

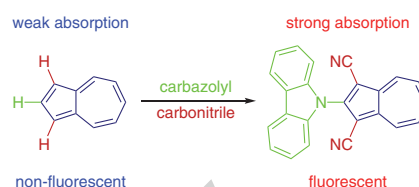
Donor-Acceptor Azulenes with Intense Absorption and Emission in the Visible Region

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Abstract New donor-acceptor compounds based on the azulene nucleus have been synthesized that demonstrate intense light absorption in the visible spectrum (380–600 nm) and emit light in the blue photoluminescence range. The appearance of photoluminescence is a unique feature of the resulting compounds and is absent from the original azulene. This ability was achieved by introducing a donor substituent at position 2 and acceptors at positions 1 and 3 of azulene. This led to a restructuring of its electronic structure, which created the prerequisites for the permitted π - π^* transition.

Key words azulene, azulenecarbonitrile, donor-acceptor azulene, carbazoyl-azulene, optoelectronics, photoluminescence

The increased interest in π -conjugated derivatives of aromatic hydrocarbons is associated with their important contribution to the development of functional materials for organic optoelectronics. In this context, the focus of research is mainly on the development of benzoid and heteroaromatic structures modified with donor and/or acceptor fragments.^{1–10}

However, aromatic hydrocarbons of a non-benzoid structure have not yet been widely used as starting materials for creating new materials with demanded electronic properties.

Azulene occupies a special place among non-benzoid hydrocarbons.^{11–20}

The nonalternant aromatic structure of azulene determines its special properties, such as dipole structure ($\mu = 1.08 \text{ D}^{21}$) (Figure 1a) and abnormal fluorescent behavior that does not obey Kasha's rule.^{21–24} In addition, azulene is

characterized by high HOMO energies and low LUMO.^{11–15} In azulene, atoms C₁ and C₃ show high HOMO values, while atoms C₂ and C₆ show high HOMO-1 and LUMO parameters (Figure 1b).^{11–15}

Azulene is colored blue, indicating the absorption of light caused by the transition of electrons from the S₀ state to the S₁ state with a maximum at 581 nm and a small extinction coefficient ($350 \text{ M}^{-1} \text{ cm}^{-1}$).²⁵

Controlling the energy levels of azulene FMO will open up new horizons in the creation of materials with unique optoelectronic properties.

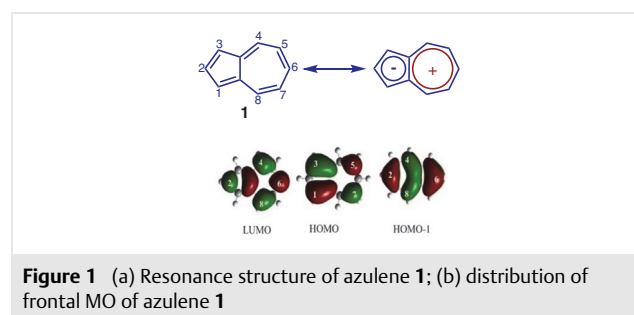
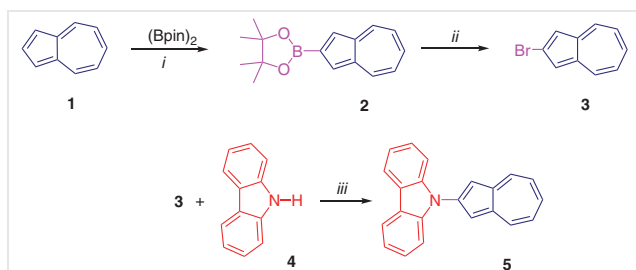


Figure 1 (a) Resonance structure of azulene **1**; (b) distribution of frontal MO of azulene **1**

In this study, we introduced a donor carbazoyl group at positions 2, and acceptor carbonitrile groups at positions 1 and 3 of azulene **1**, and then investigated the optical properties (electron absorption and fluorescence) of the resulting donor-acceptor derivatives.

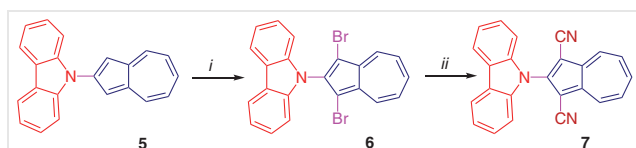
Schemes 1 and 2 demonstrate routes to 2-(9H-carbazoyl)azulene **5** and 2-(9H-carbazoyl)azulene-1,3-dicarbonitrile **7**.

As can be seen (Scheme 1), boryl **2** was synthesized by coupling **1** with (Bpin)₂.²⁶ Its bromination with CuBr in DMF then gave compound **3** in 71% yield.²⁷ Further, 2-carbazoyl-substituted azulene **5** was obtained by cross-coupling of compounds **3** and **4** in 82% yield.²⁸



Scheme 1 Synthesis of **5**: (i) $[\text{IrCl}(\text{cod})_2]$, 2,2'-bpy, cyclohexane, reflux (14 h), 70%; (ii) CuBr, DMF, 90 °C (3 h), 71%; (iii) Pd(OAc)₂, *t*-BuOK, [(*t*-Bu)₃PH]BF₄, toluene, reflux (3 h), 82%.

Further regioselective reaction (Scheme 2) of carba-azulene **5** with NBS led to dibromide **6** in 90% yield.²⁹ Reaction of bromide **6** with copper cyanide in DMF then gave the final dicyanitrile **7** in 80% yield.



Scheme 2 Synthesis of **7**: (i) NBS, CH₂Cl₂, -78 °C (2 h), 90%; (ii) CuCN, DMF, reflux (5 h), 80%.

The azulenes **5** and **7** obtained are stable dark brown solids showing good solubility in CH₂Cl₂, CHCl₃, toluene, and chlorobenzene under normal temperature conditions.

Structures **5** and **7** were confirmed by physicochemical methods (¹H and ¹³C NMR and infrared and mass spectrometry) (Supporting Information).

The UV-visible spectrum of compound **7** (compared to **5**²⁸) is shown in Figure 2; Table 1 shows the characteristics of compounds **5** and **7**.

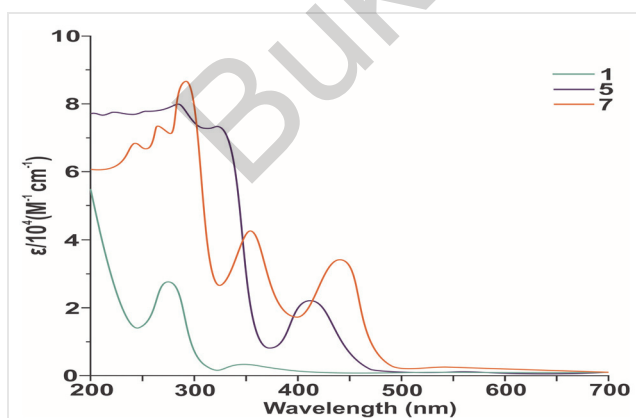


Figure 2 UV-Vis spectra of compounds **5**, **7**, and **1**

Table 1 Photophysical Properties of **5** and **7**^a

Compound	Absorption		Fluorescence ^b	
	λ_{abs} (nm)	ϵ (M ⁻¹ cm ⁻¹)	λ_{em} (nm)	Intensity (a.u.)
5	284	80,000	450	566
	323	73,474		
	412	22,100		
7	292	86,652	400	871
	354	42,640		
	441	34,117		

^a CH₂Cl₂, ambient temperature, concentration 1×10^{-4} M.

^b λ_{ex} (excitation wavelength) 360 nm for **5** and 320 nm for **7**.

In the UV-Vis spectrum of **7** in dichloromethane, a new intense absorption band was observed with a λ_{max} of 441 nm ($\epsilon = 34,117 \text{ M}^{-1} \text{ cm}^{-1}$) (Table 1). Derivative **5** also shows a visible absorption band with λ_{max} at 412 nm (Table 1).

Strong light absorption in the visible range, characterized by large extensions, indicates an effective donor-acceptor interaction between the substituents and the azulene nucleus.

The absorption peak of **7** is shifted (bathochromic shift of 29 nm) with increasing intensity compared to **5** (Figure 2). This can be caused by an extension of the π -conjugation and a reduction in the gap between the frontal MO (Figure 4).

Absorption in these regions of visible light in **5** and **7** ($\epsilon = 22,100$ and $34,117 \text{ M}^{-1} \text{ cm}^{-1}$) is much stronger than in azulene **1** ($\epsilon = 350 \text{ M}^{-1} \text{ cm}^{-1}$).²⁵

Electron absorption of **7** (compared to **5**) in thin films was investigated (Supporting Information). In thin films, the absorption spectrum shows general similarity to the spectrum in dichloromethane (Figure S7b, Figure 2), except for visible bands. They are observed in the longer wavelength part of the spectrum than in solution, shifting by 16 and 14 nm, respectively (Table 1). Such a shift is characteristic of interatomic interactions of **7** (or **5**) in the solid state.²⁹

Substances widely used as functional materials have absorption regions at 380–500 nm.^{30–36} Absorption wavelengths of **7** and **5** are located in the same spectral region.

The fluorescence spectrum of derivative **7** (compared to **5**²⁸) is presented in Figure 3 (Table 1).

Spectrum of **7** is characterized by a new emission with λ_{em} at 400 nm ($\lambda_{\text{ex}} = 320$ nm), and **5** by an emission band with a peak at 450 nm.

The emission maximum of **7** is significantly shifted to the blue part of the spectrum (50 nm) and is more intense than the emission band of **5**.

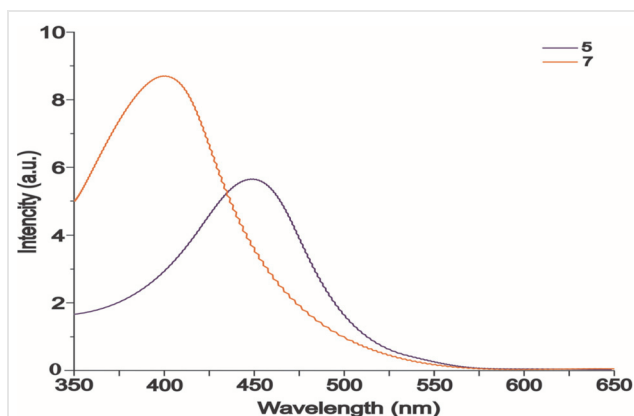


Figure 3 Fluorescence spectra of compounds 5 and 7

It should be noted that the blue photoluminescence of donor-acceptor azulene **7** is special, since the original molecule **1** does not have such ability.^{24,25}

Thus, it has been found that the addition of acceptor and donor substituents to the carbon atoms of C₁ (and C₃) and C₂ azulene leads to electron absorbances and fluorescent emissions in the visible spectrum.

To clarify the electron structure of donor-acceptor azulene **7** (compared to azulene **5**²⁸) and the structure-optical property relationship, quantum chemical calculations were performed (DFT method B3LYP/6-31G*) (Figure 4, Supporting Information).

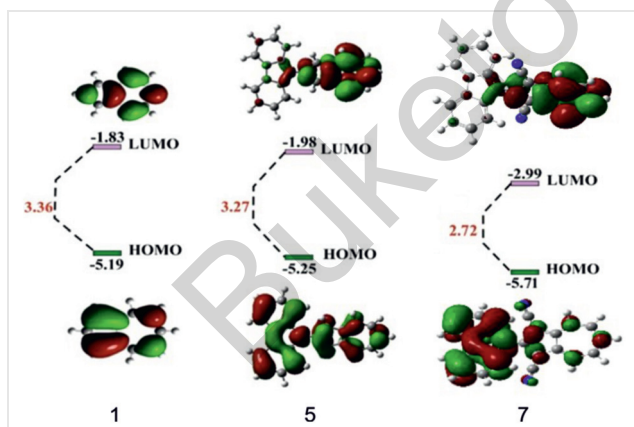


Figure 4 Distribution of frontal MO of 5 and 7 vs azulene 1

It has been shown that the delocalization of the highest occupied molecular orbital occurs both in the structure of azulene moiety and in the carbazolyl and carbonitrile substituents **7** and **5** (Figure 4). This may result from the interaction of the highest occupied molecular orbital **4** and HOMO-1 of original **1**,²⁹ since in the highest occupied MO of **1** the carbon atom C₂ is nodal, while in the HOMO-1 it is absent in this nodal plane and has a significant atomic-orbital parameter (Figure 1b).

Figure 4 also demonstrates that the levels of the highest occupied and lowest unoccupied molecular orbitals of derivative **7** are significantly lower than the corresponding levels of molecules **1** and **5**. At the same time, the energy gap between FMO levels is reduced by 0.64 eV. Such FMO changes make the electronic $\pi \rightarrow \pi^*$ transition permitted.²⁵ As a result, long-wave absorption and emission bands are recorded in the spectra of molecules **7** and **5** (Figures 2 and 3, Table 1).

We have successfully synthesized donor-acceptor compounds with an azulene core, which have a high absorption and emissivity. This became possible due to the introduction of donor substituents in the C₂ position and acceptors in the C₁ and C₃ positions of azulene. This modification of the structure caused significant changes in the energy levels of the original azulene, which created the prerequisites for a permitted electronic transition between HOMO and LUMO.

Conflict of Interest

The authors declare no conflict of interest.

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Supporting Information

Supporting information for this article is available online at <https://doi.org/10.1055/s-0043-1775501>.

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