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Short communication

The Temperature Dependent HFS EPR and Conformation of 9-substituted Octahydrocarbazole Cation Radical

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Abstract

The conformational motion of cyclohexene rings in six octahydrocarbazole N-derivatives was studied by EPR spectroscopy. Additionally the potential energy surface for the conformational change of one cyclohexene ring was calculated using the semiempirical method AM1.

Keywords: EPR, conformation, radical, AM1, PES

The conformational motion of cyclohexene rings in the octahydrocarbazole cation radicals was studied by EPR spectroscopy. The six octahydrocarbazole N-derivatives (*tert*-butyl, tolyl, 1-naphtyl, phenyl, cyclohexyl, adamantyl) were prepared by Paal - Knorr syntheses from primary amine and 2,2'-diketodicyclohexyle. The cation radicals were generated *in situ* by the potential controlled electrolysis in dichloromethane (0.1 M $TBAPF_6$). The EPR spectra were recorded at whole liquid range of CH_2Cl_2. The HFS of the spectra shows line-width alternation (Figure 1). All three types of HFS were registered: frozen, coalescent, and time-averaged. This phenomenon can be interpreted in terms of nonsynchronized cyclohexene rings movement using the four-jump model [1], describing the exchange between four populated sites. The series of spectra has been simulated by application of this model. Comparison of the experimental and computer simulated spectra at various temperatures yields the rate constant and thermodynamic parameters for the process. The mean lifetime of conformers spans the interval 10^{-10} to 10^{-7}s. The energy barrier amounts about 30 kJ/mol. The dynamics of the conforma-

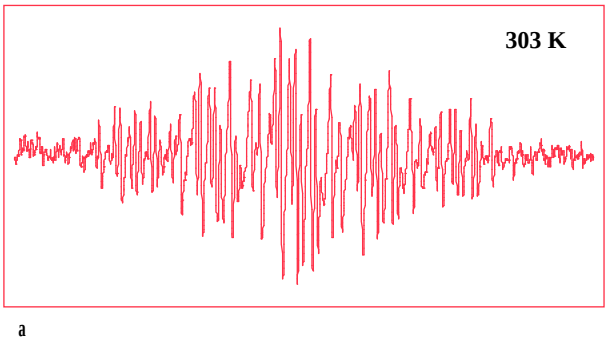

Figure 1a. *EPR spectra of 9-adamantyl octahydrocarbazole (9-AOHC) radical cation in dichloromethane at 303 K.*

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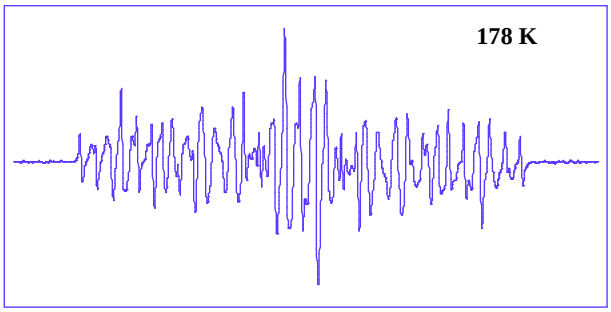
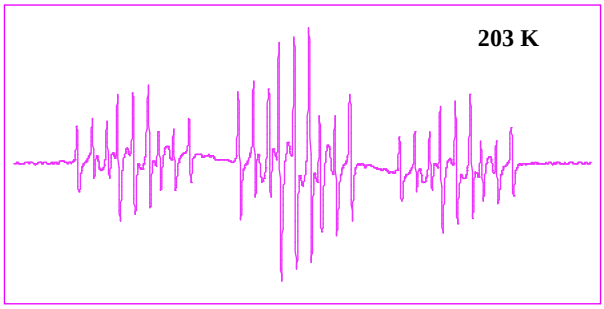


c

Figure 1c. *EPR spectra of 9-AOHC radical cation in dichloromethane at 178 K.*



b

Figure 1b. *EPR spectra of 9-AOHC radical cation in dichloromethane at 203 K.*

tional movement is beyond the time scale of NMR spectroscopy.

The potential energy surface (Figure 2) for the conformational change of one cyclohexene ring in 9-H-octahydrocarbazole radical cation was calculated by AM1 [2] (AMPAC 2.1). According the calculation the saddle points are 10.9 kJ/mol above the minima and the planar structure lies still 2.5 kJ/mol higher. The conformation of the molecule switches between the chair-chair C_s and the chair-chair C_2 geometry by movement of either cyclohexene ring, the boat conformation of the ring being the transition state.

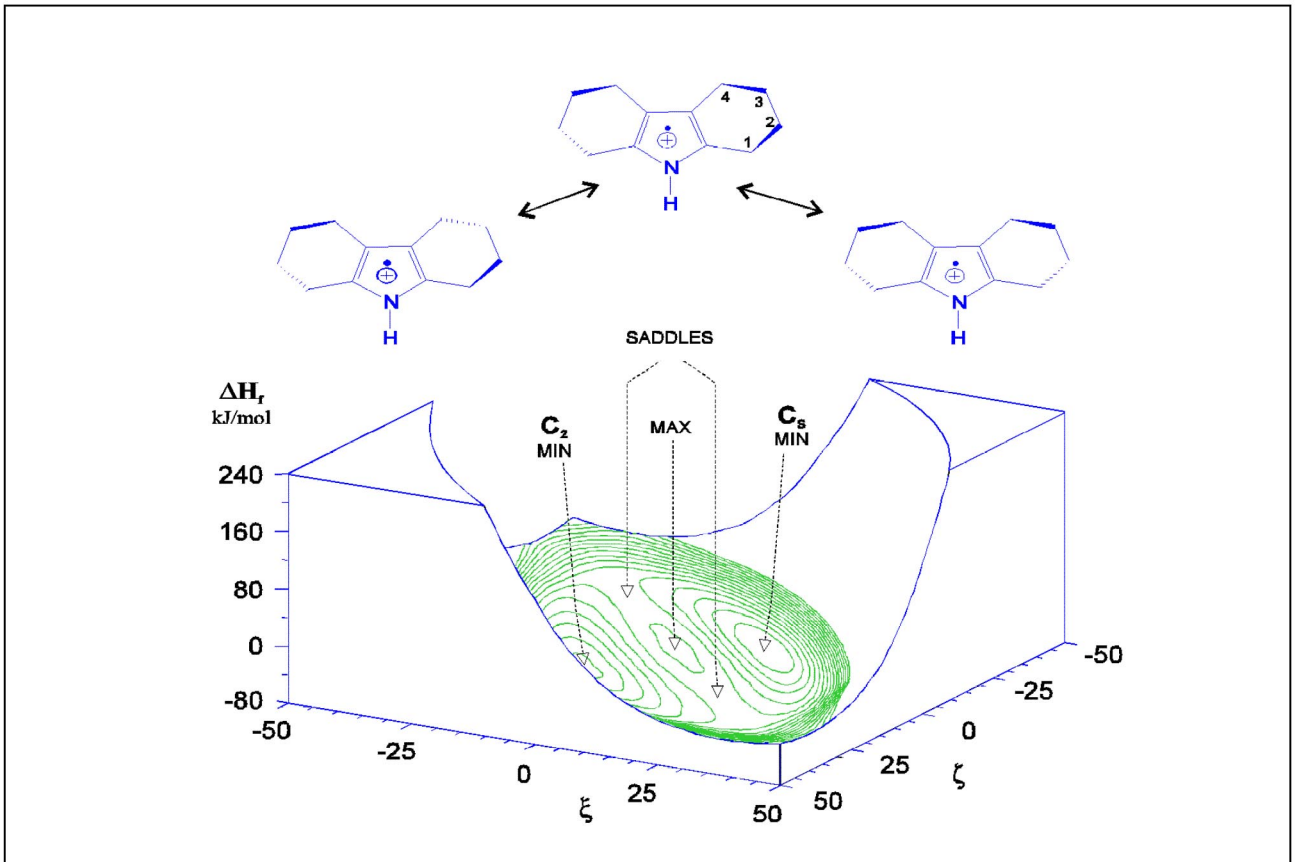


Figure 2. *The potential energy surface (AMPAC 2.1 - AM1) for conformational change of one cyclohexene ring in 9-H-octahydrocarbazole. The coordinates ξ and ζ are the torsion angles of the bond 1-2 and 3-4 with respect to the pyrrole plane. Only those coordinates were fixed at each point of the surface, all others were allowed to relax.*

Reference

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2. Dewar M. J. S., et al., *J. Am. Chem. Soc*. **1985**, *107*, 3902.