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SYNTHESIS AND PROPERTIES OF AZULENO[2,1-a]-3,8-METHANO[10]ANNULENE AND ITS 2-METHYL DERIVATIVE

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Key Words: peripheral conjugation, azulene, diatropicity.

Summary: The cata-condensed system of azulene fused with 1,6-methano[10]annulenes was synthesized. The ^{1}H NMR spectra revealed the existence of diatropicity as 18-pi electron periphery.

Although the contribution of the peripheral 18-pi electron conjugation in azuleno-azulenes has not been reported,1) the MIND/3 calculation of the new cata-condensed system of 1,6-methano[10]annulene fused with azulene 1,2) a system similar to that with azuleno-azulenes, suggests the contribution to some extent of a peripheral conjugation (Fig. 1). Furthermore, in this system, the tropicity could be estimated more precisely than that of the azuleno-azulenes;1) also, the difference in the degree of aromaticity between 1,6-methano[10]annulene and azulene (calculated REs are -17.5 and -12.8 Kcal/mol, respectively)3) could be directly known by ^{1}H NMR spectroscopy. Now we describe here the synthesis and properties of azuleno[1,2-b]-3,8-methano[10]annulene 1 and its 2-methyl derivative 2 as a new cata-condensed peripheral 18-pi electron diatropic system containing an azulene nucleus.

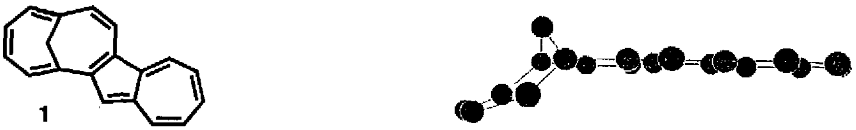
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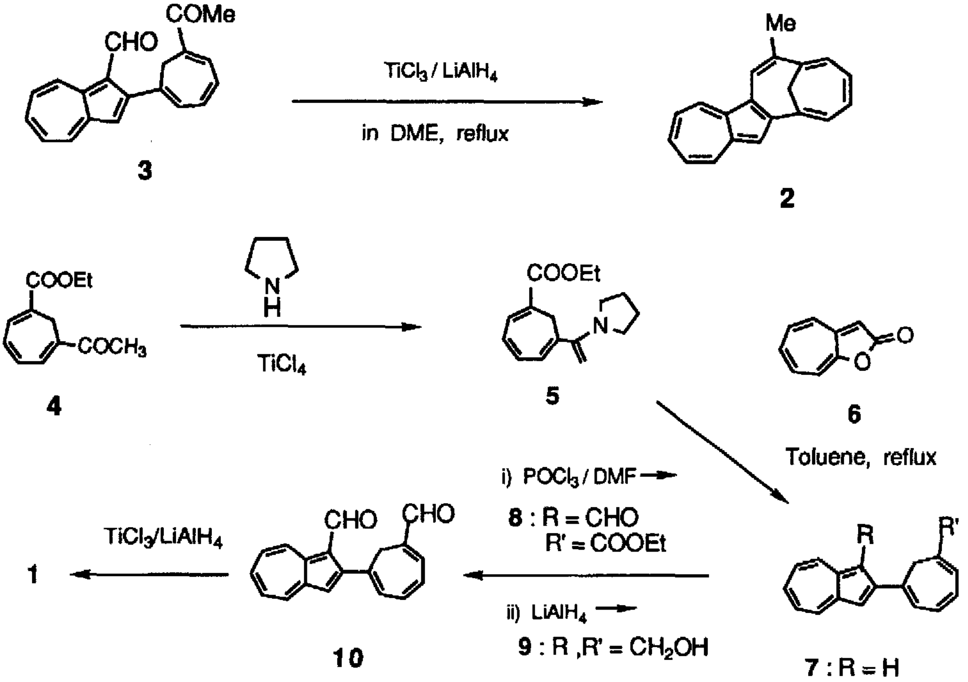
Fig. 1. 1 and side view of its calculated molecular structure.

First, the intramolecular reductive coupling of 2-(6-acetylcyclohepta-1,3,5-triene-1-yl)-1-formylazulene 34) with low valent titanium (Ti^0) prepared from TiCl$_3$ and LiAlH$_4$ in refluxing dry dimethoxyethane (DME) for 8 h gave 2-methyl azuleno[2,1-a]-3,8-methano[10]annulene 2 in ca. 3-5% yield (Scheme 1). In order to know the ^{1}H-^{1}H coupling constant between 1-

and 2-position, the parent compound was synthesized by the following procedures. The reaction of ethyl 6-acetyl-1,3,5-cycloheptatriene-1-carboxylate **4**[5)] chosen as a suitable starting material with pyrrolidine in the presence of titanium tetrachloride ($TiCl_4$) gave enamine **5**.



Scheme 1

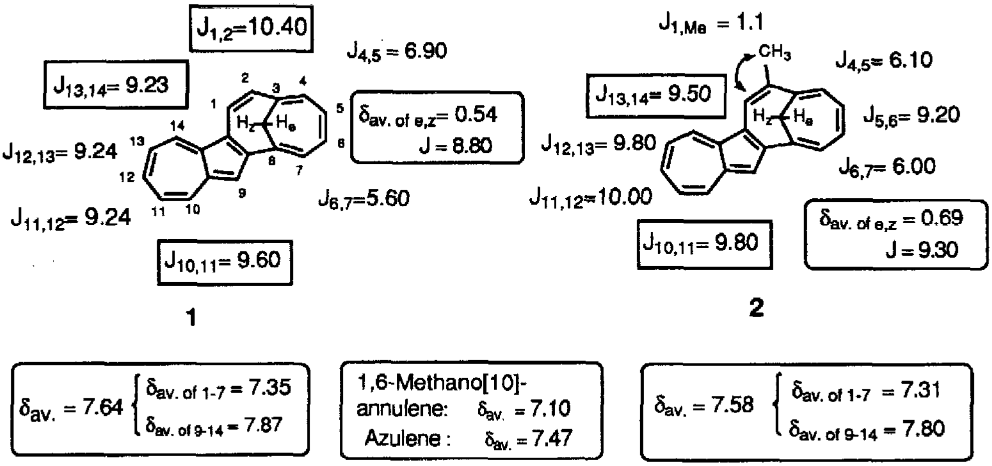
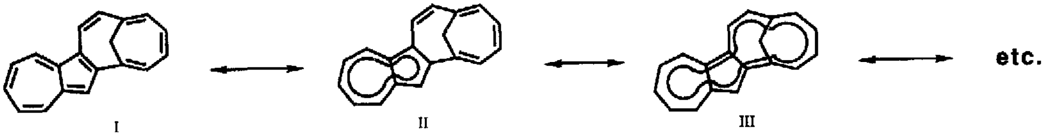


Fig. 2. The ^1H - ^1H coupling constants (J in Hz) and the averages of the ^1H-chemical shifts ($\delta_{av.}$ in ppm) of **1**, **2** and reference compounds

The reaction of 2H-cyclohept[b]furan-2-one **6** with the enamine **5** in refluxing dry toluene for 3.5 h gave azulene derivative **7** in 76% yield. Formylation of **7** by Vilsmeier procedure gave 1-formyl-2-[(6-ethoxycarbony)cyclohept-1,3,5-trien-1-yl]azulene **8** in 86% yield. The reduction of **8** with $LiAlH_4$ in dry ether at r. t. for 1 h gave diol **9** in 87% yield. Oxidation of **9** with $BaMnO_4$ in refluxing CH_2Cl_2 for 5 h gave diformyl compound **10** in 67% yield. Intramolecular reductive coupling of **10** with low valent titanium (Ti^0) gave the desired azuleno-bridged[10]annulene **1** in ca. 5-10% yield. All the spectral data are consistent with the assigned structures of **1** and **2**, respectively.[6] As shown in Fig. 2, the ^1H NMR resonances for ring protons of **1** and **2** are observed at lower field than those corresponding to azulene[7] and 1,6-methano[10]annulene[8], respectively, indicating the greater diatropicity of **1** and **2** than the latter. The high field shifts of ring protons and the low field shifts and large coupling constant of methylene protons of **1** compared to those of **2** indicate that the methyl substitution on 2-position slightly decreases the tropicity raised from peripheral conjugation by distortion of planearity of bridged[10]annulene moiety due to the steric repulsion between the methyl group and proton on 4-position. The difference in coupling constants between H-10-H-11 and H-13-H-14 of both **1** ($\Delta J=0.37Hz$) and **2** ($\Delta J=0.30Hz$) is much smaller than those of corresponding protons to the azulene moiety on azulen[2,1-a]azulene [$\Delta J_{(8,9)-(11,12)}=1.20Hz$][1] and benz[a]azulene **11** ($\Delta J_{(6,7)-(11,12)}=2.90Hz$)[9], indicating less bond alternation in the azulene moiety of **1** and **2** than in the others. The ^1H-^1H coupling constants of H-1 and H-2 on bridged annulene moiety of **1** is smaller than those of corresponding protons to 2,3-benzo-1,6-methano[10]annulene **12** ($J_{1,2}=11.05Hz$)[10], indicating less localization of the double bond on C-1,2 of **1** than that of **12**. The ^1H NMR resonances for ring protons of [10]annulene moiety and those of the bridged methylene protons of **1** and **2** are observed at lower field and higher field, respectively, than those of **12**. This evidence indicates that the contribution of both resonance forms II and III is predominant in **1** and **2** (Scheme 2). It interestingly shows that the degree of the diatropicity of azulene is larger than that of 1,6-methano[10]annulene contrary to the evaluated resonance energy.[3] The ^{13}C NMR spectra of **2** also showed similar results, namely, that the average chemical shift of peripheral ring carbons and that of bridged carbon [**1**: δ 135.9 & 37.1 ppm; **2**: δ 128.6 & 36.5 ppm] is in good agreement with the calculated values [δ 130.1 & 35.6 ppm] for a peripheral conjugation system according to Hunadi's method[11]. The above interpretation is consistent with the calculated molecular structure (Fig. 1), comprising the planar azulene extended to C-1, C-2, and C-8 and distorted bridged [10]annulene with a dihedral angle of about 130° at C-3 and C-8 similar to that of 1,6-methano[10]annulene.[12)]



Scheme 2

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6) Physical properties of the new compounds

1: green needles, mp 132.5-133 °C (methanol); IR(KBr) 3020w, 1578m, 798m, 729vs cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$, TMS) δ =8.75 (d, J=9.23Hz, 1H, H-14), 8.38 (d, J=9.60Hz, 1H, H-10), 7.92 (s, 1H, H-9), 7.76 (d, J=10.40Hz, 1H, H-1), 7.60 (t, J=9.24Hz, 1H, H-12), 7.47 (d, J=5.60Hz, 1H, H-7), 7.35 (dd, J=9.23 & 9.24Hz, 1H, H-13), 7.29 (d, J=10.40Hz, 1H, H-2), 7.26 (m, 2H, H-5 & -6), 7.20 (dd, J=9.24 & 9.60 Hz, 1H, H-11), 7.03 (d, J=6.90Hz, 1H, H-4), 1.25 (d, J=8.76Hz, 1H, H-z), -0.17 (d, J=8.76Hz, 1H, H-e); ^{13}C NMR($CDCl_3$) δ=150.5, 141.3, 140.9, 137.6, 137.2, 132.4, 128.9, 128.7, 127.1, 126.3, 126.2, 125.4, 125.3, 124.9, 124.6, 121.0, 117.3, 115.3, 112.9; UV/VIS(CH_2Cl_2): λ_{max} 208 (log ε =4.09), 337 (4.44), 390sh(3.56), 413sh(3.51), 640(2.35), 695sh(2.29), 792sh(2.00), 892nm(1.94); MS(70 eV): m/z 242 (M^+, 100%), HRMS M. Found: 242.1093, Calcd for $C_{19}H_{14}$: 242.1110.

2: deep green needle, mp 145-146 °C(hexane); IR (KBr) 3020w, 1579m, 803m, 728s cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$, TMS) δ =8.71 (d, J=9.5Hz, 1H, H-14), 8.32 (d, J=9.8Hz, 1H, H-10), 7.84 (s, 1H, H-9), 7.55 (bs, 1H, H-1), 7.55 (dd, J=9.8 & 10.0Hz, 1H, H-12), 7.37 (d, J=6.0Hz, 1H, H-7), 7.29 (dd, J=6.1 & 9.2Hz, 1H, H-5 or H-6), 7.26 (dd, J= 9.5 &9.8Hz, 1H, H-13), 7.23 (dd, J=6.0 & 9.2Hz, 1H, H-6 or H-5), 7.14(dd, J=9.8 & 10.0Hz, 1H, H-11), 7.10 (d, J=6.1Hz, 1H, H-4), 2.69 (d, J=1.1Hz, 3H, Me), 1.51 (d, J=9.30Hz, 1H, H-z), -0.12 (d, J=9.3Hz, 1H, H-e); ^{13}C NMR($CDCl_3$) δ =148.2, 139.3, 139.0, 136.0, 135.7, 133.6, 130.6, 127.9, 127.6, 125.8, 124.0, 123.2, 121.1, 118.6, 118.3, 113.8, 36.5, 21.0; UV/VIS(CH_2Cl_2): λ_{max} 204(log ε =3.19), 229(3.38), 417sh(2,95), 658(1.59), 715sh(1.41), 900nm(0.46); MS(70 eV) m/z 256 (M^+, 100%); HRMS M, Found: 256.1196. Calcd for $C_{20}H_{16}$: 256.1249.

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