

**1,8-Diazabicyclo[6.6.6]eicosa-4,11,17-triyne and 1,8-Diazacyclotetradeca-4,11-diyne.
 Syntheses and Properties.¹**

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The syntheses of 1,8-diazacyclotetradeca-4,11-diyne and 1,8-diazabicyclo[6.6.6]eicosa-4,11,17-triyne and 1,8-diazabicyclo[6.6.6]eicosa-4,11,17-triene are reported.

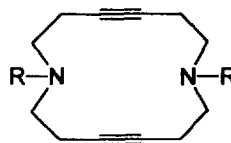
Cage-like molecules have fascinated chemists for many years.² They have been attractive not only because many of them have high symmetry but also because they are ideal model compounds for the study of topics as rearrangements, cycloadditions and interactions of π -systems on an intramolecular basis. Our interest in cage-like systems arose from our work on through space and through bond effects of π -systems, such as benzene rings, double bonds and triple bonds.³ Compounds in which three triple bonds are oriented parallel or near parallel with respect to each other are of interest as model substances to study the interaction of acetylenic units in close proximity. So far only one compound has been reported in the literature, 1,6-diazabicyclo[4.4.4]tetradeca-3,8,12-triyne **1**.⁴



1



2



3 R = H

 4 R = *i*-C₃H₇

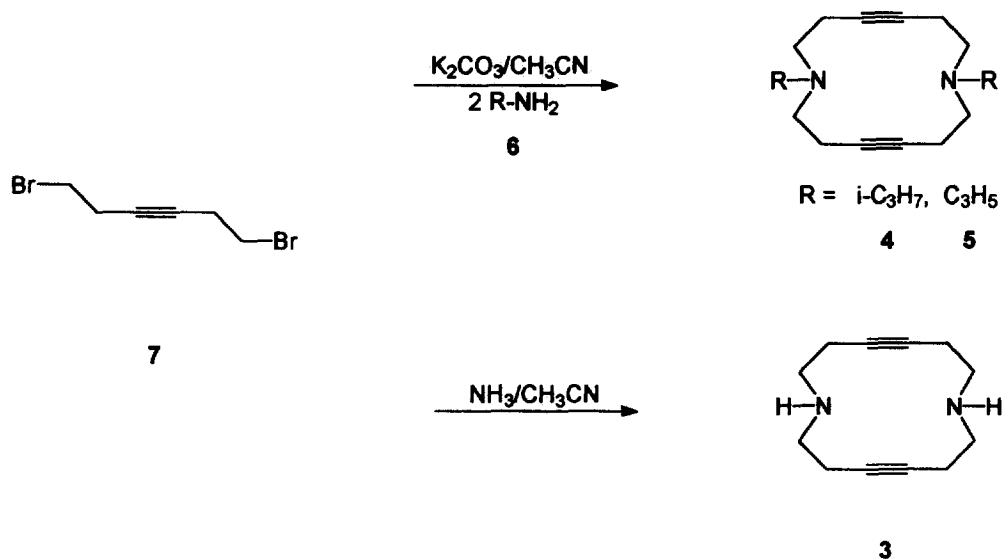
 5 R = C₃H₅

1 proved to be rather unstable, therefore a detailed study of its properties has not been possible so far. To find out more about the properties of bicyclic triynes we embarked in the synthesis of the next higher homologue of **1**, 1,8-diazabicyclo[6.6.6]eicosa-4,11,17-triyne **2**.

Starting point of our investigations was the synthesis of 1,8-diazacyclotetradeca-4,11-diyne (**3**) and some of its alkyl derivatives (**4** and **5**).

The synthesis of **2** - **5** proved to be very simple and straightforward as shown in Scheme 1.

Scheme 1

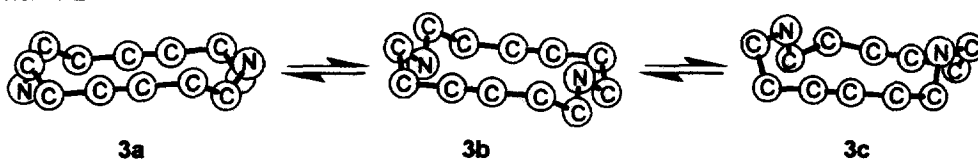


Reaction of the primary amine (isopropyl- or allylamine **6**) with 1,6-dibromohex-3-yne⁵ (**7**) in acetonitrile with K_2CO_3 as base yielded the cyclic diamines 1,8-diisopropyl-1,8-diazacyclotetradeca-4,11-diyne (**4**) and 1,8-diallyl-1,8-diazacyclotetradeca-4,11-diyne (**5**) in 25% yield. The parent compound **3** was available through the introduction of ammonia to a well stirred solution of **7** in acetonitrile.

For **3** quantum chemical procedures (MNDO/2)⁶ predict an equilibrium between boatlike conformers and chairlike conformers (Scheme 2) with **3b** as the global minimum. Only small energy differences between the various conformers are predicted by the calculations. This implies that all conformers might be present in solution at room temperature.

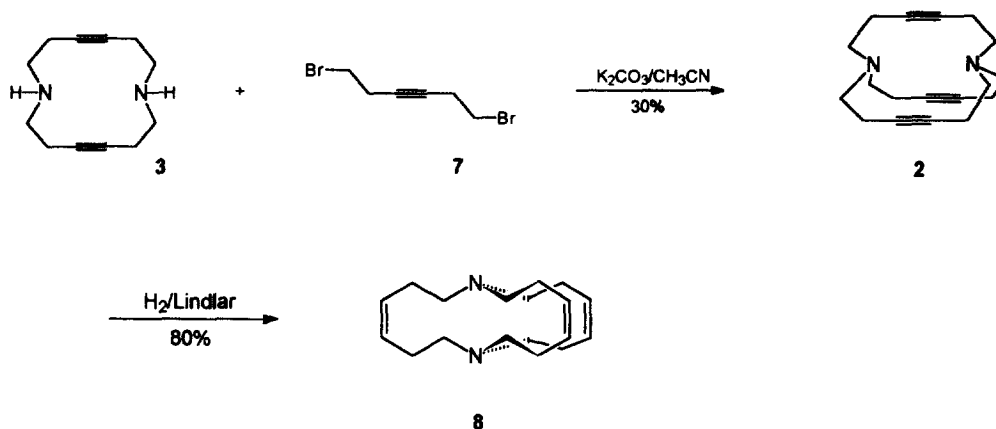
X-ray diffraction on a single crystal of **4** reveals conformation **4a** to be present in the solid state, with the isopropyl substituents in axial positions.⁷

Scheme 2



Our assumption that the boatlike conformers of **3** are present in solution is supported in so far as the reaction of **3** with **7** (Scheme 3) in acetonitrile and in presence of K_2CO_3 as base affords the bicyclic species **2** in 30% yield. Compound **2** has also been obtained by reacting NH_3 with **7**. In contrast to **1**, its homologue **2** proved to be thermally stable up to 100 °C. The hydrogenation of **2** with Lindlar's catalyst affords **1**, 8-diazabicyclo[6.6.6]eicosa-4,11,17-triene (**8**) in high yield. The structural assignment of all new compounds is based on their spectroscopic properties (see Table 1). The new bicyclic systems are promising models for the study of the interaction of their π -systems and their bridgehead nitrogens.⁸

Scheme 3



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Table 1 Spectroscopic data of **2**, **3**, **4**, **5**, and **8**

- 2:** ^1H NMR (300 MHz, CDCl_3): δ = 2.22 (t, 12 H), 2.41 (t, 12 H); ^{13}C NMR (75 MHz, CDCl_3): δ = 19.09 (s), 53.39 (s), 79.65 (q); HRMS (EI): calcd. 268.1939, found 268.1942.
- 3:** ^1H NMR (300 MHz, CDCl_3): δ = 2.30 (t, 8 H), 2.57 (t, 8 H), 1.74 (2 H, NH); ^{13}C NMR (75 MHz, CDCl_3): δ = 19.14 (s), 48.80 (s), 79.51 (q).
- 4:** ^1H NMR (300 MHz, C_6D_6): δ = 0.96 (d, 12 H), 2.42 (t, 8 H), 2.71 (t, 8 H), 2.75 (m, 2 H); ^{13}C NMR (75 MHz, C_6D_6): δ = 18.6 (p), 20.8 (s), 49.5 (s), 52.3 (t), 80.9 (q); HRMS (EI): calc. 274.2409, found 274.2388.
- 5:** ^1H NMR (300 MHz, CDCl_3): δ = 2.29 (t, 8 H), 2.76 (t, 8 H), 3.07 (d, 4 H), 5.91-5.94 (m, 2 H), 5.20-5.06 (m, 4 H); ^{13}C NMR (75 MHz, CDCl_3): δ = 17.55 (s), 51.80 (s), 57.19 (s), 80.34 (q), 117.20 (s), 136.71 (t).
- 8:** ^1H NMR (300 MHz, CDCl_3): δ = 2.20-2.80 (m, 24 H), 5.32-5.71 (m, 6 H); ^{13}C NMR (75 MHz, CDCl_3): δ = 25.36 (s), 58.85 (s), 129.22 (t); HRMS: calc. 274.2489, found 274.2484.

References

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