

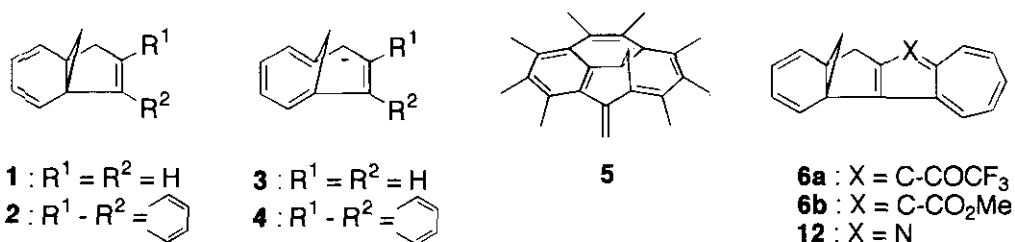
**SYNTHESIS, VALENCE ISOMERIZATION, AND CHEMICAL PROPERTIES OF 13-AZAAZULENO[1,2-*g*]BICYCLO[4.3.1]DECA-5b,6,8,10-TETRAENE**

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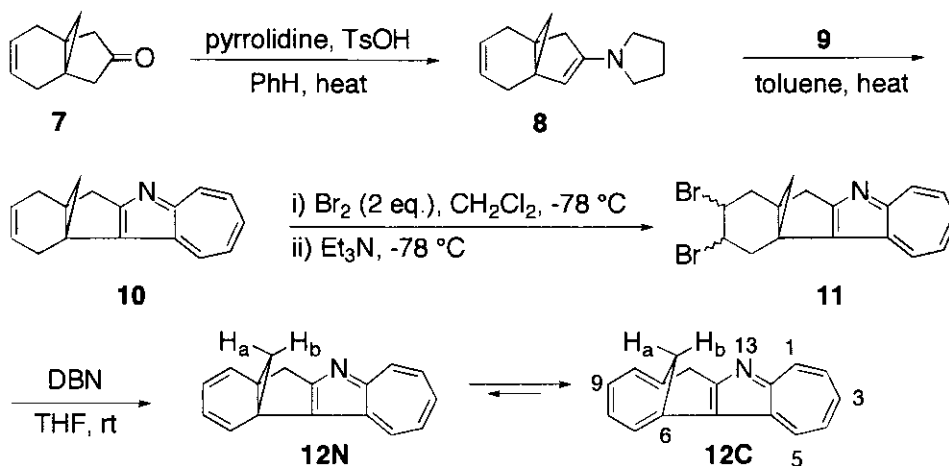
*Abstract*--1-Azaazulene-annulated tricyclo[4.3.1.0<sup>1,6</sup>]deca-2,4,7-triene ring system was synthesized, and <sup>1</sup>H- and <sup>13</sup>C-NMR spectroscopy suggested that the compound exists in equilibrium between major amount of 13-azaazuleno[1,2-*g*]bicyclo[4.3.1]deca-5b,6,8,10-tetraene and minor amount of 13-azaazuleno[1,2-*g*]tricyclo[4.3.1.0<sup>1,6</sup>]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.<sup>1</sup> These factors can be classified into four categories: (i) the placement of  $\pi$ -accepting substituent(s) such as a cyano group at the C7-position;<sup>2</sup> (ii) the extension of conjugation at appropriate positions in the NCD form;<sup>3</sup> (iii) the nonbonding interaction between the C7-substituent and proximal  $\pi$ -bonds or substituents;<sup>4</sup> (iv) the forced shortening of the C1-C6 distance as in **1**<sup>5,6</sup> and **2**.<sup>7</sup> Although [6,5] close compounds (**1**) and (**2**) react with dimsyl anion in DMSO-*d*<sub>6</sub> to produce aromatic systems, (**3**)<sup>5,6</sup> and (**4**),<sup>7</sup> an example of a [6,5] open neutral structure has been found in the chemistry of fulleroid



**Figure 1.**

(5).<sup>8</sup> We have recently succeeded in the synthesis of 13-trifluoroacetyl- and 13-methoxycarbonylazuleno[1,2-g]tricyclo[4.3.1.0<sup>1,6</sup>]deca-5b,7,9-trienes (**6a,b**), and the <sup>13</sup>C-NMR spectra revealed that the former exists in a NCD structure, while the latter is in equilibrium between a NCD and a CHT.<sup>9</sup> We report here the synthesis, spectroscopic and chemical properties of 1-azaazuleno-annulated tricyclo[4.3.1.0<sup>1,6</sup>]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<sup>1,6</sup>]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).<sup>10</sup> Reaction of enamine (**8**), which was derived from ketone (**7**)<sup>11</sup> 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<sub>2</sub>O<sub>3</sub>, hexane).<sup>12</sup> Then, the bromination of **10** was performed by using bromine (2 mol eq.) in CH<sub>2</sub>Cl<sub>2</sub> at -78 °C to give **11** in 31% yield.<sup>12</sup> 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).<sup>12</sup> The spectral data of compound (**12**) are appropriate for the structure: the <sup>1</sup>H- and <sup>13</sup>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),<sup>13</sup> **2** ( $J=3.6$  Hz),<sup>13</sup> and **6a** ( $J=4.1$  Hz).<sup>13</sup> The value is even larger than that of **6b** ( $J=5.9$  Hz),<sup>9</sup> which exists in equilibrium between a NCD and a CHT, as well as [6,5] open compounds (**3**) ( $J=7.5$  Hz)<sup>13</sup> and **4** ( $J=7.3$  Hz).<sup>13</sup> Furthermore, the <sup>13</sup>C-NMR signals of C6 and C11

for compound (**12**) appear at  $\delta=107.8$  and  $\delta=119.8$ , which are largely shifted to lower field as compared with those of compounds **1** ( $\delta=40.1$  and  $48.1$ ), **2** ( $\delta=39.6$  and  $45.6$ ),<sup>13</sup> and **6a** ( $\delta=45.7$  and  $51.5$ ).<sup>9</sup> The values are close to the corresponding values of [6,5] open anions ( $\delta=113.7$  for **3**;  $\delta=101.3$  and  $119.2$  for **4**).<sup>13</sup> Thus, <sup>1</sup>H- and <sup>13</sup>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); <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  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); <sup>1</sup>H-NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>, at 25 °C)  $\delta$  0.96 (1H, d, J=8.1 Hz, H-14), 3.39 (1H, d, J=17.6 Hz, H<sub>endo</sub>-12), 3.59 (1H, d, J=8.1 Hz, H-14), 4.17 (1H, d, J=17.6 Hz, H<sub>exo</sub>-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); <sup>13</sup>C-NMR (100.6 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  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). <sup>1</sup>H-NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>, at -95 °C)  $\delta$  0.96 (1H, d, J=8.4 Hz, H-14), 3.39 (1H, d, J=17.6 Hz, H<sub>endo</sub>-12), 3.78 (1H, d, J=8.4 Hz, H-14), 4.17 (1H, d, J=17.6 Hz, H<sub>exo</sub>-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 <sup>1</sup>H- and <sup>13</sup>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 ( $\delta_{av}=7.96$ ) and four vinyl protons on the C7-8-9-10 ( $\delta_{av}=6.62$ ) at 25 °C are shifted to low-field of  $\delta_{av}=8.08$  and  $\delta_{av}=6.70$  at

-95 °C, 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,  $^{13}\text{C}$ -NMR chemical shifts of **12** are also changed at -95 °C. A noteworthy point is the chemical shifts of C6 and C11 ( $\delta=107.8$  and  $119.8$ ) which shifted to lower field of  $\delta=113.7$  and  $126.5$ . These features clearly indicate that compound (**12**) exists in two different structures, **12N** and **12C** at 25 °C, and the equilibrium between them is further shifted to the side of **12C** at -95 °C. Thus, the [6,5] open isomer (**12C**) seems to be more stable than the [6,5] close isomer (**12N**). Unfortunately, we could not conduct  $^{13}\text{C}$ -NMR spectroscopy below -95 °C and compound (**12**) is unstable above 40 °C 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 shortening of C6-C11 distance,<sup>5-7</sup> 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  $\pi$  system.<sup>14</sup> The polarized 1-azaazulene would donate  $\pi$ -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.<sup>15</sup> 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

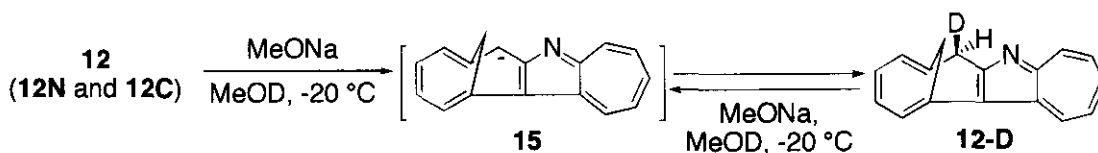


**Figure 2.**

(-8.33 eV) of 1-methoxycarbonylazulene involved in **6b**,<sup>9</sup> equilibrium between **12N** and **12C** is much shifted to the side of isomer (**12C**), as compared to that of **6b**.

The hydrogen-deuterium exchange reaction of compound (**12**) in MeOD-MeONa at -20 °C occurred stereospecifically to give **12-D**. The  $\text{H}_{\text{exo-12}}$ , 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,<sup>16</sup> as well as those for compounds (**6a**) and (**6b**).<sup>9</sup> Although the generation of the intermediate anion (**15**) is performed by treatment of **12** with dimethyl-*d*<sub>5</sub> sodium in DMSO-*d*<sub>6</sub>, 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 acetylenedicarboxylate or 3,5-dihydro-4-phenyltriazolin-3,5-dione,<sup>9b</sup> 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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