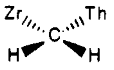
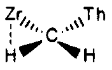
2.446 (4) and 2.543 (4) Å in $Cp'_2Th(neopentyl)_2$,[16b] 2.493 (11) Å in $Cp'_2ThCH_2SiMe_2$-*o*-C_6H_4,[16b] and 2.55 (3) Å in $Cp'_2Th(\eta^4-C_4H_6)$[16a]). Correcting for differences in Th(IV) and U(IV) ionic radii[17] yields a hypothetical U–C distance of 2.32 (1) Å, which compares favorably with the U–C "multiple bond" distance of 2.29 (3) Å in $Cp_3U(CHPMe_2Ph)$.[18,19]

Unusual aspects of the μ-CH_2 bonding are also revealed by variable-temperature NMR. At room temperature, the formally nonequivalent methylene protons are undergoing rapid exchange (T_c = 268–287 K, Table I). Low-temperature spectroscopy reveals AB pairs with *very large* chemical shift dispersions (2.4–5.8 ppm) and distinctive $^1J_{C-H}$ parameters (Table I). The low-field methylene resonance having $^1J_{C-H}$ = 124 Hz is typical of a μ-CH_2 group involving an early transition metal center.[3,4] On the other hand, the upfield displacement and small $^1J_{C-H}$ (85–95 Hz) of the second methylene resonance suggests an "agostic interaction."[16b,20] The sensitivity of these latter parameters to the identity of the group 4 metal (Zr vs. Hf) implies that the interaction is with that metal.

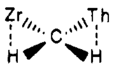
In regard to molecular dynamics, it is noteworthy that the μ-CH_2 hydrogen interchange process *does not* time-average other aspects of the instantaneous C_1 molecular symmetry (nonequivalent Cp′, nonequivalent halves of the metalated Cp, unaffected Zr–CH_3). Moreover, $\Delta G_c^\ddagger$ values for the three complexes are low, virtually identical, and insensitive to toluene vs. THF (Table I). Although further information on the methylene interchange process awaits precise determination of H atom positions, it is noteworthy that any mechanism involving $Zr(CH_2)Th$ bridge breaking must occur in such a manner that the resulting charge separation/coordination unsaturation is insensitive to the presence of THF and that "spinning" of the transitory terminal CH_2 prior to bridge closure must occur with a lower barrier than commonly observed in d^0 methylidene complexes.[21] More intriguing is the possibility, supported by preliminary EHMO calculations,[22] that hydrogen exchange occurs via a "planar" "anti van't Hoff" intermediate, possibly stabilized by agostic interactions (e.g., A–C). Of particular relevance here are the small calculated energy differences between tetrahedral and planar CH_2Li_2 structures,[23] as well as the similarity in polar metal–ligand bonding and the availability of empty metal acceptor orbitals.



A



B



C

Acknowledgment. This research was supported by the NSF under Grant CHE-8306255. The X-ray diffractometer and the computer used in data reduction and model refinement were acquired under NSF Grant CHE-8300958 and NIH Grant 1-510-RR-01672-01. We thank Profs. V. W. Day and K. Tatsumi for helpful discussions.

Supplementary Material Available: Spectroscopic and analytical data, X-ray experimental details (including positional and anisotropic displacement parameters), and tables of bond lengths and angles (19 pages); listing of observed and calculated structure factor amplitudes (32 pages). Ordering information is given on any current masthead page.

---

[16] (a) Smith, G. M.; Suzuki, H.; Sonnenberger, D. C.; Day, V. W.; Marks, T. J. *Organometallics* **1986**, *5*, 549–551 and references therein. (b) Bruno, J. W.; Smith, G. M.; Marks, T. J.; Fair, C. K.; Schultz, A.; Williams, J. M. *J. Am. Chem. Soc.* **1986**, *108*, 40–56.

[17] Shannon, R. D. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1976**, *32*, 751–767.

[18] Cramer, R. E.; Maynard, R. B.; Paw, J. C.; Gilje, J. W. *Organometallics* **1983**, *2*, 1336–1340.

[19] Judging from the fairly extensive data base,[12] $Cp'_2MX_2 \rightarrow Cp_3MX$ coordination number corrections to ionic radii[17] are very small.

[20] (a) Crabtree, R. H.; Holt, E. M.; Lavin, M.; Morehouse, S. M. *Inorg. Chem.* **1985**, *24*, 1986–1992 and references therein. (b) Schmidt, G. F.; Brookhart, M. *J. Am. Chem. Soc.* **1985**, *107*, 1443–1444 and references therein. (c) Jeske, G.; Schock, L. E.; Swepston, P. N.; Schumann, H.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 8103–8110. (d) Brookhart, M.; Green, M. L. H. *J. Organomet. Chem.* **1983**, *250*, 395–408. (e) No unusual ν_{C-H} features are evident in the infrared spectra.

[21] (a) Mann, B. E., ref 12b, pp 99–103 and references therein. (b) Schrock, R. R. *Acc. Chem. Res.* **1979**, *12*, 98–104.

[22] Tatsumi, K., private communication.

[23] (a) Bachrach, S. M.; Streitwieser, A., Jr. *J. Am. Chem. Soc.* **1984**, *106*, 5818–5824. (b) Laidig, W. D.; Schaefer, H. F. *J. Am. Chem. Soc.* **1978**, *100*, 5972–5973. (c) Collins, J. B.; Dill, J. D.; Jemmis, E. D.; Apeloig, Y.; Schleyer, P. v. R.; Seeger, R.; Pople, J. A. *J. Am. Chem. Soc.* **1976**, *98*, 5419–5427. (d) Nilssen, E. W.; Skancke, A. *J. Organometal. Chem.* **1976**, *116*, 251–256.

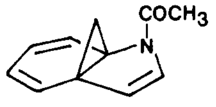
Synthesis of 9-Acetyl-9-azatricyclo[4.3.1.0^{1,6}]deca-2,4,7-triene, a Valence Isomer of 1-Acetyl-2,7-methanoaza[9]annulene

Norihiro Tokitoh and Renji Okazaki*

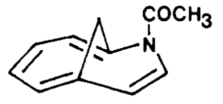
Department of Chemistry, Faculty of Science
The University of Tokyo, Hongo, Tokyo 113, Japan

Received October 20, 1986
Revised Manuscript Received January 2, 1987

We report here the synthesis of 9-acetyl-9-azatricyclo[4.3.1.0^{1,6}]deca-2,4,7-triene (**1**), a valence isomer of 1-acetyl-2,7-methanoaza[9]annulene (**2**).

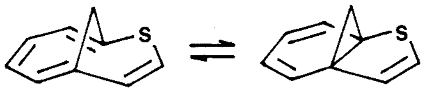


1



2

Although there has been much current interest in bridged annulenes and heteroannulenes,[1] only a few examples have been reported for the latter.[2] It is probably due to the limited availability of useful synthetic methods for such heterocycles. Recently we have reported the synthesis of 2,7-methanothia[9]annulene (**3**) starting from 1,6-diiodo-1,3,5-cycloheptatriene (**4**) and the existence of an equilibrium between **3** and its valence isomer **3′**.[3] The diiodide (**4**) is a very useful starting material for this type of heterocycle,[4,5] and the title compound (**1**), a nitrogen analogue of bridged thia[9]annulene **3**, has now been synthesized from **4** by a route as shown in Scheme I.[6] One of the iodines was converted into a 2-hydroxyethyl group by selective monovinylation followed by hydroboration to give alcohol **6**. After introduction of a carboxyl group by halogen–metal exchange and subsequent carboxylation, the resulting carboxylic acid **7** was



3 3′

---

[1] Vogel, E. In *Current Trends in Organic Synthesis*; Nozaki, H., Ed.; Pergamon: New York, 1983; pp 379–400 and references cited therein.

[2] (a) Tückmantle, W.; Andree, G.; Seidel, A.; Schmickler, H.; Lex, J.; Kraka, E.; Haug, M.; Cremer, D.; Vogel, E. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 592 and references cited therein. (b) Kato, H.; Toda, S. *J. Chem. Soc., Chem. Commun.* **1982**, 50. (c) Kato, H.; Arikawa, Y.; Hashimoto, M.; Masuzawa, M. *Ibid.* **1983**, 938.

[3] Okazaki, R.; Hasegawa, T.; Shishido, Y. *J. Am. Chem. Soc.* **1984**, *106*, 5271.

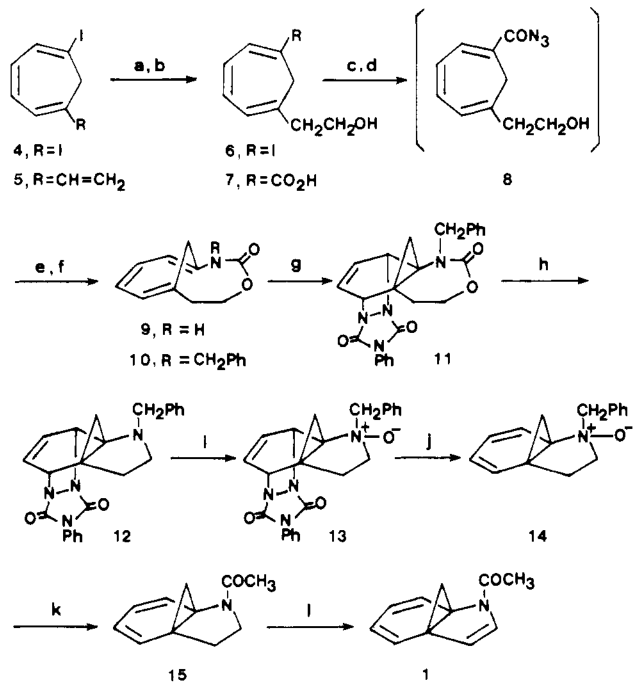
[4] Okazaki, R.; O-oka, M.; Tokitoh, N.; Shishido, Y.; Inamoto, N. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 799.

[5] Okazaki, R.; O-oka, M.; Tokitoh, N.; Shishido, Y.; Hasegawa, T. *Phosphorus Sulfur* **1983**, *16*, 161.

[6] All the new compounds (**1**, **7**, **9–15**, and **17**) were identified by spectral (^1H, ^{13}C NMR, IR, and MS) and analytical (exact mass and/or elemental analyses) data. See supplementary material for the details.

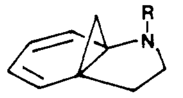
0002-7863/87/1509-1856$01.50/0

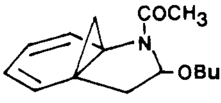
Scheme I[a]



[a] (a) $CH_2{=}CHMgBr$–catalytic Li_2CuCl_4; 87%. (b) 9-BBN, $NaOH-H_2O_2$; 82%. (c) *n*-BuLi (2 equiv)–CO_2, H_3O^+; 60%. (d) $(PhO)_2P(O)N_3-NEt_3$. (e) PhH reflux, high dilution; 80%. (f) *i*-Pr_2NLi/THF-HMPA, $PhCH_2Br$; 76%. (g) PTAD/CH_3CN, −10 °C; 62%. (h) $Me_3SiI/CHCl_3$, aqueous NaOH; 81%. (i) MCPBA; 93%. (j) Na/EtOH, Δ; 75%. (k) $(MeCO)_2O$, NEt_3; 87%. (l) $(t\text{-}BuO_2CO)_2$/PhH; 5%.

converted into the corresponding acyl azide **8**.[7] It was subjected, without isolation, to the Curtius reaction under high-dilution conditions, and the resulting isocyanate underwent an intramolecular cyclization to give the bicyclic urethane **9**. After N-benzylation, **10** was subjected to the Diels–Alder reaction with 4-phenyl-1,2,4-triazoline-3,5-dione (PTAD) to give adduct **11**. The reaction with trimethylsilyl iodide followed by treatment with aqueous alkaline solution smoothly converted **11** into the corresponding pyrrolidine derivative **12**. Various attempts to remove PTAD from **12** to give **16** (R = CH_2Ph) were unsuccessful probably because of the instability of the product, **16**. However,

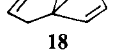

16


17

treatment with sodium in ethanol[8] of the corresponding *N*-oxide **13**, obtained by *m*-chloroperbenzoic acid oxidation, gave desired tricyclic *N*-oxide **14**, the Polonovski reaction of which afforded acetamide **15**. Radical oxidation of **15** using di-*tert*-butyl peroxyoxalate[9] afforded the target enamide **1** as a pale yellow oil along with a similar amount of *tert*-butoxy-substituted acetamide **17**. The enamide **1** was also obtained in 53% yield by treatment of **17** with a catalytic amount of oxalic acid in benzene.

The structure of **1** was confirmed by the following spectral data:[10] ${}^1H$ NMR ($CDCl_3$ at 0 °C) δ 0.24 (d, 1 H, J = 4.4 Hz), 1.39 (d, 1 H, J = 4.4 Hz), 2.18 (s, 3 H), 5.56 (d, 1 H, J = 4.6 Hz), 6.14 (d, 1 H, J = 4.6 Hz), 5.7–7.3 (m, 4 H); ${}^{13}C$ NMR ($CDCl_3$ at 0 °C) δ 19.61 (dd), 22.59 (q), 40.87 (s), 50.14 (s), 115.25 (d), 119.61 (d), 119.89 (d), 123.73 (d), 126.25 (d), 126.44 (d), 166.83 (s); MS, m/z 173 (M^+, 6%), 130 (100%); high-resolution MS, m/z 173.0843 (calcd for $C_{11}H_{11}NO$, 173.0841). Variable-temperature ${}^{13}C$ NMR spectra of **1** indicated slight but regular changes in chemical shifts for the bridgehead carbons, which are thought to be most susceptible to temperature changes. In Table I is listed the temperature gradient (Δ) of the chemical shifts of **1** along with those for some other related compounds. In contrast to the fluxional system **3** ⇌ **3′** having a large value, that of **1** is considerably small and close to those of adamantane and **18**, both of which are incapable of cycloheptatriene–norcaradiene equilibrium. This fact, along with the observation that the value of **1** is also similar to those of **15** and **17**, suggests that the azacycle obtained here exists mostly as a norcaradiene form **1** and the contribution of **2** is minute to such an extent that it cannot be detected by NMR spectroscopy, if any exists. Positive evidence for the existence of **2**, however, was obtained by its electronic spectrum, which showed a very weak shoulder at 350 nm ($\epsilon \lesssim 50$), a region similar to the longest wavelength absorption of **3** (350 nm). Although a quantitative argument is difficult at the present time, the contribution of **2** would be $\lesssim$2% at ambient temperature.[12] Since the lesser contribution of the bicyclic annulenyl structure **2** in the present system compared with the **3** ⇌ **3′** system is most probably due to the presence of an electron-withdrawing acetyl group on nitrogen,[13] we are currently continuing our efforts to obtain the parent 2,7-methanoaza[9]annulene[14] by deacetylation of **1**.[15]

Table I. ${}^{13}C$ Shift Temperature Gradients (Δ)[a] for Bridgehead Carbons of **1** and Related Systems[b]

compd	Δ	compd	Δ
1	0.57	**3** ⇌ **3′**	5.37
15	0.26	 **18**	0.52
17	0.48	adamantane	0.58

[a] In 10^{-2} ppm/K units. All the chemical shift values for the bridgehead carbons decrease upon lowering temperatures. The value of adamantane, which is the average of the tertiary and secondary carbons, is considered to be intrinsic for a compound of relatively high rigidity.[11] [b] The averages of the chemical shifts for the two bridgehead carbons are listed.

In summary, we have succeeded in the synthesis of the fluxional system between azapropellane **1** and bridged aza[9]annulene **2**. Although the NMR spectra suggest that the system exists essentially as **1**, the electronic spectrum indicates the existence of **2** as an equilibrium mixture, though to a minor extent.

Acknowledgment. R.O. thanks the Kurata Foundation (the Kurata Research Grant) for financial support. The generous supply of the silyl halides from Shin-etsu Chemical Co., Ltd., is also gratefully acknowledged.

Supplementary Material Available: ${}^1H$ and ${}^{13}C$ NMR, infrared, mass spectral, and elemental analytical data for the compounds **7**, **9–15**, and **17** (3 pages). Ordering information is given on any current masthead page.

---

(7) Ninomiya, K.; Shioiri, T.; Yamada, S. *Tetrahedron* **1974**, *30*, 2151.

(8) Barton, D. H. R.; Shioiri, T.; Widdowson, D. A. *J. Chem. Soc., Chem. Commun.* **1970**, 939.

(9) We thank Prof. Vogel of the University of Cologne for informing us of the detailed procedure of the oxidation using di-*tert*-butyl peroxyoxalate. For the use of this reagent in the synthesis of azaannulenes, see ref 2a.

(10) Only a single rotamer was observed by NMR spectra although, in principle, two rotamers due to the restricted rotation around the N—(C=O) bond were possible.

(11) Schneider, H.-J.; Freitag, W. *J. Am. Chem. Soc.* **1976**, *98*, 478.

(12) The value of 2% was estimated by assuming that the absorption coefficient of **2** was the same as that of **3** (i.e., 2200).

(13) An electron-withdrawing substituent on nitrogen is known to decrease the aromaticity of azonines. Anastassiou, A. G.; Kasmai, H. S. *Adv. Heterocycl. Chem.* **1978**, *23*, 55.

(14) The parent 2,7-methanoaza[9]annulene has been predicted to have a resonance energy similar to that of **3**. Jurić, A.; Sablijć, A.; Trinajstić, N. *J. Heterocycl. Chem.* **1984**, *21*, 273.

(15) Attempts of the deacetylation have been so far unsuccessful probably because of kinetic instability of the parent system under the reaction conditions.