Zeitschrift für Physikalische Chemie, Bd. 180, S. 135–158 (1993)
 – 0942-9352/93 $ 3.00+0.00

Magnetic Resonance Studies and Ab-Initio Calculations as Structure Probes for Radical Cations – Hexa-1,5-diene Systems*, [1,2]

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Radical cations / Molecular structure / Cope rearrangement / CIDNP

Magnetic resonance (CIDNP and/or ESR) data as well as ab-initio calculations have established three distinct structure types for radical cations derived from 1,5-hexadiene sytems: a) "dissociative" radical cations (e.g. **1**) containing two separate allylic moieties; b) cyclohexane-1,4-diyl radical cations (e.g. **6**) in a chair conformation, the apparent products of "arrested" 1,6-cycloadditions; and c) several bridged cyclooctadiene-diyl structures (boat conformers, e.g., **2** or **3**). The third radical cation type can be viewed, formally, as a cyclic conjugated "bis-homo-cyclohexatriene" structure with 5 π electrons; however, the degree of interaction between the two allylic moieties appears to be quite small.

The three radical cation types are striking examples of fundamental structure changes upon one-electron oxidation in systems combining σ and π donor functions. In general, significant differences can be expected for the potential surfaces of radical cations and their neutral diamagnetic precursors.

Aus CIDNP- and ESR-Untersuchungen sowie aus ab-initio-Rechnungen wurden drei ungewöhnliche Radikalkation-Strukturen erschlossen, die sich von Hexa-1,5-dien-Systemen ableiten lassen: a) „dissoziative" Radikalkationen mit zwei deutlich getrennten Allyl-Systemen (z. B. **1**); b) Cyclohexan-1,4-diyl-Radikalkationen (in der Sesselform, z. B. **6**), offensichtlich Cycloadditionsprodukte, die nach dem ersten Teilschritt „eingefroren" sind; und c) überbrückte Cyclooctadien-diyl-Radikalkationen (in der Bootform, z. B. **2** oder **3**). Der dritte Radikalkationentyp kann formal als eine cyclisch konjugierte „Bis-homo-cyclohexatrien"-Struktur mit 5 π-Elektronen aufgefaßt werden; allerdings dürfte die Überlappung der beiden Allylsysteme nur äußerst geringfügig sein.

Die drei Strukturtypen sind Musterbeispiele für die dramatischen Strukturveränderungen, die als Folge von Ein-Elektronen-Oxidationen in Systemen mit

* Presented as an Invited Lecture at the International Symposium "Magnetic Field and Spin Effects in Chemistry and Related Phenomena", 26–31 July 1992, Konstanz, Germany.

[1] This paper is dedicated to the memory of Professor Gerhard Ludwig Closs, whose significant and elegant contributions in such divergent areas as carbene chemistry, magnetic polarization, and electron transfer processes have been an inspiration to the author.

[2] Support of this work by the National Science Foundation through grants CHE-9110487 and CHE920022N is greatly appreciated.