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Atropisomerism of phosphorus-containing N-aryl carbamates. Experimental and computational data

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Abstract

Studies by 1H NMR spectroscopy and X-ray diffraction analysis revealed hindered rotation of the aromatic substituent about the C Ar-N bond in ortho-substituted (except for o-fluorin--substituted) phosphorus-containing carbamates. The energy barriers to rotation (AG c ≠) and coalescence temperatures (Tc) determined by the coalescence method increase with increasing volume of the ortho substituent. Conformations resulting from rotation of the ortho-substituted aryl group about the CAr-N bond were analyzed by quantum-chemical methods, potential curves were constructed, and differences between the conformational energies and the heights of rotation barriers were estimated. The theoretical rotation barriers change in parallel with the experimental values of ΔGc ≠ however, the theoretical values are much smaller in magnitude.

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Keywords

Atropisomerism, Low-temperature NMR spectroscopy, Ortho effect, Phosphorus- containing carbamates, Quantum-chemical calculations, X-ray diffraction analysis