SYNTHESIS, VALENCE ISOMERIZATION, AND CHEMICAL PROPERTIES OF 13-AZAAZULENO[1,2-*g*]BICYCLO[4.3.1]DECA-5b,6,8,10-TETRAENE

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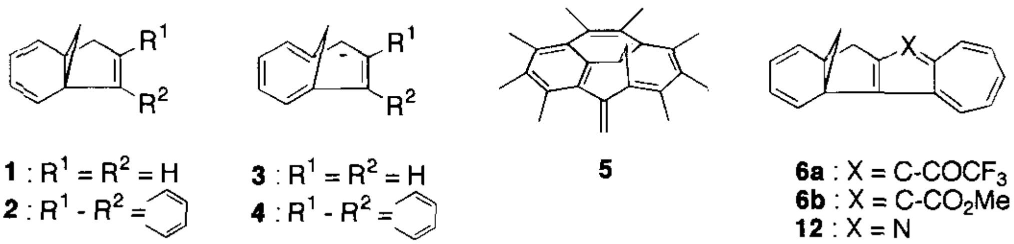
Abstract--1-Azaazulene-annulated tricyclo[4.3.1.0^{1,6}]deca-2,4,7-triene ring system was synthesized, and ^{1}H- and ^{13}C-NMR spectroscopy suggested that the compound exists in equilibrium between major amount of 13-azaazuleno[1,2-*g*]bicyclo[4.3.1]deca-5b,6,8,10-tetraene and minor amount of 13-azaazuleno[1,2-*g*]tricyclo[4.3.1.0^{1,6}]deca-5b,7,9-triene.

Cycloheptatriene (CHT)-norcaradiene (NCD) tautomerism has received much attention from the theoretical and synthetic points of view. Several structural factors have been found to transform a CHT form to a NCD form.[1] These factors can be classified into four categories: (i) the placement of π-accepting substituent(s) such as a cyano group at the C7-position;[2] (ii) the extension of conjugation at appropriate positions in the NCD form;[3] (iii) the nonbonding interaction between the C7-substituent and proximal π-bonds or substituents;[4] (iv) the forced shortening of the C1-C6 distance as in **1**[5,6] and **2**.[7] Although [6,5] close compounds (**1**) and (**2**) react with dimsyl anion in DMSO-d_6 to produce aromatic systems, (**3**)[5,6] and (**4**),[7] an example of a [6,5] open neutral structure has been found in the chemistry of fulleroid



1 : R^1 = R^2 = H
2 : R^1 - R^2 =

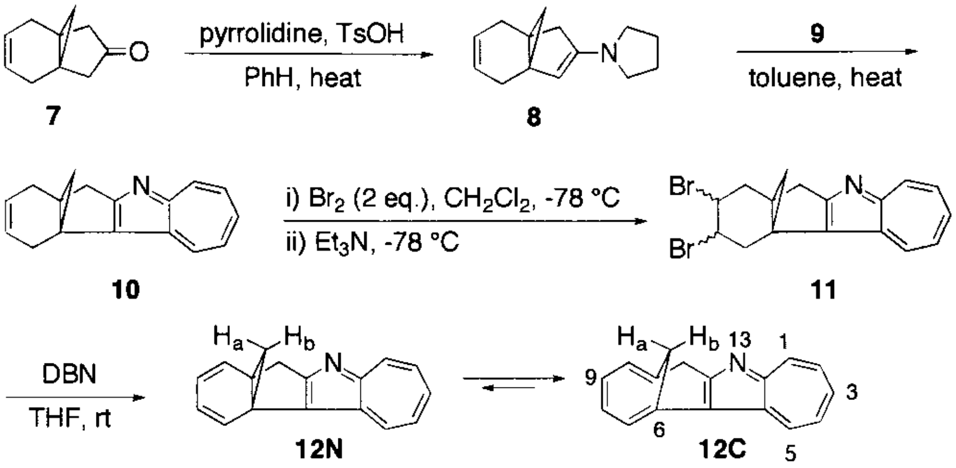
3 : R^1 = R^2 = H
4 : R^1 - R^2 =

5

6a : X = C-COCF$_3$
6b : X = C-CO$_2$Me
12 : X = N

Figure 1.

(**5**).[8] We have recently succeeded in the synthesis of 13-trifluoroacetyl- and 13-methoxycarbonylazuleno[1,2-*g*]tricyclo[4.3.1.0^{1,6}]deca-5b,7,9-trienes (**6a**,**b**), and the ^{13}C-NMR spectra revealed that the former exists in a NCD structure, while the latter is in equilibrium between a NCD and a CHT.[9] We report here the synthesis, spectroscopic and chemical properties of 1-azaazuleno-annulated tricyclo[4.3.1.0^{1,6}]deca-2,4,7-triene (**12**), which exists in equilibrium between major amount of 13-azaazuleno[1,2-*g*]bicyclo[4.3.1]deca-5b,6,8,10-tetraene (**12C**) and minor amount of 13-azaazuleno[1,2-*g*]tricyclo[4.3.1.0^{1,6}]deca-5b,7,9-triene (**12N**).



Scheme 1.

Compound (**12**) was prepared through the enamine method synthesizing the 1-azaazulene ring system, explored by our research group (Scheme 1).[10] Reaction of enamine (**8**), which was derived from ketone (**7**)[11] in a usual manner, with tropone oxime (**9**) (1.5 mol eq.) in toluene under reflux for 4 h gave **10** in 29% yield after purification by column chromatography (Al_2O_3, hexane).[12] Then, the bromination of **10** was performed by using bromine (2 mol eq.) in CH_2Cl_2 at -78 °C to give **11** in 31% yield.[12] Since compound (**11**) is unstable and it decomposes gradually, it was subsequently treated with excess DBN in THF at rt for 12 h to result in the formation of **12** in quantitative yield (Scheme 1).[12] The spectral data of compound (**12**) are appropriate for the structure: the ^{1}H- and ^{13}C-NMR spectra at 25 °C are assigned by using H-H and C-H COSY spectra.

The geminal coupling constant of the methylene protons at C14 for **12** (J=8.1 Hz) is larger than those for [6,5] close NCDs **1** (J=3.5 Hz),[13] **2** (J=3.6 Hz),[13] and **6a** (J=4.1 Hz).[13] The value is even larger than that of **6b** (J=5.9 Hz),[9] which exists in equilibrium between a NCD and a CHT, as well as [6,5] open compounds (**3**) (J=7.5 Hz)[13] and **4** (J=7.3 Hz).[13] Furthermore, the ^{13}C-NMR signals of C6 and C11 for compound (**12**) appear at δ=107.8 and δ=119.8, which are largely shifted to lower field as compared with those of compounds **1** (δ=40.1 and 48.1), **2** (δ=39.6 and 45.6),[13] and **6a** (δ=45.7 and 51.5).[9] The values are close to the corresponding values of [6,5] open anions (δ=113.7 for **3**; δ=101.3 and 119.2 for **4**).[13] Thus, ^{1}H- and ^{13}C-NMR spectra suggest that **12** exists mainly in the [6,5] open CHT isomer **12C**.

Table 1. Selected physical data of new compounds (**10**) and (**12**).

10: reddish viscous oil (picrate: mp 154-160 °C); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.61 (1H, d, J=4.3 Hz, H-14), 1.40 (1H, d, J=4.3 Hz, H-14), 2.46-3.14 (4H, m, H-7 and H-10), 3.19 (1H, d, J=19.0 Hz, H-13), 3.39 (1H, d, J=19.0 Hz, H-13), 5.64-5.66 (2H, m, H-8 and H-9), 7.42 (1H, dd, J=10.0 Hz, 9.4 Hz, H-2), 7.52 (1H, dd, J=10.0 Hz, 9.8 Hz, H-3), 7.64 (1H, dd, J=10.2 Hz, 9.8 Hz, H-4), 8.32 (1H, d, J=10.2 Hz, H-5), 8.37 (1H, d, J=9.4 Hz, H-1).

12: purple viscous oil (picrate: mp 145-150 °C); ^{1}H-NMR (400 MHz, CD_2Cl_2, at 25 °C) δ 0.96 (1H, d, J=8.1 Hz, H-14), 3.39 (1H, d, J=17.6 Hz, H_{endo}-12), 3.59 (1H, d, J=8.1 Hz, H-14), 4.17 (1H, d, J=17.6 Hz, H_{exo}-12), 6.41 (1H, d, J=5.9 Hz, H-7 or H-10), 6.53 (1H, d J=5.7 Hz, H-10 or H-7), 6.66 (1H, dd, J=8.8 Hz, 5.9 Hz, H-9 or H-8), 6.86 (1H, dd, J=8.8 Hz, 5.7 Hz, H-8 or H-9), 7.53 (1H, dd, J=10.1 Hz, 9.5 Hz, H-2), 7.58 (1H, d, J=10.3 Hz, 9.5 Hz, H-3), 7.75 (1H, d, J=10.3 Hz, 9.3 Hz, H-4), 8.37 (1H, d, J=9.3 Hz, H-5), 8.57 (1H, d, J=10.1 Hz, H-1); ^{13}C-NMR (100.6 MHz, CD_2Cl_2) δ 38.7 (C12), 44.3 (C14), 120.2 (C7 or C10), 121.0 (C10 or C7), 125.0 (C8 or C9), 127.6 (C9 or C8), 127.9 (C2), 128.8 (C3), 133.2 (C1), 135.3 (C5), 137.2 (C4), 107.8 and 119.8 (C-6 and C7), 130.8, 136.2, 158.5, and 184.8 (quart. C). ^{1}H-NMR (400 MHz, CD_2Cl_2, at -95 °C) δ 0.96 (1H, d, J=8.4 Hz, H-14), 3.39 (1H, d, J=17.6 Hz, H_{endo}-12), 3.78 (1H, d, J=8.4 Hz, H-14), 4.17 (1H, d, J=17.6 Hz, H_{exo}-12), 6.48 (1H, d, J=5.3 Hz, H-10 or H-7), 6.58 (1H, d, J=5.5 Hz, H-7 or H-10) , 6.75 (1H, dd, J=9.9 Hz, 5.3 Hz, H-9 or H-8), 6.97 (1H, dd, J=9.9 Hz, 5.5 Hz, H-8 or H-9), 7.66 (1H, dd, J=9.7 Hz, 9.1 Hz, H-2), 7.76 (1H, dd, J=10.1 Hz, 9.7 Hz, H-3), 7.86 (1H, dd, J=10.1 Hz, 9.7 Hz, H-4), 8.45 (1H, d, J=9.7 Hz, H-5), 8.65 (1H, d, J=9.1 Hz, H-1).

The ^{1}H- and ^{13}C-NMR spectral studies of compound (**12**) were conducted at the temperature ranging from 25 °C to -95 °C. The average chemical shift of the seven-membered ring moiety (δ_{av}=7.96) and four vinyl protons on the C7-8-9-10 (δ_{av}=6.62) at 25 °C are shifted to low-field of δ_{av}=8.08 and δ_{av}=6.70 at

-95 ℃, respectively. Noteworthy points are the geminal coupling constant (J=8.1 Hz) at C14 and vicinal coupling constant between H-8 and H-9 (J=8.8 Hz) and they became larger values of J=8.4 Hz and J=9.9 Hz, respectively. The other proton chemical shifts and vicinal coupling constants are also changed. In addition, ^{13}C-NMR chemical shifts of **12** are also changed at -95 ℃. A noteworthy point is the chemical shifts of C6 and C11 (δ=107.8 and 119.8) which shifted to lower field of δ=113.7 and 126.5. These features clearly indicate that compound (**12**) exists in two different structures, **12N** and **12C** at 25 ℃, and the equilibrium between them is further shifted to the side of **12C** at -95 ℃. Thus, the [6,5] open isomer (**12C**) seems to be more stable than the [6,5] close isomer (**12N**). Unfortunately, we could not conduct ^{13}C-NMR spectroscopy below -95 ℃ and compound (**12**) is unstable above 40 ℃ in solution, thus, further detailed dynamic behavior of **12C** and **12N** could not be clarified at this stage.

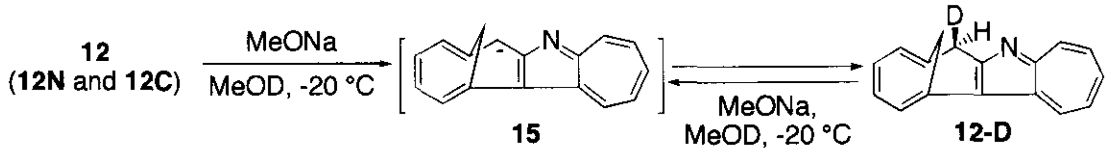
The unusual valence isomerization between **12N** and **12C**, which experiences the forced shortning of C6-C11 distance,[5-7] is rationalized on the basis of the interaction between the Walsh orbital of cyclopropane with the highest occupied molecular orbital (HOMO) or the lowest unoccupied molecular orbital (LUMO) of π system.[14] The polarized 1-azaazulene would donate π-electron to the cyclopropane ring as depicted in **13**, which represents the interaction between the LUMO of the Walsh orbital of cyclopropane and HOMO of 1-azaazulene (**14**). The calculated energy level and coefficients of HOMO for 1-azaazulene (**14**) are depicted in Figure 2.[15] Thus, the LUMO (cyclopropane)-HOMO (**12N**) interaction (overlapping of the lobes at C5b and C6) occurs effectively as to weaken the basal C6-C11 bond in **13** (**12N**), and the valence isomerization between isomer (**12N**) and isomer (**12C**) easily occurs. The isomer (**12C**) is stabilized by conjugation between cycloheptatriene and 1-azaazulene moieties as compared to **12N**. Although the energy level of HOMO (-8.49 eV) of 1-azaazulene (Figure 2.) is slightly lower than that (-8.33 eV) of 1-methoxycarbonylazulene involved in **6b**,[9] equilibrium between **12N** and **12C** is much shifted to the side of isomer (**12C**), as compared to that of **6b**.

13 (12N)

14

Figure 2.

The hydrogen-deuterium exchange reaction of compound (**12**) in MeOD-MeONa at -20 ℃ occurred stereospecifically to give **12-D**. The H_{exo}-12, which is assigned by using NOE effect, was completely exchanged. The exo selectivity (to the bridgemethylene) is in good accordance with the results obtained for **1** by Takahashi and co-workers,[16] as well as those for compounds (**6a**) and (**6b**).[9] Although the generation of the intermediate anion (**15**) is performed by treatment of **12** with dimsyl-d_5 sodium in DMSO-d_6, anion (**15**) seemed to be unstable and only decomposition of compound (**12**) was observed. Although compounds (**6a**) and (**6b**) underwent a Diels-Alder reaction with dimethyl acetylenesicarboxylate or 3,5-dihydro-4-phenyltriazolin-3,5-dione,[9b] the attempted reaction of **12** with 3,5-dihydro-4-phenyltriazolin-3,5-dione at 0 °C afforded only tarry materials and significant decomposition of **12** was observed.



Scheme 2.

Further studies including substituent effects on the valence isomerization are now underway.

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