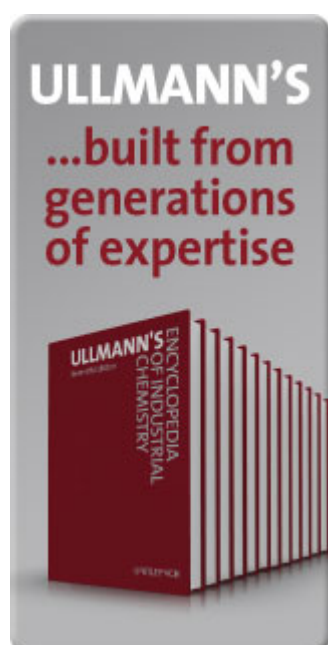


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Article

Experimental appraisal of solvent effects on internal rotation barriers and stabilization energies of disubstituted methyl radicals

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- Abstract

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Keywords:

- EPR;
- Capto-dative radicals;
- Rotational barriers;
- Solvent effects;
- Stabilization energies

Abstract

The EPR spectra of aminopropynyl and aminocyanomethyl radicals were recorded in a variety of solvents with different dielectric constants. For the former radical the spectra showed exchange broadening due to restricted rotation about the $\text{H}_2\text{N}-\text{C}^\cdot$ bond. Arrhenius parameters for the bond rotation, i.e. for the interconversion of the two rotamers, were obtained by computer simulation of the exchange-broadened spectra. The rotational barrier height was found to change only marginally in solvents with dielectric constants ranging from 2.1 to 37.5. For both radicals the temperature dependences of the $\alpha(\text{NH}_2)$ values also indicated little change in their $\text{H}_2\text{N}-\text{C}^\cdot$ rotation barriers in solvents of differing polarity.

Because rotation barriers are directly related to the stabilization energies (*SE*) of the radicals, it was concluded that solvent polarity has little effect on the *SE* of a capto-datively substituted radical.

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