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## 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>

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Paul G. Mezey<sup>a</sup>; Ronald P. Steer<sup>a</sup>; Anil Kapur<sup>a</sup>

<sup>a</sup> 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>

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# 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 analogy with the corresponding carbonyls, are expected to be non-planar in their  $S_1$  and  $T_1$  states.<sup>(1,2)</sup> 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.<sup>(3)</sup> 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  $\text{FCIC}=\text{S}$ , a barrier of 5.80 kcal/mole were obtained).

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