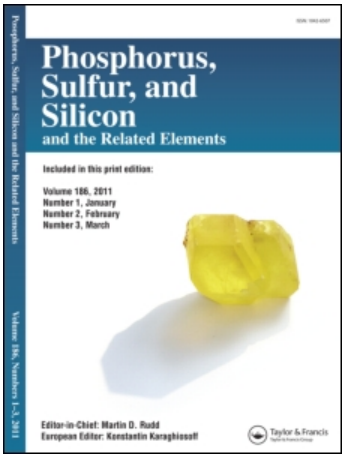

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SELENIUM-CONTAINING HYDANTOINS

Francesco A. Devillanova[a]; Francesco Isaia[a]; Gaetano Verani[a]
[a] Istituto di Chimica Generale, Inorganica ed Analitica, Cagliari, ITALY

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SELENIUM-CONTAINING HYDANTOINS

FRANCESCO A. DEVILLANOVA, FRANCESCO ISAIA AND GAETANO VERANI
Istituto di Chimica Generale, Inorganica ed Analitica, Via Ospedale 72, 09124 Cagliari, ITALY

Abstract. The influence of the exo-chalcogen atoms on the hydantoin skeleton of the complete series of molecules NH C(=X) NH C(=Y)CMe_2 (X,Y = O,S,Se) has been studied from several points of view.

INTRODUCTION

Molecules containing a hydantoin structure are of interest as drugs both for their antiepiletic and sedative activities[1]. It has been verified that the simple substitution at C-5 can enhance either activity. For this reason, we have thought that it would be of interest to prepare the complete series of hydantoin derivatives in which one, or both oxygen atoms are substituted by sulphur and/or selenium, and to study this series of molecules from several points of view.

INFRARED SPECTRA

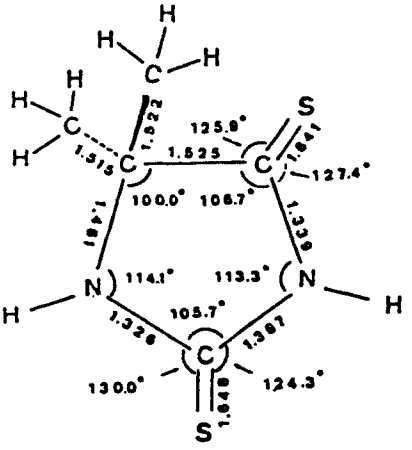
i) This investigation has been carried out for two purposes: the spectra in the solid state have been used to identify the characteristic vibrations originating from the C=S and C=Se bonds[2], using the quasi-isotopic effect of selenium with respect to sulphur as the principal tool. This study has shown that the υ(NH)'s contribute to bands falling below 550 cm^{-1};

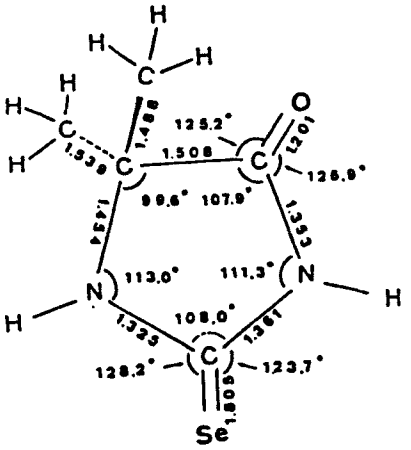
ii) the spectra in CH_2Cl_2 solution[3] have confirmed the influence of the exochalcogen atoms on the vibrational properties of the two NH groups and revealed the existence of a meaningful correlation between the υ(NH)'s and the charge densities, calculated by CNDO/2.

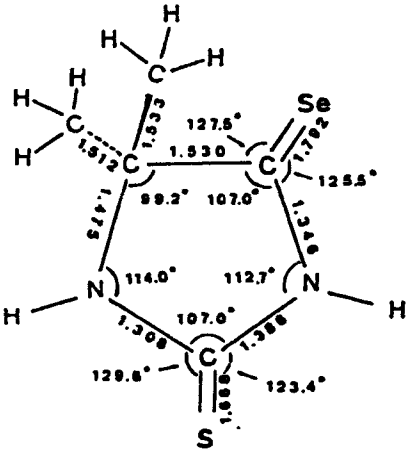
X-RAY STRUCTURES

In order to observe the influence of various chalcogen atoms on the imidazolidine ring, we have solved several X-ray structures. The verified small variations in bond distances and angles are explainable in terms of the different electronic effects of oxygen, sulphur and selenium[4].

On the basis of the structural parameters, simple HOSE calculations[5] have allowed for an evaluation of the contributions of the various resonanting forms on changing the chalcogen atoms.







ADDUCTS WITH MOLECULAR IODINE

The donor abilities of sulphur and/or selenium towards molecular iodine have been quantified by measuring the stability constants[6] of the following equilibria in CH_2Cl_2 solutions where D is an hydantoin

$$D + I_2 \rightleftarrows D\ I_2$$

of the series. In all cases, only the formation of a adduct has been verified, although two potential donor centers are present. These values reveal that the higher reactivity of the chalcogen bonded at C-2 than at C-4 (for X = Y) and to confirm that Se binds I_2 more strongly than S or O.

PHOTOELECTRONIC SPECTRA

The substitution of oxygen by sulphur or selenium is easily observable from ultraviolet photoelectron (UP) spectra. The assignment of the UP bands has been made on the basis both of CNDO/S calculations and of the two by two cross comparisons of isologous compounds, i.e., compounds which differ only with respect to a single exochalcogen atom. The validity of the assignments has been tested by correlating the B.E. of the long pairs involved in the coordination with molecular iodine[7] with the stability constants.

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