NOTA EDITORIAL

Ao iniciar as suas funções, a nova equipa editorial acha oportuno dirigir algumas palavras aos autores e leitores da Revista Portuguesa de Química. Aos autores, deseja exprimir todo o seu empenho no sentido de que a Rev. Port. Quím. possa oferecer uma publicação expedita dos artigos aceites e uma saída regular dos vários números de cada volume. Para atingir tais objectivos, os autores são convidados a seguir estritamente as normas de publicação que encontram no final de cada número. Almejando uma maior projecção para a Rev. Port. Quím., parece conveniente aos editores que os artigos sejam, na medida do possível, publicados na língua científica comummente aceite, o inglês. Isto permitirá não apenas alargar o número de leitores bem como facilitar, sempre que oportuno, a avaliação científica, por parte de especialistas estrangeiros, do conteúdo dos artigos submetidos para publicação. Aos leitores, pede-se uma análise crítica construtiva a fim de que com o empenho expresso dos editores e, certamente, da Comissão Redatorial, se possa assegurar um nível que garanta a utilidade da Rev. Port. Quím. para a comunidade Química Nacional e Internacional.

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NORMAL COORDINATE CALCULATIONS ON ROTATIONAL ISOMERS OF ETHYL DITHIOACETATE, METHYL DITHIOPROPIONATE AND *N*-ACETYLGLYCINE ETHYL DITHIOESTERS

Normal coordinate calculations have been carried out for different rotamers of ethyl dithioacetate, methyl dithiopropionate and N-*acetylglycine ethyl dithioester and a number of their isotopically substituted analogs. The results of the calculations are compared to existing experimental data. In addition, CNDO/2 calculations were performed on* $CH_3C(=X)YCH_3$ $(X, Y = O, S)$ *and* $CH_3(C=O)NHCH_2C(=S)SC_2H_5$ *in its A and B conformational states. The differences in overlap populations in the ground and first excited states offer an explanation for the extensive number of intense peaks in the RR spectra of these molecules. The calculations for the B form of* $CH_3C(=O)NHCH_2C(=S)SC_2H_5$ *provide evidence that the contact between the N and S (thiol) atoms, characteristic of conformer B, is of an attractive kind.*

INTRODUCTION

The normal coordinate analyses reported in this paper were undertaken as part of an effort to understand the vibrational properties of dithioesters. In turn, these studies are motivated by our use of dithioesters as resonance Raman (RR) probes of enzyme mechanism; the RR spectrum of a dithioester, created between a substrate and an enzyme in the active site, enables us to monitor the vibrational spectrum of the group undergoing catalytic transformation [1, 2]. In an earlier publication [3], we reported a vibrational analysis of methyl and ethyl dithioacetate, with the heavy atom skeleton in the latter compound in its planar zig-zag conformation. The resultant force field was able to reproduce the IR and Raman (and RR) spectra of various D and ^{13}C substituted analogs. A major aspect of the present work is to use this force field in the vibrational analyses of more complex dithioesters. There are two reasons for this approach; it can be used as a test of the validity of the original force field and, in addition, it can be used in an attempt to explain the experimental results for more complex dithioesters. The analysis of the spectra of complex dithioesters is concerned in large part with the characteristic vibrational spectra of different rotamers [4-8]. In the calculations detailed here we have made certain approximations concerning these rotamers *e. g.*, we have considered that rotation about a given bond occurs within the rigid rotor approximation and, moreover, that different rotamers have the same force constants. Further approximations, in common with the earlier work [3], are that a general valence harmonic force field is used and, thus, non-bonding interactions are not taken into account explicitly. In spite of these approximations it will be seen that the calculations are capable of accounting for some of the experimental features of the complex dithioester spectra and to provide useful insight into their normal mode behaviour. No attempt was made to refine the force field for the complex molecules because, although better agreement may be reached between theory and experiment, for example by adding numerous substantial off-diagonal force constants, it was felt that this would be achieved by artificially over parameterising the problem and would not provide further insight into the physical nature of the molecular vibrations.

Additionally, we have performed CNDO/2 calculations for $CH_3C(=S)SCH_3$, $CH_3C(=S)OCH_3$, $CH_3C(=O)SCH_3$ and $CH_3C(=O)OCH_3$ with a view to comparing the electron distribution of these molecules in the ground and first excited state and thereby gaining insight into the RR intensity enhancement associated with dithioesters. CNDO/2 calculations were also performed on the two preferred conformational forms, designated conformers A and B [5, 7], of $CH_3C(=O)NHCH_2C(=S)SC_2H_5$.

METHODS

The computer programs used to perform the normal coordinate analysis were adapted to a Univac Sigma 5 computer from FUHRER *et al.* [9] and are the same as in reference [3]. The conformations chosen for ethyl dithioacetate and methyl dithiopropionate (figs. 1 and 2) were based on previously considered structural parameters of methyl dithioacetate (Table 2 of ref. [3]). Methyl and methylene groups were assumed to have tetrahedral angles. Apart from the usual changes in bond lengths and bond angles, we have included four torsion coordinates around the C-C, C-S and S-C bonds and an out-of-plane wagging coordinate for C=S in the set of internal coordinates. In order to eliminate any redundant coordinates, local symmetry coordinates were considered [10].

The majority of force constants were simply transferred from a previously optimized force field for methyl dithioacetate [3] while those associated with a methyl or methylene group not directly bound to a sulphur atom were assumed to be the same as those derived for alkanes [11]. The same force constants were used in all the rotational isomers of a given compound.

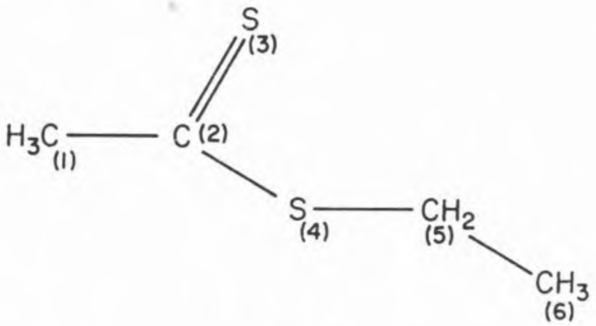

Fig. 1

Numbering of skeleton atoms for ethyl dithioacetate.

The geometry of conformer B was taken from the X-ray crystallographic analysis of *N*-acetylglycine ethyl dithioester [7] and the geometry of conformer A from the X-ray crystallographic results for *N*-(p-nitrobenzoyl) glycine ethyl dithioester [7], replacing the *p*-nitrophenyl ring of the latter by a methyl group. The same force constants, taken from [3] and [12] without further refinement, were used in both conformations. Regarding the force field for the amide group, we also tested a set of force constants taken from [13], though without significantly different results.

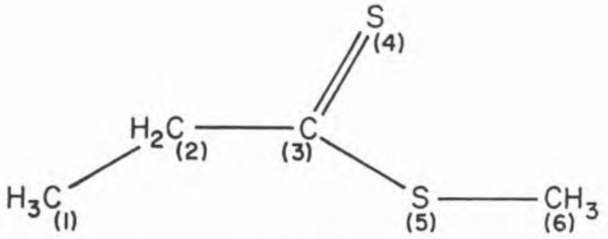

Fig. 2

Numbering of skeleton atoms for methyl dithiopropionate.

The computer program used to perform the CNDO/2 calculation was from reference [14] and the basis set of atomic orbitals included