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Theoretical Investigations on the Valence Tautomerism between 1,6-Methanol[10]annulene and Tricyclo[4.4.1.0^{1,6}]undeca-2,4,7,9-tetraene

By *Dieter Cremer** and *Bernhard Dick*

1,6-Methano[10]annulene **1** must, on the basis of its physical and chemical properties, be described as a Hückel aromatic system with a delocalized π-electron decet[1a-d]. Investigations on C-11-substituted 1,6-methano[10]annulenes, however, suggest that **1** can transform into the valence tautomer tricyclo[4.4.1.0^{1,6}]undeca-2,4,7,9-tetraene **2** in solution[1c,d]. There is the possibility of a rapid reversible valence tautomerism of the type **1 ⇌ 2**, similarly to that assumed for the system cycloheptatriene **3** – norcaradiene **4**[1e-g].

| 1, R = H | 2, R = H |
| 5, R = CN | 6, R = CN |

3 ⇌ 4
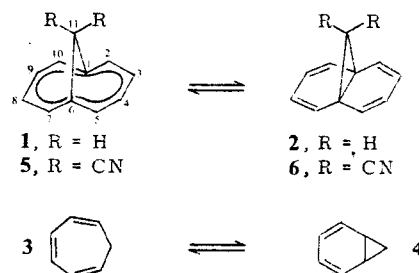
According to experimental and theoretical estimates[2], **4** is destabilized by about 4–12 kcal/mol compared to **3**. Accordingly, the equilibrium **3 ⇌ 4** is shifted far over to the side of the cycloheptatriene. However, detection of the norcaradiene component has so far only been possible in an indirect way. Thus, **3** reacts like **1** with dienophiles to give Diels-Alder products, indicating a previous rearrangement **3 ⇌ 4** or **1 ⇌ 2**. However, it cannot be ruled out that the norcaradiene component is first formed at the moment of reactive collision with the dienophile[2a].

To clarify this problem we have determined the energy profile of the valence tautomeric processes **1 ⇌ 2** and **3 ⇌ 4**, respectively, by *ab initio* calculations and therefrom obtained the energy differences $\Delta E = E(2) - E(1)$ and $\Delta E = E(4) - E(3)$[3]. After taking into account vibration and entropy effects values of 4.5 and 5.6 kcal/mol, respectively, result for the difference in the free energies ΔG^0, which corresponds to concentrations of about 0.05% **2** and 0.01% **4** at room temperature.

The valence tautomerization of **1**, like that of **3**, is characterized by an asymmetric double-well potential (Fig. 1). According to our calculations, an asymmetric single-well potential, as has been discussed for the 11-cyano-11-methyl derivative[4a], can be ruled out for the rearrangement **1 → 2**. For the energy barriers ΔE^{*} of the forward and reverse reactions, we find values of 7.3 and 2.3 kcal/mol, respectively. These values are about 3 kcal/mol smaller than the barriers calculated for the equilibrium **3 ⇌ 4**. Appar-

[*] Priv.-Doz. Dr. D. Cremer, Dr. B. Dick
    Lehrstuhl für Theoretische Chemie der Universität
    Greinstrasse 4, D-5000 Köln 41 (Germany)

ently formation of the cyclopropane bond is favored as a result of the shorter 1,6-distance in **1** (2.26 Å as opposed to 2.50 Å in **3**[3]), whereas in **2** the interaction of the Walsh orbitals of the three-membered ring with the π-orbitals of the butadiene moieties indicates the far better π-conjugation in **1**.
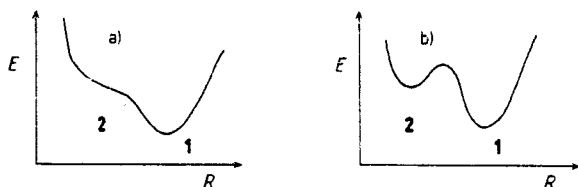

Fig. 1. Schematic representation a) of an asymmetric single-well potential and b) of an asymmetric double-well potential for the valence tautomeric equilibrium $1 \rightleftharpoons 2$. R is distance between C-1 and C-6.

According to experimental and theoretical investigations on cycloheptatrienes, substituents can shift the valence tautomeric equilibrium to the side of the norcaradiene[4b-e]. Thus, *Ciganek* synthesized 7,7-norcaradienedicarbonitrile as the first norcaradiene derivative in this way[4b].

The electronic influence of the two CN groups has been calculated to amount to about 10 kcal/mol[3] in the case of the cycloheptatriene. If this value is extended to the system $1 \rightleftharpoons 2$, then it can be predicted that tricyclo[4.4.1.0^{1,6}]undeca-2,4,7,9-tetraene-11,11-dicarbonitrile **6** is more than 5 kcal/mol more stable than the valence tautomeric 1,6-methano[10]annulene-11,11-dicarbonitrile **5**. This prediction is confirmed by the synthesis of **6** and its spectroscopic and structural chemical characterization carried out by *Vogel et al.*[5].

CAS Registry numbers:
1, 2443-46-1; **2**, 174-23-2; **3**, 544-25-2; **4**, 14515-09-4; **5**, 61997-35-1; **6**, 61997-37-3.

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[3] The equilibrium geometries of **1** to **4** were determined by means of the MNDO method and by Hartree-Fock (HF) calculations with minimal basis (STO-3G). The potential curve for the transformation $1 \rightleftharpoons 2$ was determined by HF/4-31G calculations. The absolute energies for **1** and **2** are -421.67075 and -421.66278 Hartree, respectively. In the case of **3** and **4** additional HF/6-31G* calculations were carried out [$E(3) = -269.68035$, $E(4) = -269.67128$ Hartree]. Correlation effects were estimated according to the Møller-Plesset perturbation method (2nd order). Finally, the zero point vibration energies as well as vibration contributions to enthalpy and entropy have been determined by force field calculations (D. Cremer, B. Dick, D. Christen, unpublished results).

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