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Synthesis and Properties of Azuleno[1,2-*a*]acenaphthylene and Dimethyl acenaphthyleno[1,2-*d*]heptalene-8,9-dicarboxylate

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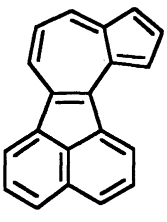
The parent compound of azuleno[1,2-*a*]acenaphthylene (**8**) was synthesized, and its ^{1}H NMR spectrum suggests no bond alternation in the azulene moiety. The cycloaddition of **8** with dimethyl acetylenedicarboxylate gave an acenaphthyleno[1,2-*d*]heptalene derivative.

Although the synthesis of azulenes fused with acenaphthylene such as azuleno[4,5-*a*]acenaphthylene (**1**) and azuleno[1,2-*a*]acenaphthylene derivative (**2**) was reported two decades ago,1) the detailed discussion on the aromaticity from a viewpoint of bond alternation has not been made so far. Azuleno[1,2-*a*]acenaphtylene is considered to consist formally of two parts, that is, either azulene and naphthalene moieties or acenaphtylene and heptafulvene moieties, and the calculation of DEPE (Delocalization Energy per Pi-electron) for each parts; azulene (0.023), naphthalene (0.055), acenaphthylene (0.039), and heptafulvene (-0.002),2) predicted the greater contribution of the former pair. Now, we describe here the synthesis and properties of azuleno[1,2-*a*]acenaphthylene **8** and its 3,4-dimethoxycarbonyl derivative (**9**) in order to discuss the aromaticity of them from the above viewpoint. Further, another condensed system of dimethyl acenaphthyleno-[1,2-*d*]heptalene-8,9-dicarboxylate (**12**), a valuable reference compound to **8** and **9**, was prepared by the reaction of **8** with dimethyl acetylenedicarboxylate in one step.



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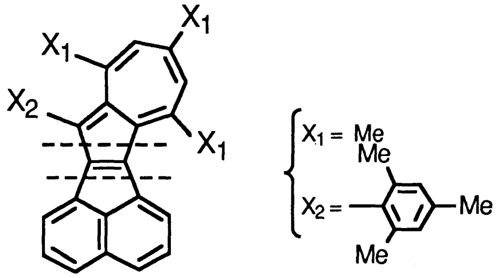

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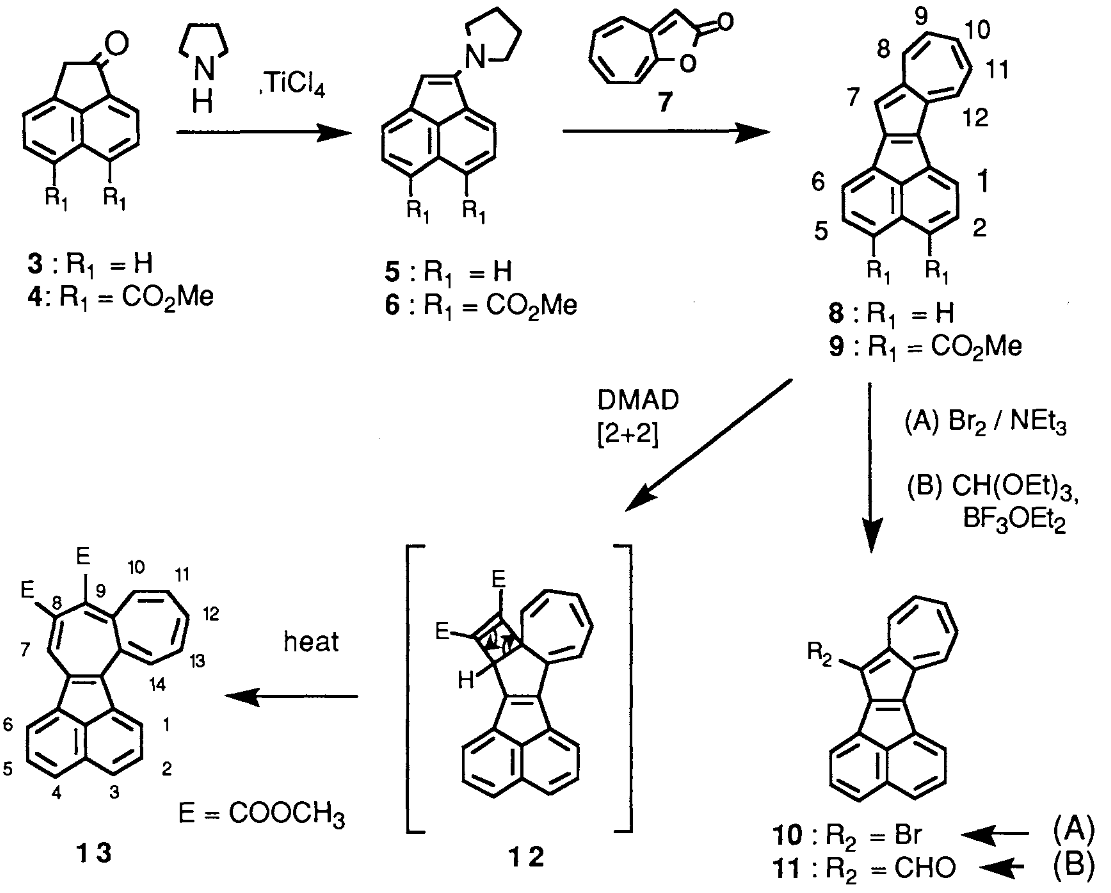
The reaction of pyrrolidine enamine (**5**), derived from acenaphthen-1-one (**3**), with 2*H*-cyclohepta-[*b*]furan-2-one (**7**)4) in refluxing dry toluene for 4 h gave **8**10) in 34% yield. All spectral data are consistent with the assigned structure of **8**. The ^{1}H NMR signals for ring protons of **8** were observed in the aromatic region of δ 7.15-8.57 ppm. The signals at δ 8.57 and δ 8.19 were assigned for H-12 and H-8 protons, having coupling constants with neighboring protons, $J_{H11\text{-}H12}$ = 9.82 Hz and $J_{H8\text{-}H9}$ = 9.21 Hz, respectively, and

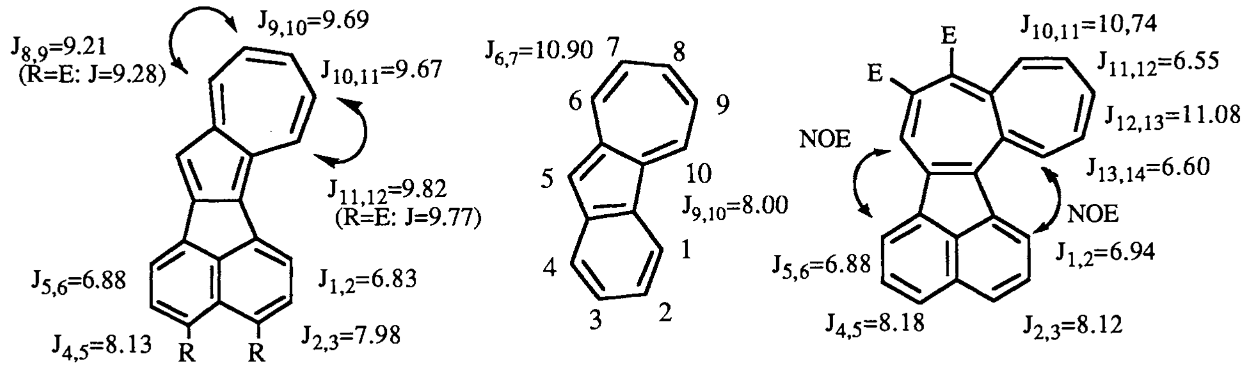


Scheme 1.

the other signals were also assigned by the ^{1}H-^{1}H decoupling and 2D method (COSY) as shown in references. To confirm the assignment of the ring protons on naphthalene ring, and with an expectation to be a potential synthetic starting material for more condensed systems, 3,4-dimethoxycarbonyl derivative **9** was synthesized in the similar manner in 58% yield by using dimethyl 1-pyrrolidylacenaphtylene-5,6-dicarboxylate (**6**) obtained from **4**.[5] The differences in coupling constants between $J_{H8\text{-}H9}$ and $J_{H11\text{-}H12}$ in both **8** and **9** (ΔJ = 0.61Hz, and 0.49Hz, respectively) are very small compared with that of benz[*a*]azulene (**14**) ($\Delta J_{(H6\text{-}H7)\text{-}(H9\text{-}H10)}$ = 2.90Hz) in which bond alternation clearly exists.[6] Furthermore, the ^{1}H-chemical shifts of azulene moiety and naphthalene moiety are very close to those corresponding to parent azulene and naphthalene, respectively.[7] These observations indicate no contribution of 20π electron diatropicy of **8** and **9**, but these molecules are regarded as a composite of two 10π electron systems, that is, of mainly azulene and naphthalene moieties rather than that of acenaphthylene and heptafulvene moieties. Since the degree of the contribution of acenaphthylene moiety to the condensed system is too small to be detected, these results suggest the greater aromaticity of the pair of azulene and naphthalene than that of acenaphthylene and heptafulvene as indicated by the DEPE calculation. And also the longer absorption maxima of **8** and **9** in UV-vis spectra than that of **2** indicate the planar form of these compounds.

The reaction of **8** with bromine in CH_2Cl_2 at r. t. for 30 min gave 10-bromo derivative (**10**) in 87% yield. Also the reaction of **8** with ethyl orthoformate in the presence of $BF_3\cdot OEt_2$[8] gave 10-formyl derivative (**11**) in 60% yield. These regioselective reactions suggest the stability of azulenium ion formed as an intermediate.

The reaction of **8** with DMAD in refluxing xylene for 5 h gave **13** in 13% yield. The structure of **13** was



8 and **9** **14** **13**

Fig. 1. ^{1}H NMR coupling constants of **8** , **9**, **13**, and **14** in Hz.

assigned by the spectral data, especially based on the NMR spectra; the ^{1}H-^{1}H cosy revealed the relationship of all the ring protons and the NOE between the protons at 6- and 7-positions and 1- and 14-positions, respectively, and ^{13}C NMR spectrum showed none of methine carbons in the region of alkyl carbons in the range of 0 to 60 ppm. This compound is the first example that heptalene is condensed with acenaphthylene. The heptalene derivative **13** is considered to be formed through cycloaddition of DMAD with **8** at its 7 and 7a positions and following ring opening of the [2+2] cycloadduct (**12**).[9] The large difference in coupling between $J_{\mathrm{H}12\text{-}\mathrm{H}11}=6.60$ Hz, and $J_{\mathrm{H}8\text{-}\mathrm{H}9}=10.86$ Hz and no bond shift in the heptalene skeleton of **13** observed even at decaline refluxing indicate the clear bond alternation and the localization of double bond at 1-position of acenaphtylene, which might be a consequence of the aromatic stability of acenaphthylene moiety over non-aromatic heptalene [9] contrary to the above case of azulene vs. acenaphtylene.

We are grateful to YKK Co., Ltd. for measuring the ^{1}H NMR spectra of compounds **10** and **11**.

References

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3) The enamines were obtained by the reaction of **3** and **4** with pyrrolidine and $TiCl_4$ in dry benzene in 70% and 65% yields, respectively.

4) P.- W. Yang, M. Yasunami, and K. Takase, *Tetrahedron Lett.*, **1971**, 4275; M. Yasunami, T. Hioki, Y. Kitamori, I. Kikuchi, and K. Takase, *Bull. Chem. Soc. Jpn.*, **66**, 2273 (1993) and references cited therein.

5) The ketone **4** was prepared as follows: the oxidation of 5,6-dicarbomethoxy acenaphthene with Pb_3O_4 in AcOH at 90 °C for 5 h gave 1-acenaphthyl acetate in 76% yield, and followed by basic hydrolysis gave alcohol in 89% yield. Finally the oxidation of the alcohol with PCC gave ketone **4** in 79% yield.

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9) K. Hafner, H. Diehl, and H. U. Süss, *Angew. Chem., Intern. Ed. Engl.*, **15**, 104 (1976). The fast π-bond shift of heptalene (Ea=14.7 kJ/mol) is observed by E. Vogel, H. Königshofen, J. Wassen, K.

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Physical properties of new compounds.

10) **8**: Green needles, mp 155-156 °C; IR (KBr) 3040w, 1609w, 1563m, 1393m, 830s, 772s, 736m, 716s cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.57 (d, *J*=9.82Hz, H-12), 8.19 (d, *J*=9.21Hz, H-8), 7.95 (d, *J*=6.88Hz, H-6), 7.91 (d, *J*=6.83Hz, H-1), 7.80 (d, *J*=8.13Hz, H-4), 7.66 (d, *J*=7.98Hz, H-3), 7.60 (dd, *J*=7.02, 8.12Hz, H-5), 7.59 (dd, *J*=6.95, 7,97Hz, H-2), 7.52 (s, H-7), 7.46 (t, *J*=9.69Hz, H-10), 7.15 (t, *J*=9.67Hz, H-11), 7.11 (t, *J*=9.27Hz, H-9); ^{13}C NMR ($CDCl_3$) δ 153.8, 148.8, 136.5, 136.4, 134.8, 133.9, 133.6, 132.7, 130.9, 130.5, 128.3, 127.9, 127.5, 124.5, 124.1, 123.9, 122.2, 118.9, 110.0; UV-vis (CH_2Cl_2) λmax 229.6 (logε=4.41), 288.0 (4.33), 310.2 (4.44), 340.4 (4.66), 353.0 (4.62), 404.4 (3.92), 426.8 (3.76), 454.0 (3.26), 625.4 (2.29), 674.6 (2.78), 739.8 nm (2.41); MS *m/z* 252 (M$^+$, 100%). HRMS M. Found: 252.0493. Calcd for $C_{20}H_{12}$: 252.0498.

9: Green needles, mp 247-248 °C; IR (KBr) 3040w, 1720vs, 1492m, 1295s, 1270s, 1200s, 1122m, 800m, 758m, 720m cm^{-1}; ^{1}H NMR (400MHz, $CDCl_3$) δ 8.43 (d, *J*=9.77Hz, H-12), 8.15 (d, *J*=9.28 Hz, H-8), 8.01 (d, *J*=7.32Hz, H-5), 7.98 (d, *J*=7.33Hz, H-2), 7,82 (d, *J*=7.32Hz, H-6), 7.74 (d, *J*= 7.33Hz, H-1), 7.46 (t, *J*=9.77Hz, H-10), 7.43 (s, H-7), 7.14 (t, *J*=9.77Hz, H-11), 7.12 (t, *J*=9.52 Hz H-9), 3.93 (s, 2X-Me); UV-vis (CH_2Cl_2) λmax 227.2 (logε=4.46), 260.4 (4.37), 343.0,(4.69), 423.8 (3.92), 451.4 (3.94), 479.4 (3.66), 627 (2.97), 676.0 (3.00), 737.4nm (2.67); MS *m/z* 368 (M$^+$, 100%), HRMS M. Found: 368.1044. Calcd for $C_{24}H_{16}O_4$: 368.1046.

10: Green needles, mp 178-179.5 °C; IR (KBr) 3050w, 1570w, 1410w, 800m, 770s, 738s, 712s cm^{-1}; ^{1}H NMR (600MHz, $CDCl_3$) δ 8.51 (d, *J*=9.78Hz, H-12), 8.24 (d, *J*=6.92Hz, H-6), 8.23 (dd, *J*=10.01 & 0.75Hz, H-8), 7.91 (d, *J*=6.86Hz, H-1 or H-3), 7.85 (d, *J*=8.14Hz, H-4), 7.69 (d, *J*=8.17 Hz, H-3 or H-1), 7.65 (dd, *J*=8.14, 6.92 Hz, H-5), 7.60 (dd, *J*=8.17, 6.86Hz, H-2), 7.50 (t, *J*=9.78 Hz, H-10), 7.20 (dd, *J*=10.01, 9.78Hz, H-9), 7.16 (d, *J*=9.78Hz, H-11); UV-vis (CH_2Cl_2) λmax 236.8 (logε=4.39), 342.4 (4.60), 427.8 (3.77), 455.4 (3.30), 643.0 (2.81), 695.6nm (2.82); HRMS M. Found: 332.0024, 330.0049. Calcd for $C_{20}H_{11}Br$: 332.0024, 332.0044.

11: Green needles, mp 179-179.5 °C; IR(KBr) 3040w, 1600vs, 1420m, 1290m, 1080m, 830s, 770s, 752s cm^{-1};^{1}H NMR (400MHz, DMSO) δ 10.85 (s, -CHO), 9.35 (d, *J*=10.27Hz, H-8), 9.10 (d, *J*= 9.27Hz, H-12), 8.74 (d, *J*=7.08Hz, H-6), 8.37 (d, *J*=7.08Hz, H-1), 8.11 (d, *J*=8.05Hz, H-4), 7.97 (t, *J*=9.76Hz, H-10), 7.94 (d, *J*=8.06Hz, H-3), 7.82 (dd, *J*=8.05, 7.08Hz, H-5), 7.75 (dd, *J*=8.06, 7.08Hz, H-2), 7.73 (dd, *J*=10.26 & 9.76Hz, H-11), 7.70 (dd, *J*=9.76, 9.27Hz, H-9); UV-vis (CH_2Cl_2) λmax 239.0 (logε=4.51), 269.0 (4.31), 352.0 (4.68), 376.0 (4.74), 418.2 (3.95), 582.8 (2.74), 623.8 (2.72), 776.4 (2.01), 832.8 (2.03), 866.4 (1.64), 878.0 nm (1.31); HRMS M. Found: 280.0881. Calcd for $C_{21}H_{12}O$: 280.0886.

13: Red needles, mp 217-218 °C; IR (KBr) 3030w, 1720s, 1580m, 1430s, 1240m, 1120m, 768s, 720m cm^{-1}, ^{1}H NMR (600MHz, $CDCl_3$) δ 8.19 (bs, H-7), 7.91 (d, *J*=8.12Hz, H-3) 7,90 (d, *J*=8.18, H-4), 7.83 (d, *J*=6.88Hz, H-6), 7.75 (d, *J*=6.94Hz, H-1), 7.64 (dd, *J*=8.18 & 6.88Hz, H-5), 7.57 (dd, *J*=8.12, 6.94Hz, H-2), 6.62 (dd, *J*=11.08, 6.60Hz, H-13), 6.53 (dd, *J*=11.08, 6.55, H-12), 6.34 (dd, *J*=10.74 ,6.55Hz, H-11), 6.21 (d, *J*=6.60Hz, H-14), 5.86 (d, *J*=10.74Hz, H-10), 3.81 (s, -Me), 3.68 (s, -Me); UV-vis (CH_2Cl_2) λmax 211.6 (logε=4.26), 228.0 (4.48), 335.8 (4.31), 514.6nm (3.06); MS m/z 394 (M$^+$, 100%), HRMS M. Found: 394.1206. Calcd for $C_{26}H_{18}O_4$: 394.1205.

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