SHORT PAPER

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A novel polycyclic system: synthesis of 1,3,5-tri(1-azulenyl)benzenes by cyclotrimerization of 1-acetylazulenes

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Synthesis of 1,3,5-tri(1-azulenyl)benzene was accomplished by tetrachlorosilane-mediated cyclotrimerization of 1-acetyl-3-methoxycarbonylazulene followed by de-esterification.

Azulenes are nonalternant 10π aromatic systems and exhibit specific physical and chemical properties. Recently, synthesis and properties of a series of (1-azulenyl)methyl cations: *i.e.*, tri(1-azulenyl)methyl **1a–f**, di(1-azulenyl)phenylmethyl **2a–e**, and (1-azulenyl)diphenylmethyl **3a–e** hexafluorophosphates, have been reported.[1] These cations showed extreme stabilities with high pK_R+ values (**1f**, 24.3). Their high stabilities can be explained by the large π-conjugative effect between the central cationic carbon and the three azulene rings. In extension of these studies, it is of interest to investigate the synthesis and properties of 1,3,5-tri(1-azulenyl)benzenes. It was reported that tetrachlorosilane is very useful for trimerization of a variety of acetophenones to 1,3,5-triarylbenzenes.[2] This method was applied to conversion of 2-acetylthiophenes in to 1,3,5-tri(2-thienyl)benzenes.[3] It was also found that gaseous hydrogen chloride was useful for trimerization of acetophenones.[4] In this communication, we report that these procedures can be applied to the preparation of 1,3,5-tri(1-azulenyl)benzene (**4**) which is expected to be a useful starting material for the synthesis and characterization of novel poly carbocations, radicals, and anions, and is also a new C_3-symmetric building block[5] in azulenoid chemistry.

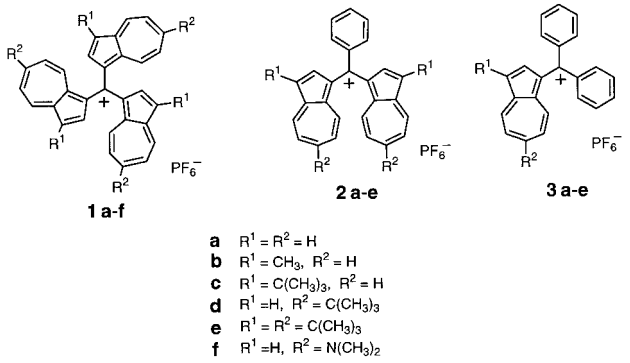
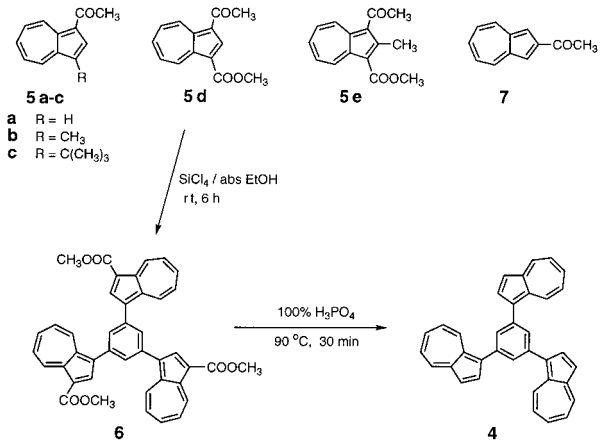


Fig. 1

Synthesis

To a solution of 1-acetylazulene (**5a**) in absolute ethanol was added tetrachlorosilane at room temperature. The mixture was stirred at the same temperature to give no desired trimer. From the treatment of 3-methyl- and 3-(1,1-dimethylethyl-substituted 1-acetylazulenes **5b,c** with tetrachlorosilane, the starting materials were also recovered. Then, a solution of 1-acetyl-3-methoxycarbonylazulene (**5d**) and tetrachlorosilane in absolute ethanol was stirred for 6 h at room temperature to afford 1,3,5-tris(3-methoxycarbonyl-1-azulenyl)benzene (**6**) in 43% yields as dark violet needles, m.p. > 300°C. Hydrogen chloride gas was also passed into a solution of **5d** in triethyl orthoformate to afford **6** in 38% yield. The compound **6** was heated in 100% phosphoric acid for 30 min at 90°C according to the usual procedure.[6] The reaction mixture was purified by chromatography on silica gel to afford 1,3,5-tri(1-azulenyl)benzene (**4**) in 93% yield as deep greenish blue prisms, m.p. 243–244°C.



Scheme 1

Although the cyclotrimerization of various acetophenones gave 1,3,5-triarylbenzenes in good yields regardless of whether the starting acetophenone contained electron-withdrawing or electron-donating group,[2a,c] a remarkable substituent effect was observed in the reactions of 1-acetylazulenes **5a–d**. Probably, these differences are caused by resonance interaction between the acetyl group and the

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seven-membered ring in azulenes **5a–c**. On the other hand, 1-acetyl-3-methoxycarbonyl-azulene (**5d**) has an additional electron-withdrawing methoxycarbonyl group which is able to conjugate with the seven-membered ring. The resonance interaction between the acetyl group and the seven-membered ring might be reduced. Consequently, the enolic tautomer of the compound **5d** acts as the nucleophile and attacks at the protonated acetyl carbonyl carbon atom of the second molecule of the compound **5d** followed by additional condensation with the third molecule, cyclization, and aromatization to yield 1,3,5-tri(1-azulenyl)benzene (**6**). However, 1-acetyl-3-methoxycarbonyl-2-methylazulene (**5e**) having an additional methyl group at the 2-position, gave no product due to steric hindrance. In addition, the investigation of synthesis and properties of the sterically less hindered, 1,3,5-tri(2-azulenyl)benzene is very interesting. Although cyclotrimerization of 2-acetylazulene (**7**) was carried out in the same conditions, the expected 1,3,5-tri(2-azulenyl)benzene was not obtained.

Properties

The structure of compound **4** was established by means of satisfactory elemental analysis and spectral data. In the high-resolution mass spectrum, the correct M^+ ionpeak, *m/z* 456.1885 (calcd for $C_{36}H_{24}$, 456.1878) was observed. The UV spectrum showed the bathochomic shift in comparison with that of azulene itself and the absorptions in the visible region were observed at λ_{max} 602 (log ε 3.00) and 723 nm (sh, 2.40). The ^{1}H NMR spectrum exhibited very clear signals in chloroforom-*d* as time-averaged results at δ 7.13 (3H, t, *J* 9.8, 7′-H × 3), 7.14 (3H, t, *J* 9.8, 5′-H × 3), 7.48 (3H, d, *J* 3.6 3′-H × 3), 7.57 (3H, t, *J* 9.8, 6′-H × 3), 7.87 (3H, s, 2-,4-,6-H), 8.16 (3H, d, *J* 3.6, 2′-H × 3), 8.36 (3H, d, *J* 9.8, 4′-H × 3), 8.76 (3H, d, *J* 9.8, 8′-H × 3). These chemical shifts are closely comparable to those of 1-phenylazulene. In the ^{1}H NMR spectra in dichloromethane-d_2/carbon disulfide at various temperature, the freezing of rotation around the C–C single bond between the azulene and the benzene ring was not observed at even low temperature (–90 °C), except for the separation of the signals of 5′-H and 7′-H protons.

The redox potentials (V *vs* Ag/Ag^+) of compound **4** were measured by cyclic voltammetry in *N, N*-dimethylformamide. It was found that the redox processes were irreversible. The oxidation showed a wave at +0.52 V which is comparable to those of azulene (+0.61 V) and 1-phenylazulene (+0.52 V). The reduction showed a wave at –1.86 V which is also close to those of azulene (–2.00 V) and 1-phenylazulene (–1.93 V).

Conclusion

1,3,5-Tri(1-azulenyl)benzene (**4**) was readily prepared in moderate yield *via* condensation of 1-acetyl-3-methoxycarbonylazulene (**5d**) followed by de-esterification. It was found that the substituent at the 3-position exhibited a remarkable influence in the cyclotrimerization process.

The star-shaped compound **4** is expected to be a useful starting material for the synthesis of novel carbocations, radicals and anions. A π–π interaction among the three azulene rings through the central benzene ring might be negligibly small from the spectral data and the redox potentials.

Experimental

The melting points were determined with a Yanagimoto MP-S2 apparatus and are uncorrected. The IR and UV spectra were taken on a Perkin-Elmer Paragon 1000 and a Hitachi U-4000 spectrophotometer, respectively. The ^{1}H and ^{13}C NMR spectra were measured with a JEOL JNM-AL300 spectrometer (300 MHz for ^{1}H and 75.5 MHz for ^{13}C measurements) with tetramethylsilane as the internal standard. The ^{1}H NMR temperature-dependent spectra were recorded on a Bruker AM 600 spectrometer (600 MHz). The MS spectra were performed with a JEOL JMS-DX 303HF apparatus. The CV potentials were determined with a BAS 100B/W apparatus.

Cyclotrimerization of 1-Acetyl-3-methoxycarbonylazulene (**5d**): (a) Treatment with tetrachlorosilane: A solution of **5d** (61 mg, 0.25 mmol) and tetrachlorosilane (0.1 ml, 0.8 mmol) in absolute ethanol (2.0 ml) was stirred for 6 h at room temperature. The reaction mixture was diluted with water and extracted with chloroform. After removal of the solvent, the residue was chromatographed on a column (Merck silica gel 60, 15 g) with hexane-ethyl acetate (2:1) as an eluent to give 1,3,5-tris(3-methoxycarbonyl-1-azulenyl)benzene (**6**) (44 mg, 43%) and the starting material **5d** (25 mg, 22%).

6: Dark violet needles (from benzene-hexane), m.p. > 300°C; ν_{max} (KBr) 1689 cm^{-1} (C=O), δ_H ($CDCl_3$) 3.98 (9H, s, $COOCH_3$ × 3), 7.43 (3H, t, *J* 9.8, 7′-H × 3), 7.55 (3H, t, *J* 9.8, 5′-H × 3), 7.80 (3H, t, *J* 9.8, 6′-H × 3), 7.83 (3H, s, 2-,4-,6-H), 8.61 (3H, s, 2′-H × 3), 8.83 (3H, d, *J* 9.8, 8′-H × 3), 9.71 (3H, d, *J* 9.8, 4′-H × 3); δ_C ($CDCl_3$) 51.2 (CH_3 × 3)), 115.8 (3C, 3′-C × 3), 127.3 (3C, 7′-C × 3), 127.9 (3C, 5′-C × 3), 129.5 (3C, 2-,4-,6-C), 130.3 (3C, 1′-C × 3), 137.0 (3C, 8′-C × 3), 137.5 (3C, 1-,3-,5-C), 138.3 (3C, 4′-C × 3), 139.9 (3C, 6′-C × 3), 140.1 (3C, 8′a-C × 3), 140.2 (3C, 2′-C × 3), 141.7 (3C, 3′a-C × 3), 165.7 (3C, C=O × 3); *m/z* (%) 630 (M^+, 6), 307 (28), 154 (100), 136 (65), 107 (19); (Found: *m/z* M, 630.2014, C, 80.24; H 4.87. $C_{42}H_{30}O_6$ requires M, 630.2042. C, 79.98; H, 4.79%).

(b) Treatment with hydrogen chloride: Hydrogen chloride gas was passed for 2 h into a solution of **5d** (455 mg, 0.25 mmol) in chloroform (5 ml) in the presence of triethyl orthoformate (360 mg, 2.4 mmol). The reaction mixture was worked up, as described above, to give the trimer **6** (159 mg, 38%) and the starting material **5d** (145 mg, 35%).

Preparation of 1,3,5-Tris(1-azulenyl)benzene (**4**): A mixture of **6** (65 mg, 0.1 mmol) and 100% phosphoric acid (9 ml) was stirred for 30 min at 90°C. The mixture was diluted with water and extracted with chloroform. The evaporation residue was chromatographed on a column (Merck silica gel 60, 15 g) with chloroform to afford, 1,3,5-tri(1-azulenyl)benzene (**4**) (44 mg, 93%).

4: Deep greenish blue prisms (from benzene-hexane), m.p. 243–244 °C; λ_{max} (log ε) ($CHCl_3$) 375 (4.44), 602 (3.00), 637 (2.93), 723 nm (2.40); δ_H ($CDCl_3$), 7.13 (3H, t, *J* 9.8, 7′-H × 3), 7.14 (3H, t, *J* 9.8, 5′-H × 3), 7.48 (3H, d, *J* 3.6, 3′-H × 3), 7.57 (3H, t, *J* 9.8, 6′-H × 3), 7.87 (3H, s, 2-,4-,6-H), 8.16 (3H, d, *J* 3.6, 2′-H × 3), 8.36 (3H, d, *J* 9.8, 4′-H × 3), 8.76 (3H, d, *J* 9.8, 8′-H × 3); δ_C ($CDCl_3$) 117.5 (3C, 3′-C × 3), 123.1 (3C, 5′-C × 3), 123.5 (3C, 7′-C × 3), 129.1 (3C, 2-,4-,6-C), 131.4 (3C, 1′-C × 3), 135.4 (3C, 8′a-C × 3), 135.9 (3C, 8′-C × 3), 137.3 (3C, 4′-C × 3), 137.4 (3C, 2′-C × 3), 138.2 (3C, 6′-C × 3), 138.3 (3C, 1-,3-,5-H), 141.8 (3C, 3′a-C × 3); *m/z* (%) 456 (M^+, 100), 326 (14), 228 (29); (Found: M, 456.1885. C, 94.80; H, 5.20. $C_{36}H_{30}O_6$ requires M, 456.1878. C, 94.70; H, 5.30%).

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Paper 00/243

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