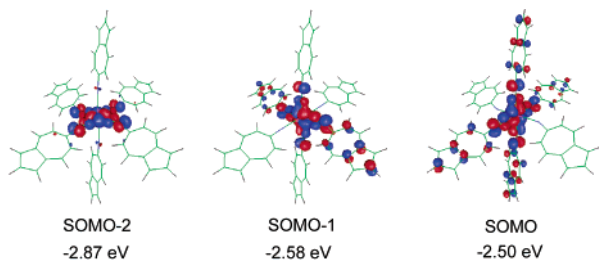
The energies of the “T_{1u}”-like ν_{CN} bands for **3** (1950 cm⁻¹) and **4** (2053 cm⁻¹) compare well with the ν_{CN} values for other binary aryl isocyanides of Cr(0) and Cr(I), respectively.^{4a,9} In both cases, the ν_{CN} values are depressed with respect to that of **2**, indicating substantial back-bonding in **3** and **4**. The low-spin d⁵ formulation of **4** is in accord with the μ_{eff} (25 °C) of 1.71 μ_B measured for **4[BF₄]**.

The molecular structure of **4[BF₄]** (Figure 2) features a nearly octahedral Cr(CN)₆ core with the Cr atom located on the inversion center. The Cr–C, C–N(Az) bond lengths and C–N–C angles observed for **4[BF₄]** are comparable to the corresponding parameters obtained for [Cr(CNPh)₆][CF₃SO₃]¹⁰ and, recently, [Cr(CNFc)₆]-[V(CO)₆] (Fc = ferrocenyl).¹¹ The peripheral C–C distances within the azulenyl groups in **4** are close to those in azulene¹² and range from 1.378(8) to 1.409(8) Å. As in azulene, the C–C bonds at the

Table 1. $E_{1/2}$ Potentials (in V) for $[\text{Cr}(\text{CNR})_6]^{z/z+1}$ versus $[\text{FcH}]^0/[\text{FcH}]^+$

couple	R			
	$\text{C}_6\text{H}_5^{a,c}$	$\text{Fc}^{b,d}$	$\text{Ph}^{a,e}$	${}^t\text{Az}^b$
$[\text{Cr}(\text{CNR})_6]^{0/1+}$	-1.54	-0.92	-0.83	-0.36
$[\text{Cr}(\text{CNR})_6]^{1+/2+}$	-0.77	-0.40	-0.21	-0.08

^a In CH_2Cl_2 . ^b In THF. ^c Reference 14. ^d Reference 4a. ^e Reference 9.

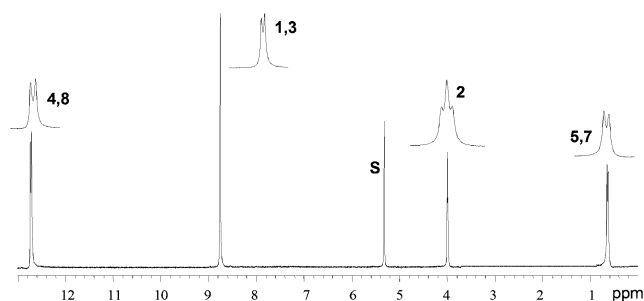
**Figure 4.** The nearly degenerate set of the highest occupied MOs of $4[\text{BF}_4]$ (solid state structure, SOMO = singly occupied molecular orbital).

five- and seven-membered ring junctions in **4** are ca. 0.1 Å longer than the peripheral C–C bonds.¹²

Cyclic voltammograms of $4[\text{BF}_4]$ in THF exhibit quasi-reversible cathodic and anodic waves signifying generation of zerovalent **3** and divalent $[\text{Cr}(\text{CN}^6\text{Az})_6]^{2+}$, respectively. The relatively high $E_{1/2}$ potential recorded for the $[\text{Cr}(\text{CN}^6\text{Az})_6]^{0/1+}$ couple (Table 1) reflects a superb π -accepting character of **2**. Given the very low energy of its lowest unoccupied molecular orbital (LUMO) displayed in Figure 3, **2** should be especially appropriate for stabilizing highly electron-rich metal ions by means of back-bonding. Thus, **2** may prove indispensable for advancing the emerging chemistry of isocyanometalates (i.e., isocyanide complexes of metals in subzero oxidation states).^{3c,13}

Due to its degenerate ideal 2T ground state, the paramagnetic cation **4** exhibits a very short electron-spin relaxation time (T_{1e})¹⁵ and gives narrow ${}^1\text{H}$, ${}^{13}\text{C}$, and ${}^{14}\text{N}$ NMR signals. Figure 4 suggests that $\text{Cr}(d\pi) \rightarrow \text{CN}^6\text{Az}(p\pi^*)$ back-donation places unpaired spin density directly into the p-orbitals of C², C^{5,7}, and the carbon atoms at the ring junctions of the azulenyl groups in **4**. Consequently, the ${}^{13}\text{C}$ resonances for these nuclei undergo downfield paramagnetic shifts,¹⁶ while the ${}^{13}\text{C}$ peaks for the remaining carbon atoms of the azulenyl substituents exhibit upfield paramagnetic shifts¹⁶ because of the spin polarization¹⁵ of the azulenic π -systems. The atomic exchange coupling¹⁵ polarizes (i.e., unpairs) electrons of the $\text{C}(\text{sp}^2)\text{-H}$ bonds, resulting in upfield paramagnetic shifts¹⁶ of the ${}^1\text{H}$ resonances for the H² and H^{5,7} nuclei and downfield paramagnetic shifts¹⁶ of the ${}^1\text{H}$ peaks for the H^{4,8} and H^{1,3} nuclei. This phenomenon is eloquently illustrated by Figure 5, in which the remarkably resolved ${}^1\text{H}$ NMR spectrum of $4[\text{BF}_4]$ is reproduced. The ${}^1\text{H}$ paramagnetic shifts for **4** exhibit approximately Curie behavior at $200\text{ K} < T < 300\text{ K}$ and are practically contact in origin because of the high symmetry of **4** (small Jahn–Teller distortions expected for **4** are very likely to be dynamic on the NMR time scale).

The spin delocalization pattern for **4** is topologically analogous to those observed for similar complexes containing benzenoid π -systems (e.g., $[\text{Cr}(\text{CNXyl})_6]^+$).^{13a} Indeed, the paramagnetic shifts of the ${}^1\text{H}$ and the corresponding ${}^{13}\text{C}$ resonances for **4** occur in opposite directions, and the ${}^{13}\text{C}$ paramagnetic shifts alternate their

**Figure 5.** ${}^1\text{H}$ NMR spectrum of $4[\text{BF}_4]$ in CD_2Cl_2 at $25\text{ }^\circ\text{C}$ (S = solvent).

sign throughout the *peripheral* (ten-membered) rings of the azulenyl fragments. To the best of our knowledge, **4** represents the only azulenic π -system studied by paramagnetic NMR.

In summary, we have described the first isocyanozulene, **2**, and demonstrated its superb π -accepting potential as a ligand. Syntheses of 1-, 2-, 4-, and 5-isocyanozulenes are underway in our laboratory. As their chemistry unfolds, isocyanozulenes are likely to gain substantial interest across scientific disciplines.

Acknowledgment. We thank the University of Kansas and NSF (Grant CHE-0079282) for financial support and Professors A. S. Borovik and K. Bowman-James for fruitful discussions.

Supporting Information Available: Experimental procedures, spectroscopic and analytical data for **1**, **2**, **3**, and $4[\text{BF}_4]$, X-ray data for $4[\text{BF}_4]$, and details of the DFT calculations (PDF and CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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JA034706F