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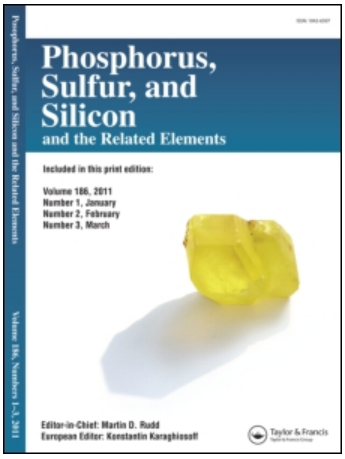

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THE SULFENAMIDE CHIRAL UNIT. TORSIONAL BARRIERS IN TRINITROBENZENESULFENAMIDES AND PERHALOBENZENSULFENAMIDES

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The Sulfenamide Chiral Unit. Torsional Barriers in Trinitrobenzenesulfenamides and Perhalobenzensulfenamides.

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The free energies of activation for degenerate racemization of sulfenamides, measured by DNMR spectroscopy provide information about the N-S formal single bond since stereomutation is accomplished by torsion about this bond. The S-N torsional barrier in benzenesulfenamides ($arSNR_1R_2$) is significantly increased by the presence of substituents which are electron withdrawing (by resonance). However, while the barrier is increased by para and single ortho substituent, the introduction of a second ortho substituent lowers the barrier.

This behavior must result from steric inhibition of resonance (when two ortho substituents are present) and offers evidence against the earlier conclusion that d-orbital conjugation plays an important role in determining S-N torsional barriers.

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