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Article

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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 UF-vis spectra of the obtained azulene push-pull compounds demonstrated strong electron absorption in the visible zone with λmax 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-dinitrilevinyl-azulene, mono-dinitrileazulene, donor-acceptor azulenes, π-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 benzoid 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 (μ=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 (ΔE is more than 10000 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 phenyldicianovinylated azulenes.

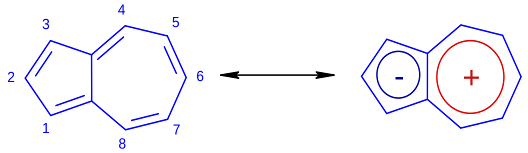

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Figure 1. The polarized resonance structure of azulene **1**

Experimental

IR spectra were recorded on an Avatar-360 Fourier spectrometer (USA) in tablets with KBr. ^{1}H and ^{13}C NMR spectra were recorded on a JeolECA-500 spectrometer (Japan) [operating frequency 500.15 MHz] in $CDCl_3$, 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 chromato-mass spectrometer (Japan) with electron impact ionization (ionization energy 70 eV, column GsBP-5MS: 0.25 μm × 0.25 mm × 30 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 $KMnO_4$. Silica gel 60 (Merck) was used for column chromatography.

Initial azulene (99.5 %), acetyl chloride (99 %), benzoyl chloride (99 %), malononitrile (≥99 %), dimethyl sulfoxide (99.5 %), pyridine (≥99.0 %), methylene chloride (≥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 SiO_2 flash column chromatography (eluent was methylene chloride) and recrystallization from methylene chloride. Yield is 0.13 g (70±0.65 %), red crystals, mp 156–157±0.15 °C. IR spectrum, ν, (cm^{-1}): 2220 (CN), 1543–1385 (C_{sp2}-C_{sp2}). ^{1}H NMR spectrum, δ (ppm): 2.28 s. (3H, CH_3), 7.31 d (1H, H^3, J4.13 Hz), 7.64 t (2H, $H^{5,7}$, J 9,6 Hz), 8.0 t (1H, H^6, J 9.6 Hz), 8.05 d (1H, H^2, J 4.13 Hz), 8.08 d (1H, H^4, J 9.6 Hz), 8.13 d (1H, H^8, J 9.6 Hz). ^{13}C NMR spectrum, δ (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_{rel},%): 218 (75.12) $[M]^+$. Found, %: C 82.62; H 4.66; N 12.94. $C_{15}H_{10}N_2$. 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±0.22 %), red crystals, mp 252–253±0.16 °C. IR spectrum, ν, (cm^{-1}): 2218 (CN), 1504–1361 (C_{sp2}-C_{sp2}). ^{1}H NMR spectrum, δ (ppm): 2.28 s. (6H, CH_3), 7.68 t (2H, H5.7, J 9.8 Hz), 8.03 t (1H, H6, J 9.8 Hz), 8.07 s (1H, H2), 8.15 d (2H, H4.8, J 9.8 Hz). ^{13}C NMR spectrum, δ (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_{rel},%): 308 (73.05) $[M]^+$. Found, %: C 77.98; H 3.96; N 18.24. $C_{20}H_{12}N_4$. Calculated, %: C 77.91; H 3.92; N 18.17.

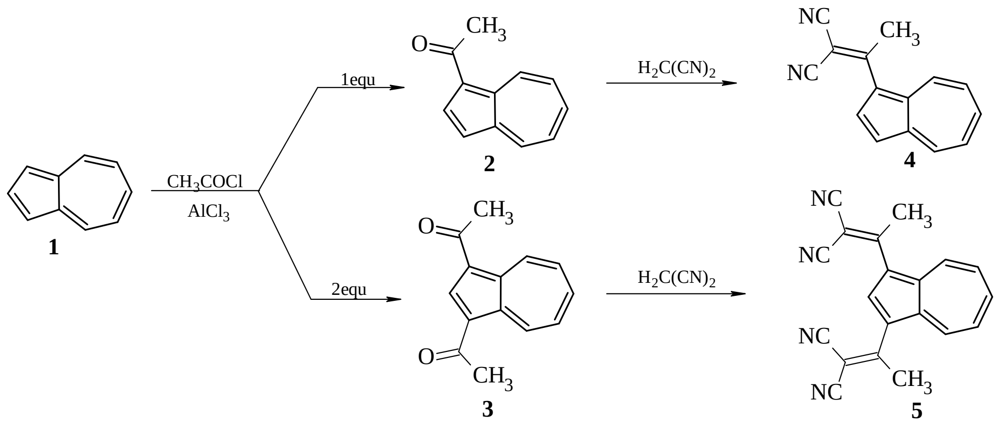
2-(Azulen-1-yl(phenyl)methylene)malononitrile (8). Monoketone 6 (201 mg, 0.87 mmol), malonitrile (100 mg, 1.5 mmol), pyridine (2 ml) and dimethyl sulfoxide (3 ml) were placed in a reaction vessel and stirred in a nitrogen atmosphere for 10 hours at 105 °C. After the end of the reaction, pyridine and dimethyl sulfoxide were distilled at reduced pressure. The product was purified by SiO_2 flash column chromatography (eluent was methylene chloride) and recrystallization from methylene chloride. Yield is 0.17 g (71±0.25 %), red crystals, mp 148–149±0.17 °C. IR spectrum, ν (cm^{-1}): 2224 (CN), 1512–1374 (C_{sp2}-C_{sp2}). ^{1}H NMR spectrum, δ (ppm): 7.35 d (1H, H3, J 4.17 Hz), 7.49–7.56 m ($3H_{arom}$), 7.63–7.66 m ($2H_{arom}$), 7.69 t (2H, $H^{5,7}$, J 9.9 Hz), 8.04 t (1H, H^6, J9.9Hz), 8.09 d (1H, H^2, J 4.17 Hz), 8.13 d (1H, H^4, J 9.9 Hz), 8.18 d (1H, H^8, J 9.9 Hz). ^{13}C NMR spectrum, δ (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_{rel},%): 280 (78.12) $[M]^+$. Found, %: C 85.61; H 4.27; No. 9.89. $C_{20}H_{12}N_2$. 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, ν (cm^{-1}): 2220 (CN), 1510–1395 (C_{sp2}-C_{sp2}). ^{1}H NMR spectrum, δ (ppm): 7.50–7.48 m (8H_{arom}), 7.63 -7.66 m (2H_{arom}), 7.64 t (2H, $H^{5,7}$, J 9.9 Hz), 8.07 t (1H, H^{6}, J 9.9 Hz), 8.09 s (1H, H^{2}), 8.17 d (2H, $H^{4,8}$, J 9.9 Hz). ^{13}C NMR spectrum, δ (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]$^{+}$. Found, %: 83.41; H, 3.71; H 12.86. $C_{30}H_{16}N_4$. Calculated, %: C, 83.32; H, 3.73; N, 12.95.

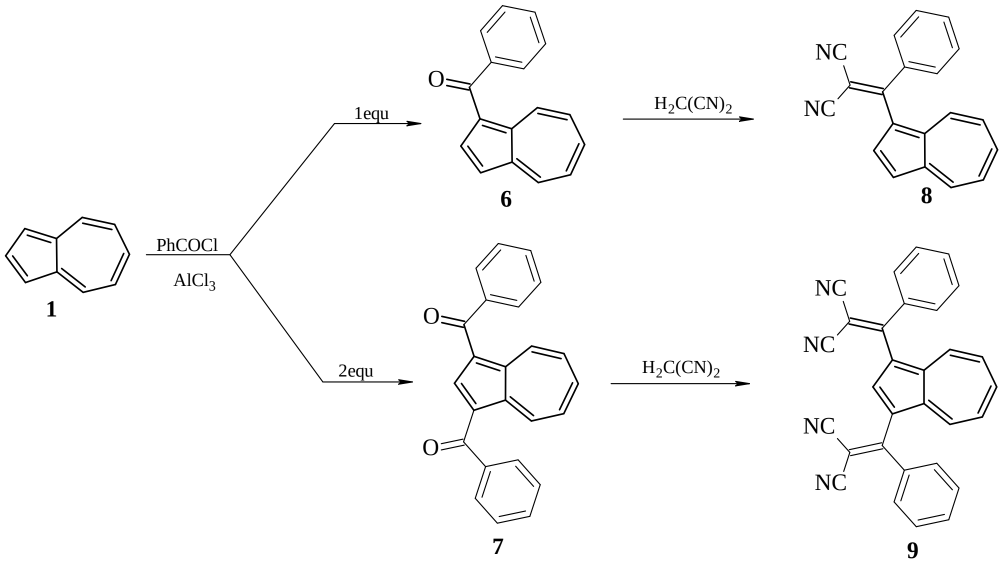
Results and Discussion

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 $CH_2(CN)_2$ 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.



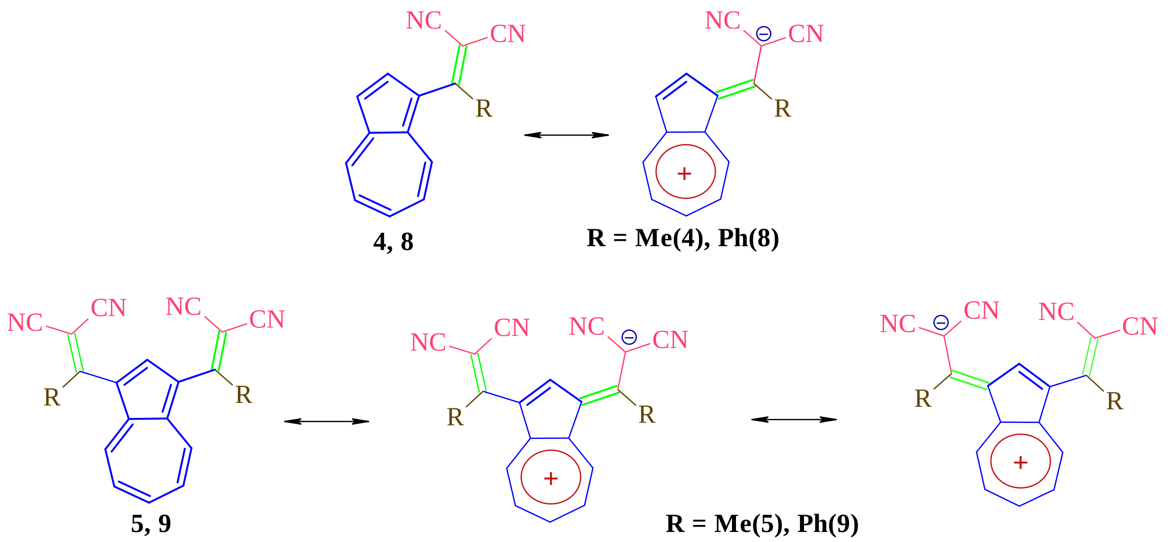
Scheme 1

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 $CH_2(CN)_2$ 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

To study the optical properties of the obtained compounds, push-pull analysis of azulenes **4, 5, 8,** and **9** was carried out using absorption spectrophotometry in the UV and visible regions. UV-Vis spectra of **4** and **5**, as well as **8** and **9** showed intense absorption in the visible spectrum with maxima at 430 and 410 nm, 452 and 434 nm, respectively (Table, Fig. 3), caused by intramolecular charge transfer between the azulene ring and dicyanovinyl group, as demonstrated on resonant structures (Fig. 2).



4, 8

R = Me(4), Ph(8)

5, 9

R = Me(5), Ph(9)

Figure 2. Resonance structures of push-pull azulenes **4, 5** and **8, 9**

Table

UV-Vis light absorption data for push-pull azulenes 4, 5 and 8, 9

Compound	Solvent	C, mol/l	λ_{abs}, nm	ε, M^{-1}cм$^{-1}$
4	dichloromethane	10^{-4}	430	9552
5	dichloromethane	10^{-4}	410	8893
8	dichloromethane	10^{-4}	450	8481
9	dichloromethane	10^{-4}	434	9186

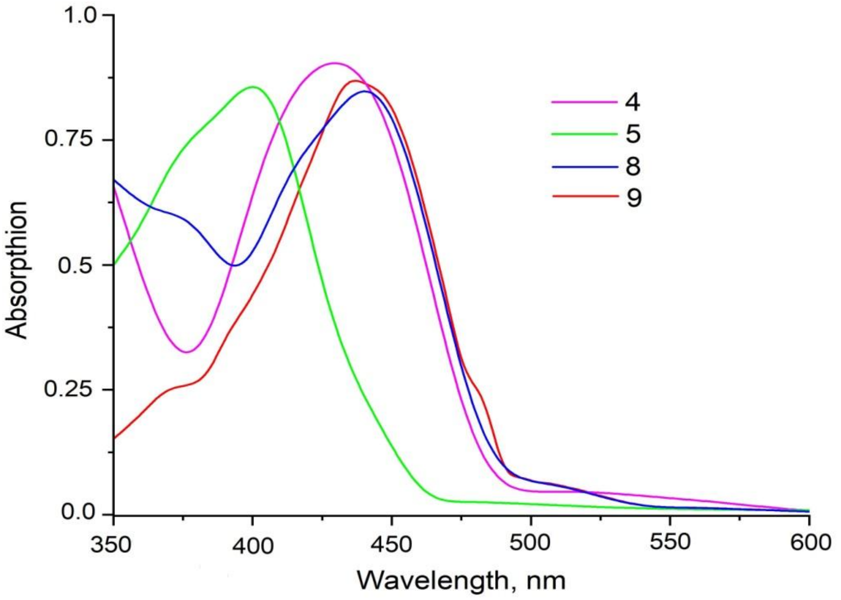


Figure 3. Push-pull absorption spectra of azulenes **4, 5** and **8, 9** in dichloromethane

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 $CH_2(CN)_2$ 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.

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References

1 Dong, J.-X., & Zhang H.-Li. (2016). Azulene-based organic functional molecules for optoelectronics. *Chin. Chem. Lett., 27,* 1097-1104. https://doi10.1016/j.cclet.2016.05.005

2 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://doi10.1021/acsmacrolett.9b00657

3 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://doi10.1039/d1cc04122c

4 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.10.1016/j.cclet.2019.08.015

5 Xin, H., Hou, B., & Gao X. (2021). Azulene-Based π‑Functional Materials: Design, Synthesis, and Applications. *Acc. of Chem. Res., 54,* 1737–1753. https://doi.10.1021/acs.accounts.0c00893

6 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.10.1021/ja504670k

7 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 π-expanded conjugated molecules. *Chem. Comm.*, *58,* 5100–5103. https://doi.org/10.1039/d2cc01061e

8 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

9 Murai, M., Abe, M., Ogi, S., & Yamaguchi, S.(2022). Diazulenylmethyl Cations with a Silicon Bridge: A π-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

10 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 Pigm., 203,* 110-311. https://doi.org/10.1016/j.dyepig.2022.110311

11 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

12 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

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