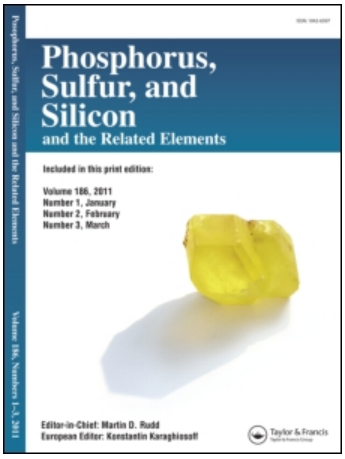

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

A NON-EMPIRICAL SCF MO STUDY ON THE GROUND STATE AND FIRST TRIPLET STATE POTENTIAL ENERGY SURFACES OF SIMPLE THIOCARBONYLS

Paul G. Mezey[a]; Ronald P. Steer[a]; Anil Kapur[a]
[a] Department of Chemistry and Chemical Engineering, University of Saskatchewan, Saskatoon, Canada

To cite this Article Mezey, Paul G. , Steer, Ronald P. and Kapur, Anil(1979) 'A NON-EMPIRICAL SCF MO STUDY ON THE GROUND STATE AND FIRST TRIPLET STATE POTENTIAL ENERGY SURFACES OF SIMPLE THIOCARBONYLS', Phosphorus, Sulfur, and Silicon and the Related Elements, 6: 1, 201 — 202
To link to this Article: DOI: 10.1080/03086647908080374
URL: http://dx.doi.org/10.1080/03086647908080374

Phosphorus and Sulfur
1979, Vol. 6, pp. 201–202

A NON-EMPIRICAL SCF MO STUDY ON THE GROUND STATE AND FIRST TRIPLET STATE POTENTIAL ENERGY SURFACES OF SIMPLE THIOCARBONYLS

Paul G. Mezey, Ronald P. Steer and Anil Kapur

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

Simple thiocarbonyls are planar in their electronic ground states but, by anology with the corresponding carbonyls, are expected to be non-planar in their S_1 and T_1 states.[1,2] Theoretical studies on the excited state geometries of these molecules are of particular interest, since the calculated potential energy surfaces may aid the interpretation of their highly structured $T_1 \leftarrow S_0$ and $S_1 \leftarrow S_0$ absorption spectra.

The geometrical features and conformational properties of small model molecules, containing the thiocarbonyl functional group have been studied with the aid of ab initio MO SCF theory. Large portions of the ground state singlet and first triplet state potential energy surfaces have been calculated and theoretical estimates have been obtained for the excited state vibrational frequencies.

The theoretical results on the triplet state vibrational frequencies show good agreement with the available experimental information obtained from the $T_1 \leftarrow S_0$ absorption spectra. The calculated triplet state double minimum potentials for the

pyramidal inversion have been analysed using a perturbation theoretical approach.[3] The calculated inversion barrier heights are of the order of $\sim$ 6-8 kcal/mole (for $F_2C{=}S$, isoelectronic with $Me_2C{=}S$, a barrier of

7.74 kcal/mole, while for FClC=S, a barrier of 5.80 kcal/mole were obtained).

REFERENCES:

1. D. C. Moule, A.K. Mehra, J. Mol. Spectorscopy, 35, 137 (1970).
2. D. C. Moule, C.R. Subramanian, Chem, Comm., 944 (1970).
3. J. B. Coon, N.W. Naugle, R. D. McKenzie, J. Mol. Spectroscopy, 20, 107 (1966).