


Nurlan Merkhately<sup>1</sup> , Amantai N. Iskanderov<sup>1\*</sup> ,  
Saltanat B. Abeuova<sup>2</sup> , Ablaykhan N. Iskanderov<sup>1</sup> 

<sup>1</sup>Karagandy University of the name of academician E.A. Buketov, Kazakhstan;

<sup>2</sup>Astana International University, Astana, Kazakhstan

(\*Corresponding author's e-mail: [dr.amantay@ya.ru](mailto:dr.amantay@ya.ru))

## Synthesis of Push-Pull Azulene-Based Compounds

Nowadays, non-benzenoid aromatic hydrocarbons are widely used as synthons for the production of new organic semiconductors with interesting photophysical characteristics. For instance, a non-benzoid azulene hydrocarbon with a polar structure, a narrow energy gap between the highest free and lowest occupied molecular orbital and the ability to form stable ions can be intended as a structural moiety for the synthesis of new conjugated compounds with important optical and electronic properties. The article discusses the synthesis and investigation of the optical properties of new push-pull azulene-based compounds. It shows that Friedel-Crafts acylation is used as the key reaction for the synthesis of methyl- and phenyl-dicyanovinylated azulenes. The interaction proceeds regioselectively at the C1 and C3 positions of the five-membered azulene ring. It is identified that the synthesis of push-pull dicyanovinylated azulenes by Knoevenagel condensation of azulenyl ketones with malononitrile proceeds easily in Py and DMSO. The UV-vis spectra of the obtained azulene push-pull compounds demonstrated strong electron absorption in the visible zone with  $\lambda_{\max}$  at 410, 430, 434 and 452 nm associated with transport of charge between the donor azulene ring and the acceptor dicyanovinyl group. The scheme of resonant structures shows the mechanism of intramolecular donor-acceptor interaction. The structure of the synthesized push-pull dicyanovinylated nonazulenes was elucidated using modern physicochemical and spectroscopic research methods.

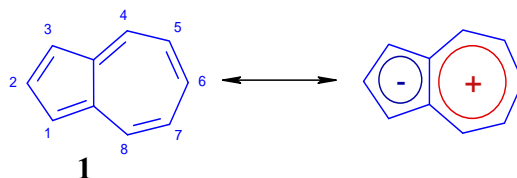
**Keywords:** functional materials, organic semiconductors, ketoazulene, diketoazulene, bis-dinitrilevinylazulene, mono-dinitrileazulene, donor-acceptor azulenes,  $\pi$ -conjugated systems.

### Introduction

The increasing interest in aromatic molecules with a stretched conjugate system due to their importance as functional materials for organic optoelectronics is largely focused on obtaining phenylated, also substituted by donor-acceptor fragments of benzenoid and heteroaromatic molecules. Nevertheless, up to now, non-alternative aromatic compounds have not found their extensive use as synthons for the production of new substances with valuable electro-optical characteristics. Such compounds include, in particular, azulene hydrocarbons [1, 2].

Azulene **1** (Fig. 1) is a unique nonalternant aromatic hydrocarbon consisting of condensed five- and seven-membered cycles [3]. The dipole structure ( $\mu=1.08$  D) of azulene can lead to stabilized ion radicals and is of interest as a structural block for obtaining donor-acceptor systems with advanced optoelectronic properties [1-3]. Azulene is unique not only for its polar nature, but also for the peculiarity of the energy transition and the small forbidden zone of HOMO – LUMO [4, 5]. This is due to its nonalternant structure, which induces frontal molecular orbitals to its mirror arrangement, thereby reducing the mutual repulsion between electrons. As a consequence, the energy gap of HOMO – LUMO **1** decreases in comparison with conventional aromatic hydrocarbons [6]. In addition, azulene gives strong absorption associated with the  $S_0$  –  $S_2$  optical transition, while the  $S_0$  –  $S_1$  transition leads to weak absorption in the visible range, which explains its blue color [7, 8]. Another feature of **1** is that its fluorescence mainly originates from the  $S_2$  state, whereas the  $S_1$ – $S_0$  transition is insignificant [9]. This nature of the transition violates the Kasha's rule [4]. The reason for this anomalous fluorescent nature is that the energy gap between the  $S_1$  and  $S_2$  states is relatively large ( $\Delta E$  is more than 10000  $\text{cm}^{-1}$ ), which leads to a decrease in the transition rate from  $S_2$  to  $S_1$ , as a result of which the radiation from  $S_2$  to  $S_0$  becomes dominant [10].

In this article, we report on the results of the directed synthesis and investigation of the optical properties of new push-pull methyl- and phenyldicyanovinylated azulenes.

Figure 1. The polarized resonance structure of azulene **1**

### Experimental

IR spectra were recorded on an Avatar-360 Fourier spectrometer (USA) in tablets with KBr.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a JeolECA-500 spectrometer (Japan) [operating frequency 500.15 MHz] in  $\text{CDCl}_3$ , internal standard TMS. Absorption spectra were recorded on a Shimadzu UV-1800 spectrophotometer (Japan) in dichloromethane ( $C=10^{-4}$  mol/l). Mass spectra were recorded on a Shimadzu GC-MSQP-2010 Ultra chromatograph-mass spectrometer (Japan) with electron impact ionization (ionization energy 70 eV, column GsBP-5MS:  $0.25 \mu\text{m} \times 0.25 \text{mm} \times 30 \text{m}$ , carrier gas helium, programmable heating from 100 to 300 °C, scanning mode for all integer  $m/z$  values in the range from 15 to 900 at a speed of 5000 amu/sec). Elemental analysis was performed on an automatic CHNS analyzer EuroVektor EA-3000 (Italy). The melting point was determined on a Melting Point M-560 instrument (Switzerland). Sorbfil PTSH-AF-UF plates (Russia) were used for TLC, eluent was hexane, hexane-ethyl acetate, and developed with a saturated solution of  $\text{KMnO}_4$ . Silica gel 60 (Merck) was used for column chromatography.

Initial azulene (99.5 %), acetyl chloride (99 %), benzoyl chloride (99 %), malononitrile ( $\geq 99$  %), dimethyl sulfoxide (99.5 %), pyridine ( $\geq 99.0$  %), methylene chloride ( $\geq 99.8$  %) produced by Sigma-Aldrich were used without additional purification.

**2-(1-(Azulen-1-yl)ethylidene)malononitrile (4).** Monoketone **2** (150 mg, 0.86 mmol), malonitrile (100 mg, 1.5 mmol), pyridine (1 ml) and dimethyl sulfoxide (2 ml) were placed in a reaction vessel and stirred in a nitrogen atmosphere for 10 hours at 105 °C. After the end of the reaction, pyridine and dimethyl sulfoxide were distilled at reduced pressure. The product was purified by  $\text{SiO}_2$  flash column chromatography (eluent was methylene chloride) and recrystallization from methylene chloride. Yield is 0.13 g (70 $\pm$ 0.65 %), red crystals, mp 156–157 $\pm$ 0.15 °C. IR spectrum,  $\nu$ , ( $\text{cm}^{-1}$ ): 2220 (CN), 1543–1385 ( $\text{C}_{\text{sp}^2}$ - $\text{C}_{\text{sp}^2}$ ).  $^1\text{H}$  NMR spectrum,  $\delta$  (ppm): 2.28 s. (3H,  $\text{CH}_3$ ), 7.31 d (1H,  $\text{H}^3$ , J4.13 Hz), 7.64 t (2H,  $\text{H}^{5,7}$ , J 9.6 Hz), 8.0 t (1H,  $\text{H}^6$ , J 9.6 Hz), 8.05 d (1H,  $\text{H}^2$ , J 4.13 Hz), 8.08 d (1H,  $\text{H}^4$ , J 9.6 Hz), 8.13 d (1H,  $\text{H}^8$ , J 9.6 Hz).  $^{13}\text{C}$  NMR spectrum,  $\delta$  (ppm): 116.08, 117.11, 120.05, 125.25, 130.84, 136.55, 141.17, 142.60, 145.49, 146.79, 151.18, 168.38. MS,  $m/z$  ( $I_{\text{rel}}$ , %): 218 (75.12) [ $\text{M}$ ] $^+$ . Found, %: C 82.62; H 4.66; N 12.94.  $\text{C}_{15}\text{H}_{10}\text{N}_2$ . Calculated, %: C 82.55; H 4.62; N 12.84.

**2,2'-(Azulene-1,3-diylbis(ethan-1-yl-1-ylidene))dimalononitrile (5)** was synthesized similarly by the interaction of diketone **3** with two equivalents of malononitrile (200 mg, 3 mmol). Yield is 0.14 g (73 $\pm$ 0.22 %), red crystals, mp 252–253 $\pm$ 0.16 °C. IR spectrum,  $\nu$ , ( $\text{cm}^{-1}$ ): 2218 (CN), 1504–1361 ( $\text{C}_{\text{sp}^2}$ - $\text{C}_{\text{sp}^2}$ ).  $^1\text{H}$  NMR spectrum,  $\delta$  (ppm): 2.28 s. (6H,  $\text{CH}_3$ ), 7.68 t (2H,  $\text{H}^{5,7}$ , J 9.8 Hz), 8.03 t (1H,  $\text{H}^6$ , J 9.8 Hz), 8.07 s (1H,  $\text{H}^2$ ), 8.15 d (2H,  $\text{H}^{4,8}$ , J 9.8 Hz).  $^{13}\text{C}$  NMR spectrum,  $\delta$  (ppm): 114.06, 115.10, 124.05, 125.19, 129.35, 130.84, 131.21, 133.35, 136.55, 139.17, 142.70, 143.39, 144.18.2, 144.18.2 MS,  $m/z$  ( $I_{\text{rel}}$ , %): 308 (73.05) [ $\text{M}$ ] $^+$ . Found, %: C 77.98; H 3.96; N 18.24.  $\text{C}_{20}\text{H}_{12}\text{N}_4$ . Calculated, %: C 77.91; H 3.92; N 18.17.

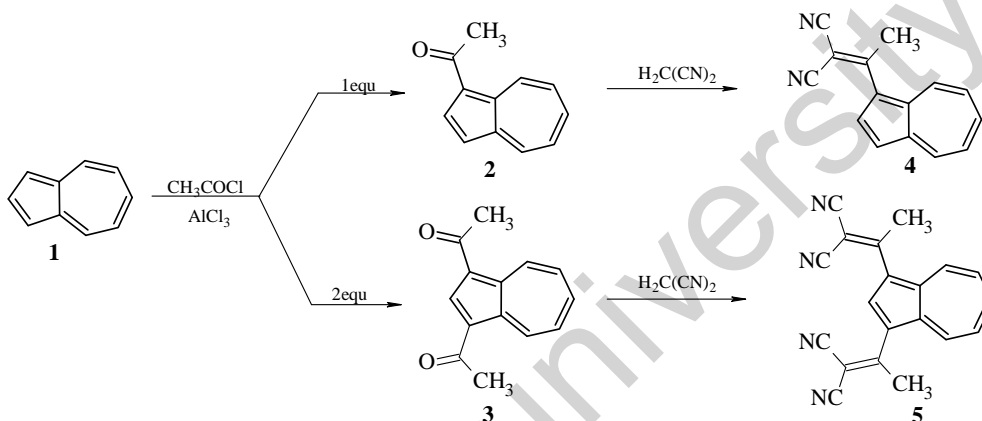
**2-(Azulen-1-yl(phenyl)methylene)malononitrile (8).** Monoketone **6** (201 mg, 0.87 mmol), malonitrile (100 mg, 1.5 mmol), pyridine (2 ml) and dimethyl sulfoxide (3 ml) were placed in a reaction vessel and stirred in a nitrogen atmosphere for 10 hours at 105 °C. After the end of the reaction, pyridine and dimethyl sulfoxide were distilled at reduced pressure. The product was purified by  $\text{SiO}_2$  flash column chromatography (eluent was methylene chloride) and recrystallization from methylene chloride. Yield is 0.17 g (71 $\pm$ 0.25 %), red crystals, mp 148–149 $\pm$ 0.17 °C. IR spectrum,  $\nu$  ( $\text{cm}^{-1}$ ): 2224 (CN), 1512–1374 ( $\text{C}_{\text{sp}^2}$ - $\text{C}_{\text{sp}^2}$ ).  $^1\text{H}$  NMR spectrum,  $\delta$  (ppm): 7.35 d (1H,  $\text{H}^3$ , J 4.17 Hz), 7.49–7.56 m (3 $\text{H}_{\text{arom}}$ ), 7.63–7.66 m (2 $\text{H}_{\text{arom}}$ ), 7.69 t (2H,  $\text{H}^{5,7}$ , J 9.9 Hz), 8.04 t (1H,  $\text{H}^6$ , J9.9Hz), 8.09 d (1H,  $\text{H}^2$ , J 4.17 Hz), 8.13 d (1H,  $\text{H}^4$ , J 9.9 Hz), 8.18 d (1H,  $\text{H}^8$ , J 9.9 Hz).  $^{13}\text{C}$  NMR spectrum,  $\delta$  (ppm): 118.07, 119.09, 122.07, 123.19, 127.26, 132.85, 133.22, 134.84, 137.52, 142.16, 143.61, 146.48, 145.75, 152.17, 166.35. MS,  $m/z$  ( $I_{\text{rel}}$ , %): 280 (78.12) [ $\text{M}$ ] $^+$ . Found, %: C 85.61; H 4.27; N 9.89.  $\text{C}_{20}\text{H}_{12}\text{N}_2$ . Calculated, %: C 85.69; H 4.31; N 9.99.

**2,2'-(Azulene-1,3-diylbis(phenylmethanylylidene))dimalononitrile (9)** was synthesized similarly by the interaction of diketone **7** with two equivalents of malonitrile (200 mg, 3 mmol). Yield is

0.18 g (70±0.17 %), red crystals, mp 237–238±0.19 °C. IR spectrum,  $\nu$  (cm<sup>-1</sup>): 2220 (CN), 1510–1395 (C<sub>sp2</sub>-C<sub>sp2</sub>). <sup>1</sup>H NMR spectrum,  $\delta$  (ppm): 7.50–7.48 m (8H<sub>arom</sub>), 7.63–7.66 m (2H<sub>arom</sub>), 7.64 t (2H, H<sup>5,7</sup>, J 9.9 Hz), 8.07 t (1H, H<sup>6</sup>, J 9.9 Hz), 8.09 s (1H, H<sup>2</sup>), 8.17 d (2H, H<sup>4,8</sup>, J 9.9 Hz). <sup>13</sup>C NMR spectrum,  $\delta$  (ppm): 116.04, 116.12, 126.05, 127.18, 128.36, 131.85, 133.22, 135.32, 137.54, 138.15, 143.68, 144.38, 145.78, 148.06, 157.16, 166.94. MS,  $m/z$  ( $I_{rel}$ , %): 432 (75.10) [M]<sup>+</sup>. Found, %: 83.41; H, 3.71; N, 12.86. C<sub>30</sub>H<sub>16</sub>N<sub>4</sub>. Calculated, %: C, 83.32; H, 3.73; N, 12.95.

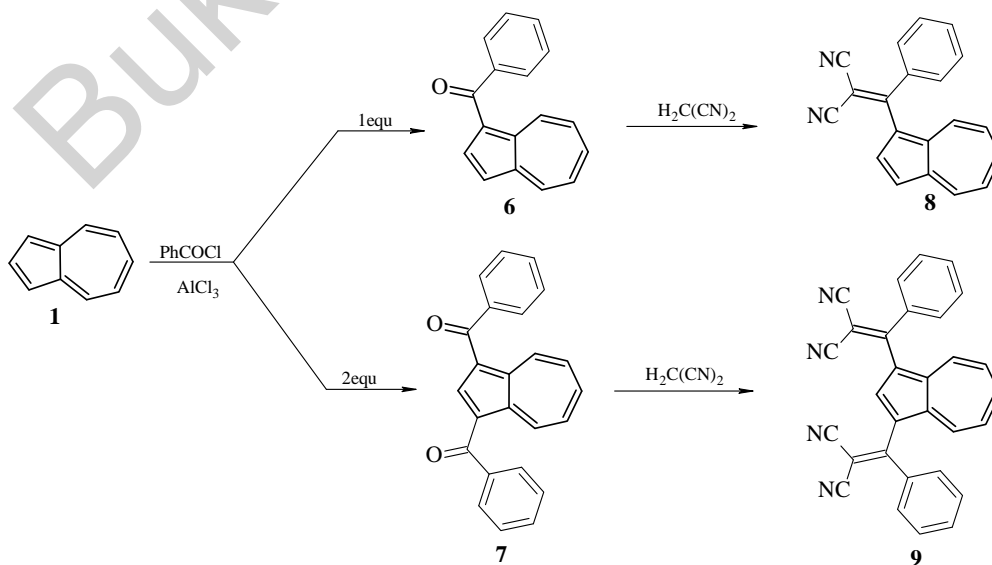
### Results and Discussion

The Friedel-Crafts acylation was used as the key reaction for the synthesis of methyl-dicyanovinylated azulenes (Scheme 1). Acylation of azulene **1** with one or two equivalents of acetyl chloride has been shown to lead regioselectively to previously described 1-mono- and 1,3-diketones **2** and **3** in 78 and 75 % yields, respectively [11]. The resulting methyl ketones then enter into a Knoevenagel condensation with CH<sub>2</sub>(CN)<sub>2</sub> in the medium of pyridine and DMSO to yield push-pull 1-mono- and 1,3-bis(methyl-dicyanovinyl)azulenes **4** and **5** as red crystals in 70 and 73 % yields, respectively.



Scheme 1

The synthesis of phenyl dicyanovinylated azulenes was carried out according to Scheme 2, also using Friedel-Crafts acylation reactions and Knoevenagel condensation. Thus, the reaction of compound **1** with one or two equivalents of benzoyl chloride in dichloromethane leads to known ketones **6** and **7** in 71 and 60 % yields [12]. Then, the resulting phenyl ketones condense with CH<sub>2</sub>(CN)<sub>2</sub> in the medium of pyridine and DMSO to form push-pull phenyl dicyanovinylazulenes **8** and **9** as red crystals in 71 and 70 % yields, respectively.



Scheme 2



### Conclusions

Acylation of azulene with acetyl- and benzoyl chloride under Friedel-Crafts electrophilic substitution conditions yielded 1-mono- and 1,3-bis(methyl) and (phenyl)azulenyl ketones in high yields. In addition, by Knoevenagel condensation of the obtained azulenyl ketones with  $\text{CH}_2(\text{CN})_2$  in pyridine, push-pull 1-mono- and 1,3-bis-methyl(phenyl)dicyanovinylazulenes were synthesized in high yields. Intense absorption bands of intramolecular charge transfer in the visible region were revealed for push-pull methyl(phenyl)dicyanovinylazulenes with absorption maxima at 430, 410, 450, and 434 nm.

### Acknowledgments

The work was carried out as part of the project № AR15473272 on grant financing of the Science Committee of the Ministry of Science and Higher Education of the Republic of Kazakhstan.

### References

- Dong, J.-X., & Zhang H.-Li. (2016). Azulene-based organic functional molecules for optoelectronics. *Chin. Chem. Lett.*, 27, 1097-1104. <https://doi.org/10.1016/j.ccllet.2016.05.005>
- Gao, H., Ge, C., Hou, B., Xin, H., & Gao, X. (2019). Incorporation of 1,3-Free-2,6-Connected Azulene Units into the Backbone of Conjugated Polymers: Improving Proton Responsiveness and Electrical Conductivity. *ACS Macro Lett.*, 8, 360-1364. <https://doi.org/10.1021/acsmacrolett.9b00657>
- Lopez-Alled, C.M., Park, S.J., Lee, D.J., Murfin, L.C., Kociok-Kohn, G., Hann, J.L., Wenk, J., James, T.D., Kim, H.M., & Lewis, S.E. (2021). Azulene-based fluorescent chemosensor for adenosine diphosphate. *Chem. Commun.*, 57, 10608-10611. <https://doi.org/10.1039/d1cc04122c>
- Ou, L., Zhou, Y., Wu, B., & Zhu, L. (2019). The unusual physicochemical properties of azulene and azulene-based compounds. *Chin. Chem. Lett.*, 30, 1903-1907. <https://doi.org/10.1016/j.ccllet.2019.08.015>
- Xin, H., Hou, B., & Gao X. (2021). Azulene-Based  $\pi$ -Functional Materials: Design, Synthesis, and Applications. *Acc. of Chem. Res.*, 54, 1737-1753. <https://doi.org/10.1021/acs.accounts.0c00893>
- Puodziukynaite, E., Wang, H.W., & Lawrence, J. (2014). Azulene methacrylate poly-421 mers: synthesis, electronic properties, and solar cell fabrication. *J. of the Am. Chem. Soc.*, 136, 11043-11049. <https://doi.org/10.1021/ja504670k>
- Chen, L.Wu, B., Qin, L., Huang, Y.Y., Zhang, X.S., & Zhang, D. (2022). A perylene five-membered ring diimide for organic semiconductors and  $\pi$ -expanded conjugated molecules. *Chem. Comm.*, 58, 5100-5103. <https://doi.org/10.1039/d2cc01061e>
- Maeng, C., Yun, Y., Son, J.Y., & Lee, P. H. (2022). Palladium-Catalyzed Oxidative Cyclization of Azulene-2-Carboxylic Acids with 1,3-Dienes for the Synthesis of Alkenyl Azulenolactones. *Adv. Synth. Catal.*, 364 (16), 2859-2864. <https://doi.org/10.1002/adsc.202200452>
- Murai, M., Abe, M., Ogi, S., & Yamaguchi, S. (2022). Diazulenylmethyl Cations with a Silicon Bridge: A  $\pi$ -Extended Cationic Motif to Form J-Aggregates with Near-Infrared Absorption and Emission. *J. of the Am. Chem. Soc.*, 144 (44), 20385-20393. <https://doi.org/10.1021/jacs.2c08372>
- Ran, F., Zheng, H.L.R., Zhang, H., Xie, F., Jin, P., Lei, Z., Wang, X.-T., & Hu, J.Y. (2022). Polarity change of OFETs based on Dithienocoronene Diimide (DTCDI)-Derived isomeric triads end-capped with Azulene. *Dyes and Pigms.*, 203, 110-311. <https://doi.org/10.1016/j.dyepig.2022.110311>
- Anderson, A.G., Scotoni, R., Cowles, E.J., & Fritz, C.G. (1957). Azulene. VI. Synthesis and Properties of Some 1,3-Disubstituted Azulenes. *J. Org. Chem.*, 22(10), 1193-1196. <https://doi.org/10.1021/jo01361a017>
- Westermayr, J., & Maure, R.J. (2021). Physically inspired deep learning of molecular excitations and photoemission spectra. *Chem. Sci.*, 12, 10755-10764. <https://doi.org/10.1021/jacs.2c08372>

### Information about authors\*

**Merkhately, Nurlan** — Doctor of Chemical Sciences, Professor, Department of Inorganic and Technical Chemistry, Karagandy University of the name of academician E.A. Buketov, Universitetskaya street, 28, 100024, Karaganda, Kazakhstan; e-mail: [merhately@ya.ru](mailto:merhately@ya.ru); <https://orcid.org/0000-0003-4588-2150>;

**Iskanderov, Amantai Nurbaevich** (*corresponding author*) — Master of Chemistry, Department of Inorganic and Technical Chemistry, Karagandy University of the name of academician E.A. Buketov, Universitetskaya street, 28, 100024, Karaganda, Kazakhstan; e-mail: [dr.amantay@ya.ru](mailto:dr.amantay@ya.ru); <https://orcid.org/0000-0001-5270-5094>;

**Abeuova, Saltanat Bolatovna** — PhD, Senior Lecturer, Astana International University, Kabanbaybatyra street, 8, Z05H0T3, Astana, Kazakhstan; e-mail: [abeuova.salta@gmail.com](mailto:abeuova.salta@gmail.com); <https://orcid.org/0000-0001-7074-3123>;

**Iskanderov, Ablaykhan Nurbaevich** — Master of Chemistry, Department of Inorganic and Technical Chemistry, Karagandy University of the name of academician E.A. Buketov, Universitetskaya street, 28, 100024, Karaganda, Kazakhstan; e-mail: [aby93@yandex.kz](mailto:aby93@yandex.kz); <https://orcid.org/0000-0002-1646-0795>

---

\*The author's name is presented in the order: *Last Name, First and Middle Names*

Buketov university