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Synthesis and Spectroscopic Properties of Azuleno[1,2-*g*]tricyclo[4.3.1.0^{1,6}]deca-5b,7,9-triene Derivatives. A Novel Cycloheptatriene Structure Bearing a Three Carbon Bridge at the C1-C6 Position

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Abstract: 13-Trifluoroacetyl- and 13-methoxycarbonylazuleno[1,2-*g*]tricyclo[4.3.1.0^{1,6}]deca-5b,7,9-trienes were synthesized, and the ^{13}C NMR spectra revealed that the former exists in a norcaradiene structure, while the latter is in equilibrium between norcaradiene and cycloheptatriene. © 1997 Elsevier Science Ltd.

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] **2**,[6,7] and **3**.[8] Regarding [6,5] close compounds **2** and **3**, they react with sodium methylsulfinyl anion in DMSO to produce aromatic systems, **4**[6,7] and **5**.[8] The incorporation of a negative charge into **2** and **3** favors the [6,5] open structures. Although the exomethylene-derivatives **6** and **7** have been shown to exist as [6,5] close isomers rather than [6,5] open nonafulvenes,[9] an example of a [6,5] open neutral structure has been found in the chemistry of fulleroid, **8**.[10] Since the theoretical calculations[11] and a large dipole moment[12] of azulene have been clearly reflected in the extremely stabilized carbocations substituted with azulene(s),[13] our interest was focused on the synthesis and structural characteristics of 13-trifluoroacetyl- and 13-methoxycarbonylazuleno[1,2-g]tricyclo[4.3.1.0^{1,6}]deca-5b,7,9-trienes **9** and **10**.

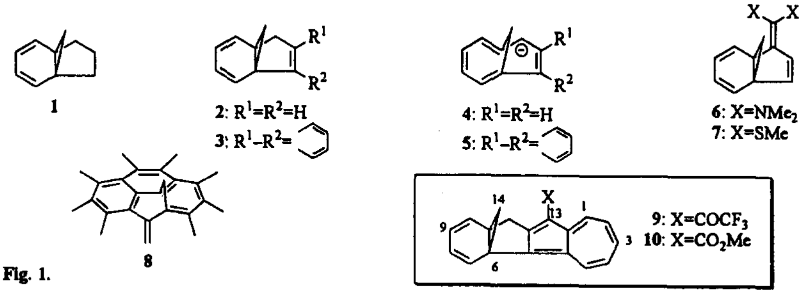
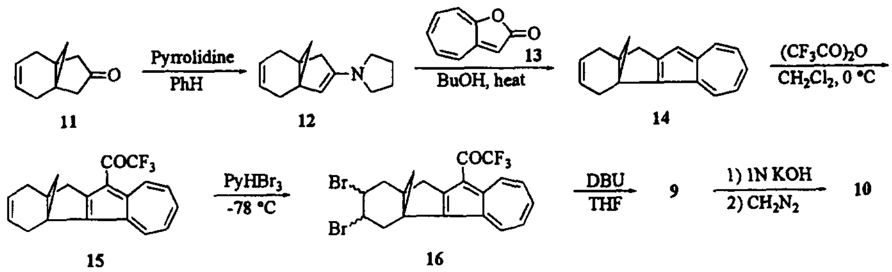


Fig. 1.

Synthesis of 13-trifluoroacetylazuleno[1,2-*g*]tricyclo[4.3.1.0^{1,6}]deca-5b,7,9-triene **9** was performed through the so-called enamine method synthesizing the azulene ring system, explored by Takase, Yasunami, and co-workers (Scheme 1).[14] Compound **12** derived from ketone **11**[15] in the usual manner reacted with 2 molar equivalents of 2*H*-cyclohepta[*b*]furan-2-one **13** in BuOH under reflux for 24 h to give **14** in 50% yield after purification by column chromatography (silica gel, hexane).[16] For protection against electrophilic attack to the azulene nucleus, **14** was converted to **15** (100%)[16] by treatment with $(CF_3CO)_2O$[15] at 0 °C for 30 min. Then, the bromination of **15** was performed by using pyridinium tribromide at -78 °C to give **16**[16] in 95% yield. Bisdehydrobromination of **16** with excess DBU in THF under reflux resulted in the formation of **9** in 33% yield.[16,17] Hydrolysis of the $-COCF_3$ group in **9** was carried out by using KOH in THF-MeOH-H_2O to give the carboxylic acid derivative, which was subsequently methylated with CH_2N_2 to give **10** in 84% yield.[16,17] The spectral data of **9** and **10** are appropriate for their structures: the ^1H and ^{13}C NMR spectra are assigned completely by using H-H and C-H COSY spectra, and marked differences are observed in the spectra between **9** and **10** [17]



Scheme 1.

The average chemical shifts of the seven-membered ring moieties of **9** (δ_{av} = 8.24) and **10** (δ_{av} = 7.99) are slightly shifted to high-field as compared with those of 1-trifluoroacetylazulene **18** (δ_{av} = 8.38) and 1-methoxycarbonylazulene **19** (δ_{av} = 8.17),[18] respectively, reflecting electron donation due to the annulation of the methanoindene ring system as well as the strong electron-withdrawing property of $-COCF_3$ as compared with $-CO_2Me$. The vicinal coupling constants of the seven-membered ring moieties suggest that bond-length alternation is small both in **9** ($J_{4,5}$ 9.7 > $J_{2,3}$ 9.6 > $J_{1,2}$ ~$J_{3,4}$ 9.5) and **10** ($J_{2,3}$ 10.3 > $J_{1,2}$ ~ $J_{4,5}$ 9.7 >$J_{3,4}$ 9.2), but the canonical structures of the azulene moieties depicted in Fig. 2 seem to be more important.

A noteworthy point is the geminal coupling constant of the methylene protons at C14 for **9** and **10**: the geminal coupling constant for **9** (J 4.1) is close to those for **2** (J 3.5)[6] and **3** (J 3.6).[8] On the other hand, the corresponding coupling constant for **10** (J 5.9) is too large for a [6,5] close NCD structure, and the value is fairly close to those of [6,5] open structures **4** (J 7.5)[6] and **5** (J 7.3). Furthermore, the ^{13}C NMR signals of C6 and C11 for **9** appearing at δ_c 45,7 and δ_c 51.5 are close to the corresponding signals of **2** (δ_c 40.1 and 48.1) and **3** (δ_c 39.6 and 45.6).[19] The signals of C6 and C11 for **10** appear at δ_c 81.3 and δ_c 90.0, which are largely shifted to lower field as compared with those of **2**, **3**, and **9**; but they are higher than those of the corresponding values of [6,5] open anion (113.7 for **4**; 101.3 and 119.2 for **5**).[19] Thus, ^1H and ^{13}C NMR spectra suggest that **9** exists as the [6,5] close NCD **9N** but **10** exists in equilibrium between a [6,5] close NCD **10N** and a [6,5] open CHT **10C** (Fig. 2). In addition, the average chemical shift of the C7-C8-C9-C10 moiety of **10** (δ_{av} = 6.49) is lower than the corresponding value of **9** (δ_{av} = 6.35) and the vicinal coupling constants in **10** ($J_{7,8}$ 8.4, $J_{9,10}$ 7.5) are smaller than those of **9** ($J_{7,8}$ 9.1, $J_{9,10}$ 9.0). This fact would be ascribed to the extension of conjugation of C7-C8-C9-C10 by participation of the eqnilibrium between **10N** and **10C**. The electronic spectrum of **10** is largely shifted to longer wave-length as compared to that of **9**, suggesting also the conjugation of C7-C8-C9-C10 with the azulene moiety by participation of the equilibrium between **10N** and **10C**.[15,19]

Although the ^{1}H NMR (600 MHz, in CD_2Cl_2) spectral studies were conducted at various temperatures, no clear change was observed for **9** and **10** at the temperature ranging from 30 °C to -100 °C. The ^{13}C NMR (150.8 MHz) of **9** was not changed at the temperature ranging from 30 °C to -100 °C in CD_2Cl_2 as well as at 30 °C to 120 °C in DMSO-d_6. This fact would support the absence of a [6,5] open CHT structure for **9**. On the other hand, ^{13}C NMR spectra of **10** in CD_2Cl_2 at various temperatures are depicted in Fig. 3. At -60 °C, the signals appearing at δ 79.2 and δ 88.2 at rt are shifted to lower field (δ 85.1 and δ 94.5), and both signals disappeared at -100 °C. The temperature dependency was also observed in signals of the aromatic and olefinic carbons as well as of the C13 and C14 carbons, which became a single peak at -100°C. In addition, signals of C6 and C11 at δ 79.2 and δ 88.2 in DMSO-d_6 shifted to higher field of δ 77.1 and δ 85.7 at 120°C, increasing the ratio of **10N** as compared to that of **10C**. These features clearly indicate that compound **10** exists in two different structures, **10N** and **10C** at rt, and the equilibrium between them is frozen at low temperature. Furthermore, on the basis of the temperature-dependent spectra, the ratio of **10C** increases at low temperature, and that of **10N** increases at higher temperature. Thus, the [6,5] open isomer **10C** seems to be more stable than the [6,5] close isomer **10N**. Unfortunately, we could not conduct ^{13}C NMR spectroscopy below -100 °C, thus, further detailed dynamic behavior of **10N** and **10C** could not be clarified at this stage.

9N: X=$COCF_3$
10N: X=CO_2Me

10C: X=CO_2Me

Fig. 2.

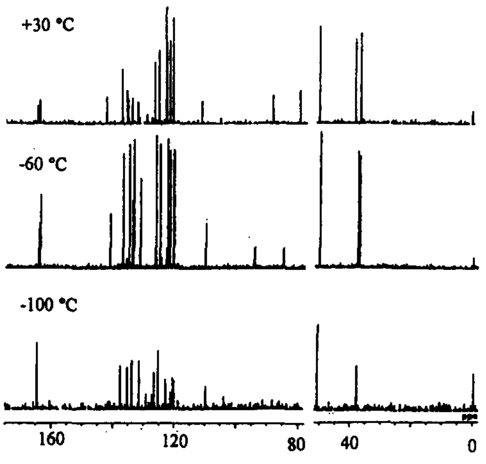
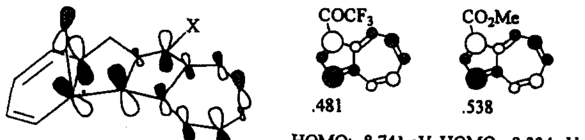


Fig. 3. ^{13}C NMR spectra of **10** at various temperatures.

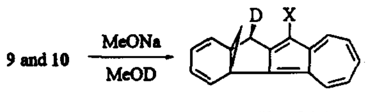
The difference in dynamic behavior between **9** and **10** is rationalized as follows. The highly polarized azulene[11-13] would donate π-electron to the cyclopropane ring as depicted in **17**, which represents the interaction between the LUMO of the Walsh orbital of cyclopropane and HOMO of azulene.[20] The calculated energy levels and coefficients of HOMO for 1-trifluoroacetylazulene **18** and 1-methoxycarbonylazulene **19** are also depicted in Fig. 4.[21] Regarding **19**, the energy level of HOMO is higher and the coefficient at C3 is larger than the corresponding values of **18**. Thus, the LUMO (cyclopropane)-HOMO (**19**) interaction occurs so effectively as to weaken the basal C6-C11 bond in **17** in the case of **10N**, as compared with the LUMO (cyclopropane)-HOMO (**18**) interaction in the



HOMO: -8.741 eV HOMO: -8.334 eV

17 **18** **19**

Fig. 4.



9-D: X=$COCF_3$
10-D: X=CO_2Me

Scheme 2.

case of **9N**. Thus, the valence isomerization between **10N** and **10C** easily occurs as compared to that of **9N**. The proton-deuterium exchange reaction of **9** and **10** in MeOD-MeONa occurred stereospecifically to give **9-D** and **10-D**, respectively. The exo selectivity (to the bridgemethylene) is in good accordance with the results obtained for **2** by Takahashi and co-workers.[22] The structural characteristics of the intermediate anions as well as the reactivities of **9** and **10** will be reported in a full paper.

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References

1. Liebman, J. F.; Greenberg, A. *Chem. Rev.* **1989**, *89*, 1225. Okamura, W. H.; Delela, A. R. *Comprehensive Organic Synthesis*, B. M. Trost and I. Fleming Eds, Pergamon, Oxford, **1991**, *5*; pp 699-750.
2. Ciganek, E. *J. Am. Chem. Soc.* **1967**, *89*, 1454. Ciganek, G. E. *J. Am. Chem. Soc.* **1967**, *89*, 1458. Hall, E.; Roberts, J. D. *J. Am. Chem. Soc.* **1971**, *93*, 2203. Ciganek, E. *J. Am. Chem. Soc.* **1971**, *93*, 2207.
3. Mukai, T.; Kubota, H.; Toda, T. *Tetrahedron Lett.* **1967**, 3581.
4. Takeuchi, K.; Fujimoto, H.; Okamoto, K. *Tetrahedron Lett.* **1981**, *22*, 4981. Takahashi, K.; Takase, K.; Toda, H. *Chem. Lett.* **1981**, 979. Takeuchi, K.; Fujimoto, H.; Kitagawa, T.; Fujii, H.; Okamoto, K. *J. Chem. Soc. Perkin Trans. 2* **1984**, 461.
5. Vogel, E.; Wiedman, W.; Kiefer, H.; Harison, W. F. *Tetrahedron Lett.* **1963**, 673.
6. Radlick, P.; W. Rosen, W. *J. Am. Chem. Soc.* **1966**, *88*, 3461.
7. Grimme, W.; Kaufhold, M.; Dettmeier, U.; Vogel, E. *Angew. Chem.* **1966**, *78*, 643.
8. Hunadi, R. J.; Helmkamp, G. K. *J. Org. Chem.* **1978**, *43*, 1586.
9. Murata, I.; Nakasuji, K.; Morita, T. *Chem. Lett.* **1974**, 743.
10. Diederich, F.; Thilgen, C. *Science* **1996**, 271. Diedrich, F.; Isaacs, L.; Philp, D. *J. Chem. Soc. Rev.* **1996**, 243.
11. Morley, J. O. *J. Am. Chem. Soc.* **1988**, *110*, 7660.
12. Anderson, Jr., A. G.; Steckler, B. M. *J. Am. Chem. Soc.* **1959**, *81*, 4941.
13. Ito, S.; Morita, N.; Asao, T. *Tetrahedron Lett.* **1991**, *32*, 773. Ito, S.; Morita, N.; Asao, T. *Tetrahedron Lett.* **1992**, *33*, 3773. Ito, S.; Morita, N.; Asao, T. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 1409.
14. Yang, P. -W.; Yasunami, M.; Takase, K. *Tetrahedron Lett.* **1971**, 4275. Yasunami, M.; Miyoshi, S.; Kanegae, N.; Takase, K. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 892.
15. Anderson, Jr., A. G.; Anderson, R. G. *J. Org. Chem.* **1962**, *27*, 3578.
16. Elemental analyses and spectroscopic data are satisfactory for all new compounds in this paper.
17. Selected physical data of new compounds. For **9**: brown plates: mp 151-152 °C (from EtOH); ^{1}H NMR (CDCl$_3$, 400 MHz) δ=0.44 (1H, d, J 4.1, H-14), 1.95 (1H, d, J 4.1, H-14), 3.82 (1H, d, J 19.0, H-12), 3.84 (1H, d, J 19.0, H-12), 6.04 (1H, dd, J 6.4, 9.1, H-8), 6.14 (1H, dd, J 6.4, 9.0, H-9), 6.45 (1H, d, J 9.0, H-10), 6.88 (1H, d, J 9.1, H-7), 7.57 (1H, dd, J 9.6, 9.8, H-3), 7.60 (1H, dd, J 9.6,9.9, H-4), 7.77 (1H, dd, J 9.7, 9.8, H-2), 8.65 (1H, d, J 9.9, H-5), 9.60 (1H, d, J 9.7, H-1); ^{13}C NMR (CDCl$_3$, 100.6 MHz) δ=29.2 (C14), 38.8 (C13), 45.7 (C6 or 11), 51.5 (C6 or 11), 115.5 (CF$_3$), 119.3 (C9), 121.0 (C8), 124.9 (C7), 127.8 (C10), 129.1 (C3), 131.1 (C4), 134.9 (C5), 136.5 (C13), 138.4 (C1), 139.2 (C2), 159.8 (C=O), 112.8, 118.4, 141.3, 148.3 (quart. C); IR (CHCl$_3$) 1645 cm^{-1}; λ_{max} (log ε) in EtOH, 200 (4.29), 231 (4.39), 283 (4.37), 327 (4.34), 414 (3.77), 432 (3.78), 532 (2.94), 657 (sh. 1.82). For **10**: purple prisms; mp 94-95 °C (decomp.) (from MeOH); ^{1}H NMR (CDCl$_3$, 400 MHz) δ=0.53 (1H, d, J 5.9, H-14), 2.76 (1H, d, J 5.9, H-14), 3.31 (1H, d, J 19.1, H-12), 3.84 (3H, s, Me), 4.03 (1H, d, J 19.1, H-12), 6.32 (1H, dd, J 7.5, 8.1, H-9), 6.48 (1H, dd, J 8.1, 8.4, H-8), 6.44 (1H, d, J 7.5, H-10), 6.73 (1H, d, J 8.4, H-7), 7.31 (1H, dd, J 9.2, 9.7, H-4), 7.36 (1H, dd, J 9.7, 10.3, H-2), 7.48 (1H, dd, J 9.2, 10.3, H-3), 8.49 (1H, d, J 9.7, H-5), 9.33 (1H, d, J 9.7, H-1); ^{13}C NMR (CDCl$_3$, 100.6 MHz) δ=37.5 (C14), 39.0 (C12), 50.9(Me), 81.3 (C6 or 11), 90.0 (C6 or 11), 121.4 (C10), 122.3 (C7), 123.4 (C9), 123.6 (C8), 125.8 (C4), 127.3 (C2), 134.4 (C5), 136.4 (C1), 137.8 (C3), 165.5 (C=O), 111.8, 132.9, 136.0, 143.0, 164.6 (quart. C); IR (CHCl$_3$) 1678 cm^{-1}; λ_{max} (log ε) in EtOH. 200 (4.61), 212 (4.65), 239 (4.62), 310 (4.80), 378 (3.97), 396 (4.00), 556 (2.94), 580 (2.89), 712 (1.76), 721 (1.47).
18. Hunadi, R. J. *J. Org. Chem.* **1982**, *47*, 1940.
19. Anderson, Jr. A. G.; Tazuma, J. J. *J. Am. Chem. Soc.* **1953**, 75, 4979.
20. Hoffmann, R.; Stohrer, W. -D. *J. Am. Chem. Soc.* **1971**, *93*, 6941. Gunther, H. *Tetrahedron Lett.* **1970**, 5173. Stohrer, W. -D.; Hoffmann, R. *Angew. Chem.* **1972**, *84*, 820.
21. AM1 calculations: MOPAC Ver. 6.00, Stewart, J. J. P. *QCPE Bull.* **1989**, *9*, 10; revised as Ver 6.12 by Athansopoulos, D. *QCPM* **1994**, 137.
22. Takahashi, K.; Takase, K.; Kagawa, T. *J. Am. Chem. Soc.* **1981**, *103*, 1186.

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