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COMMUNICATION

Poly(trifluoromethyl)azulenes: structures and acceptor properties

Cite this: DOI: 10.1039/x0xx00000x

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Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

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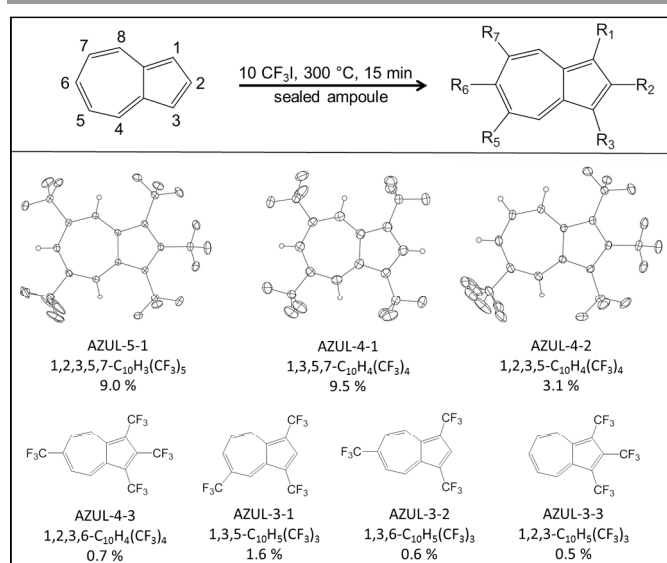
Six new poly(trifluoromethyl)azulenes prepared in a single high-temperature reaction exhibit strong electron accepting properties in the gas phase and in solution and demonstrate propensity to form regular π -stacked columns in the donor-acceptor crystals when mixed with pyrene as a donor.

Azulene is a non-alternant, non-benzenoid aromatic hydrocarbon with an intense blue colour, a dipole moment of 1.0 D,¹ positive electron affinity, and an “anomalous” emission from the second excited state in violation of Kasha’s rule.^{2,3} Azulene’s unique properties have potential uses in molecular switches,^{4,5} molecular diodes,⁶ organic photovoltaics,⁷ and charge-transfer complexes.⁸⁻¹² Introduction of electron-withdrawing groups to the azulenic core, such as CN,^{8,13,14} halogens,¹⁵⁻¹⁹ and CF₃,^{20,21} can enhance certain electrical and photophysical properties.

In this work, we report six new trifluoromethyl derivatives of azulene (AZUL), three isomers of AZUL(CF₃)₃ and three isomers of AZUL(CF₃)₄, and the first X-ray structure of a π -stacked donor-acceptor complex of a trifluoromethyl azulene with donor pyrene.

In sharp contrast to the commonly applied multi-step solution-based methods of hydrogen substitutions in AZUL with electron withdrawing groups such as CN^{7,12,13} or Hal,¹⁵⁻¹⁹ in this work, we prepared all AZUL(CF₃)_n compounds in a rapid single-step reaction carried out in the gas phase. Azulene and CF₃I gas were loaded into a sealed glass ampoule and heated in a furnace to 300 °C for 15 minutes to produce mostly a mixture of azulene(CF₃)_n (*n* = 3-5), as shown by negative-ion atmospheric-pressure chemical ionization mass spectrometry

(APCI-MS). The crude reaction mixture also contained small amounts of AZUL(CF₃)₆, and dimers (C₂₀H_{16-(*n*+1)}(CF₃)_{*n*=7,8,9}). Formation of the thermally stable dimeric AZUL species in such high-temperature reactions has not been previously reported and deserves further studies, particularly due to the relatively high electrical conductivity observed for polymeric AZUL_{*n*}.^{22,23} Doubling the reaction time resulted in more selective formation of AZUL-5-1.²¹



Scheme 1. Synthesis of AZUL(CF₃)₃₋₅. Abbreviations, formulas, and isolated yields are given. The X-ray structures of AZUL-5-1, AZUL-4-1, AZUL-4-2, are shown with thermal ellipsoids at the 50 % probability level. Overall yield = 25%.

The crude reaction mixture of the 15-minute reaction was separated by HPLC, (see Electronic Supporting Information, ESI, for details) yielding seven AZUL(CF₃)_n derivatives, i.e., three isomers of AZUL(CF₃)₃, three isomers of AZUL(CF₃)₄, and one isomer of AZUL(CF₃)₅ (for isomer notations see Scheme 1).

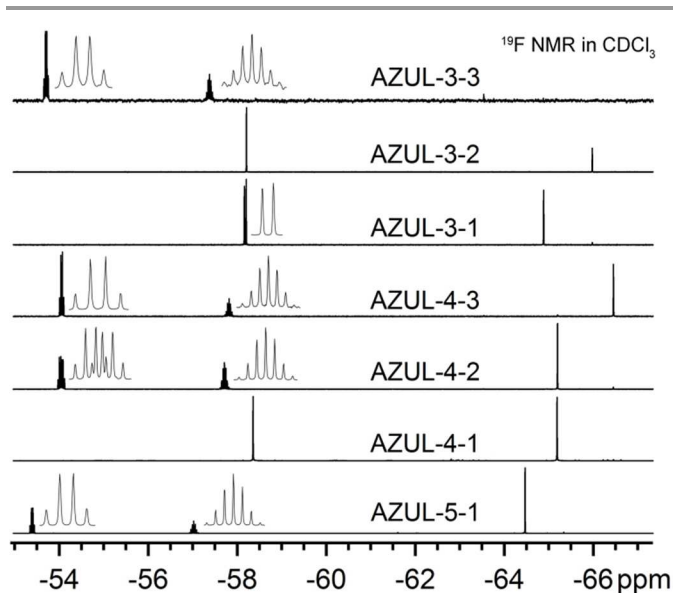


Figure 1. ¹⁹F NMR spectra (CDCl₃, 376.5 MHz, δ(C₆F₆) = -164.9 ppm) showing the CF₃ multiplets and singlets of the seven azulene derivatives. Regions where peaks are in close proximity are shown as insets for clarity. Coupling constants can be found in ESI experimental section.

Structural assignments for the new compounds were done based on negative-ion APCI-MS and the ¹H NMR and ¹⁹F NMR spectral analysis (see Figure 1 and ESI SI-1). The ¹⁹F NMR spectra were obtained in CDCl₃ and are shown in Figure 1. Multiplets corresponding to each CF₃ group appear in two distinct regions consistent to whether they are bonded to the five-membered ring (between -53.5 and -58.5 ppm) or the seven-membered ring of azulene (between -64.4 and -66.5 ppm). Through-space F–F coupling is observed between CF₃ groups bonded to adjacent carbon atoms of the azulene core resulting in quartets and apparent septets and no F–H coupling is observed. In some cases, CF₃ groups occupy all three carbon atoms of the five-membered ring, whereas CF₃ groups bonded to adjacent carbon atoms of the seven-membered ring were not observed.

The structures of the two most abundant AZUL(CF₃)₄ isomers, AZUL-4-1 and AZUL-4-2, were confirmed by single-crystal X-ray diffraction (Scheme 1); the crystals were grown by slow evaporation from dichloromethane and hexane solutions, respectively. AZUL-4-1 crystallizes in the P-1 space group with three molecules per unit cell. One molecule is ordered while the other two molecules are disordered, adopting opposite orientations at a given site. This disorder is typical and has been observed for azulene²⁴ and azulene derivatives.²⁵ Disorder in the azulene core is not observed in the structure of

AZUL-4-2; however, the fluorine atoms of the CF₃ group attached to C5 are disordered around the attached carbon atom.

The UV-vis absorption spectra of the seven poly(trifluoromethyl)azulene derivatives were obtained in hexanes and dichloromethane (see ESI for spectra). Unlike azulene, where the S₁ states become more refined in hexanes vs. dichloromethane, the solvent choice had little or no effect on the absorption spectra of the trifluoromethyl derivatives. The extinction coefficients for absorption maxima are less than parent azulene and comparable to other azulene derivatives (see ESI for values).¹⁸ Theoretical and experimental studies by Liu et. al. showed that electron withdrawing groups on odd-numbered carbon atoms blue-shift the S₁ maxima by lowering the HOMO energy while the LUMO energy remains relatively unchanged.¹⁸ Indeed, the absorption maxima in the S₁ band for all seven of the trifluoromethyl azulenes are blue shifted by 24–57 nm (see Table 1). All seven derivatives have CF₃ substituents at the C1 and C3 positions which plays a large part in blue-shifting the maxima. Two compounds (AZUL-3-2 and AZUL-4-3) have a CF₃ group bonded to an even-numbered C6 atom, which would likely cause a smaller blue shifts (24 and 27 nm), and is in agreement with the earlier prediction that electron withdrawing groups on even-numbered carbon atoms lower the LUMO energy.¹⁸ Electron withdrawing groups should lower the HOMO and LUMO+1 energy by nearly the same amount since the electron distributions of the HOMO and LUMO+1 are virtually identical, so shifts in the absorption maxima in the S₂ region are not expected to be as pronounced as the S₁ region. Absorption maxima shifts in the S₂ region are, in fact, very minor and even slightly red-shifted for one compound, AZUL-4-1.

Table 1. Absorption maxima for AZUL derivatives in hexanes (nm).

Compound	$\lambda_{\max}(S_0-S_2)$	$\Delta\lambda_{\max}$	$\lambda_{\max}(S_0-S_1)$	$\Delta\lambda_{\max}$
AZUL	341		579	
AZUL-3-1	338	-3	533	-46
AZUL-3-2	334	-7	555	-24
AZUL-3-3	329	-12	522	-57
AZUL-4-1	342	+1	537	-42
AZUL-4-2	334	-7	531	-48
AZUL-4-3	331	-10	552	-27
AZUL-5-1	338	-3	536	-43

The gas-phase electron affinity (EA) was measured experimentally by low-temperature photoelectron spectroscopy for two new isomers of AZUL-4 and compared to the electron affinity of the parent AZUL, 0.790(8),²⁶ and AZUL-5-1, 2.850(15)^{21,27} (Figure 2). Two AZUL(CF₃)₄ isomers exhibit very close EA values, 2.495(10) and 2.485(10). A plot of EA vs. number of CF₃ groups reveals a remarkable linear correlation, with a slope of 0.42 eV per CF₃ group (ESI SI-10). An extrapolation to AZUL-6 (that was observed by mass-spectrometry in the crude product as noted above) yields an estimated EA value of 3.3 eV.

No experimental data are available in the literature on EA values for any azulene derivatives for comparison. The electrochemical potentials in solution were reported for some

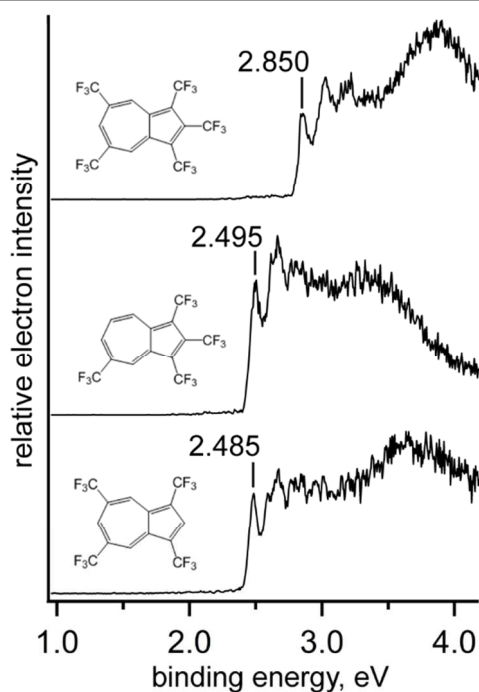


Figure 2. The low-temperature (12 K) photoelectron spectrum at 266 nm of AZUL-5-1 (top), AZUL-4-2 (middle), and AZUL-4-1 (bottom).

derivatives.^{8,13,28} Coincidentally, a similar linear correlation with nearly the same slope was observed in the half-wave reduction potentials of a series of cyano azulenes, $\text{AZUL}(\text{CN})_{2-4}$, where the $E_{1/2}(0/-)$ became more positive by 0.42 V per one CN substitution.⁸ Cyclic voltammetry in DME using TBAP electrolyte has been performed in this work for the most abundant compounds, and reversible electrochemical behaviour was only observed in the case of AZUL-4-1, $E_{1/2}(0/-) = -1.05$ V vs. $\text{FeCp}_2(+/0)$ (ESI SI-11). Comparison with the reduction potentials of $\text{AZUL}(\text{CN})_4$ shows the latter to be a stronger acceptor in solution than $\text{AZUL}(\text{CF}_3)_4$, in agreement with the theoretical predictions reported earlier for other polycyclic aromatic molecules,²⁹ including our recent work on the substituted corannulene derivatives.³⁰

Varying the degree of substitution allows for the selection of an azulene derivative to match with a proper donor to form a charge-transfer complex. The increased EA of AZUL-5-1 was utilized to form a charge-transfer complex with pyrene as the donor molecule. Dark red-purple crystalline rods of the charge-transfer complex between AZUL-5-1 and pyrene were grown by the slow evaporation from a dichloromethane solution at 2 °C. Columns of alternating AZUL-5-1 and pyrene were formed in a pseudo hexagonal close-packed formation (Figure 3A) with intermolecular, donor-acceptor distances of 3.58 and 3.61 Å (Figure 3B). The charge-transfer between AZUL-5-1 and pyrene possibly prevents AZUL-5-1 from adopting opposite orientations within its position and there was no disorder observed in the azulene core as was observed in the structure of AZUL-4-1. Solutions with varying amounts of AZUL-5-1:pyrene were made in DCM. All solutions remained the deep purple colour of AZUL-5-1 and no new absorption bands were

observed in UV-vis absorption measurements at different concentrations, even when AZUL-5-1:pyrene = 50:50 (the same ratio that formed the single-crystal charge-transfer complex). The absence of charge-transfer bands has also been observed with other azulene charge-transfer complexes,⁹ but charge-transfer bands from pyrene have been observed in other pyrene/oligomer complexes.¹⁰

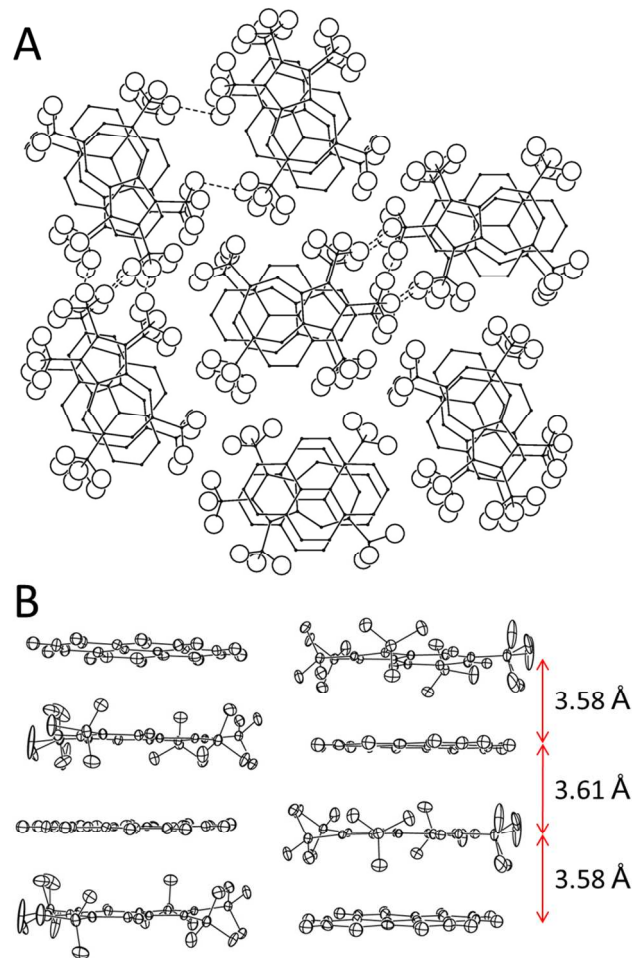


Figure 3. The packing of AZUL-5-1/pyrene columns from the top down (A) and a view of two columns from the side (B). Distances between AZUL-5-1 core plane and pyrene core planes are given.

In conclusion, we have developed an efficient trifluoromethylation method for azulene that yields a mixture of seven readily separable poly(trifluoromethyl)azulenes. Low-temperature photoelectron spectroscopy revealed a linear increase in gas-phase electron affinity of 0.42 eV per CF_3 group. Strong acceptor properties of the new compounds were utilized in the first example of a charge-transfer complex with pyrene that exhibits a regular columnar packing and strong pi-pi interactions between the aromatic cores of the donor and acceptor. Further elucidating oligomeric poly(trifluoromethyl)azulene and $\text{AZUL}(\text{CF}_3)_6$ species will result in even stronger electron acceptors and could lead to charge-transfer complexes with unique packing motifs and unusual electronic properties.

Natalia Shustova and Dmitry Peryshkov are greatly acknowledged for assistance with X-ray crystallography of AZUL-4-1. We thank the U.S. NSF (CHE-1012468), and the Colorado State University Research Foundation for partial financial support. The photoelectron spectra work was supported by the US Department of Energy (DOE), Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences, and Biosciences, and was performed at the EMSL, a national scientific user facility sponsored by DOE Office of Biological and Environmental Research and located at Pacific Northwest National Laboratory. Use of the Advanced Photon Source was supported by the U.S. Department of Energy, Office of Science, and Office of Basic Energy Sciences under Contract DE-AC02-06CH11357.

Notes and references

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† Electronic supplementary information (ESI) available: Experimental details, spectroscopic data, absorption spectra, electrochemistry, and crystallographic data. CCDC 980904 (AZUL-4-1), CCDC 980900 (AZUL-4-2), CCDC 980901 (AZUL-5-1/pyrene). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c000000x/

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