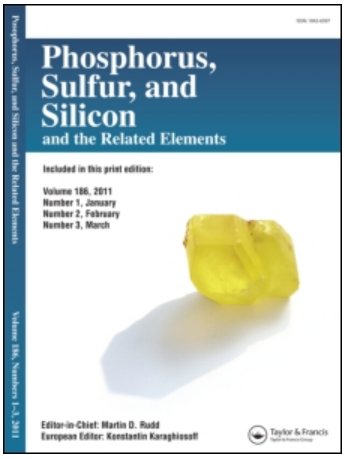

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A THEORETICAL STUDY ON THE CONFORMATIONAL PROPERTIES AND GEOMETRICAL DEFORMATIONS OF DIMETHYL SULFOXIDE

Paul G. Mezey[a]
[a] Department of Chemistry and Chemical Engineering, University of Saskatchewan, Saskatoon, Canada

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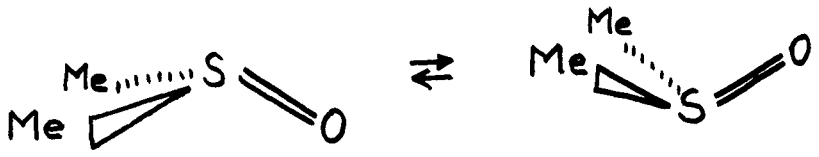
A THEORETICAL STUDY ON THE CONFORMATIONAL PROPERTIES AND GEOMETRICAL DEFORMATIONS OF DIMETHYL SULFOXIDE

Paul G. Mezey

Department of Chemistry and Chemical Engineering, University of Saskatchewan, Saskatoon, Canada.

The chemical and biological importance of DMSO and other sulfoxides is partly due to the wide variety of molecular complexes formed with these molecules[1]. The relatively large dipole moment of DMSO and the peculiar conformational properties of the sulfoxide moiety facilitates the formation of such complexes. There is experimental evidence that the formation of the molecular complex may be accompanied by extensive geometrical distortions of the DMSO molecule [2].

The unusual conformational properties of simple sulfoxide model compounds, particularly of DMSO, have been studied with the aid of ab initio potential energy surfaces. The calculated energy surface shows a systematic pattern of "soft" and "hard" domains. In the "soft" domains relatively large changes in the molecular geometry result in unusually small variations of the calculated molecular total energy. In spite of the extensive flat regions of the potential energy surface the calculated energy barrier for the



pyramidal inversion process is relatively large, 30 kcal/mole, higher than the 24 kcal/mole barrier obtained for an analogous $R_2S{=}NQ$ sulfilimine model in an earlier study[3].

The asymmetry of the two S-Me bonds, observed in the crystalline state by X-ray method, has been analysed in terms of the local properties of various components of the molecular total energy surface.

1. C.D. Leake, Ann, N.Y. Acad. Sci., 141, 1 (1967).

2. A.E. Pekary, J. Phys. Chem., 78, 1744 (1974).

3. P.G. Mezey, A. Kucsman, G. Theodorakopoulos, I.G. Csizmadia, Theor. Chim. Acta, 38, 115 (1975).