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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 $\text{CH}_3\text{C}(=\text{X})\text{YCH}_3$ ($\text{X}, \text{Y} = \text{O}, \text{S}$) and $\text{CH}_3\text{C}(=\text{O})\text{NHCH}_2\text{C}(=\text{S})\text{SC}_2\text{H}_5$ 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 $\text{CH}_3\text{C}(=\text{O})\text{NHCH}_2\text{C}(=\text{S})\text{SC}_2\text{H}_5$ 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 $\text{CH}_3\text{C}(=\text{S})\text{SCH}_3$, $\text{CH}_3\text{C}(=\text{S})\text{OCH}_3$, $\text{CH}_3\text{C}(=\text{O})\text{SCH}_3$ and $\text{CH}_3\text{C}(=\text{O})\text{OCH}_3$ 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 $\text{CH}_3\text{C}(=\text{O})\text{NHCH}_2\text{C}(=\text{S})\text{SC}_2\text{H}_5$.

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.

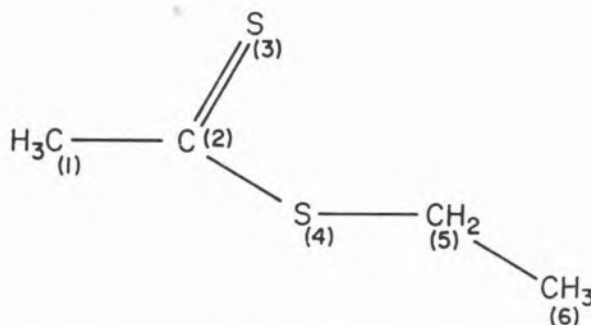


Fig. 1

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.

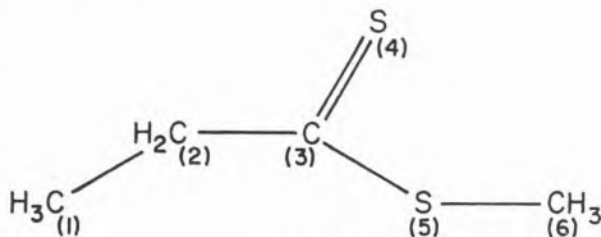


Fig. 2

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

the d -orbitals of the sulphur atoms. The «1st excited state» results mentioned in this paper refer to the electronic density obtained by promoting an electron from the highest occupied molecular orbital to the lowest unoccupied molecular orbital. These were obtained from the CNDO/2 calculation for the ground state molecule.

The electron population analyses were based in the following expressions:

$$P(\vec{r}) = \sum_i q_i d_i + \sum_{i<j} q_{ij} d_{ij},$$

where $q_i = P_{ii}$ is the i th orbital population, d_i is the i th orbital density, $q_{ij} = 2S_{ij} P_{ij}$ ($i < j$) is the i - j overlap population and d_{ij} stands for the i - j normalized overlap density, and

$$\int P(\vec{r}) dv = \sum_i q_i + \sum_{i<j} q_{ij} = n$$

where n is the total number of electrons and the integration is carried out over all the space.

For the ground state closed shell configuration the one-electron density matrix is given by

$$P = 2 T_0 \tilde{T}_0^*$$

where T_0 is the eigenvector matrix, whereas for the excited state the corresponding one-electron density matrix is given by

$$P' = T_0 \tilde{T}_0^* + T_1 \tilde{T}_1^*$$

where T_1 is the eigenvector matrix obtained by replacing the last eigenvector of T_0 that corresponds to the HOMO with the LUMO eigenvector.

In the discussion of the CNDO/2 results, the atomic charges are approximately defined as the sum, over the atomic orbitals of each atom, of the orbital populations. The overlap populations of a particular pair of interacting atoms A and B are calculated by summing the i - j overlap populations previously defined over all the i - j pairs of orbitals of atoms A and B.

RESULTS AND DISCUSSION

NORMAL COORDINATE CALCULATIONS



The normal coordinate calculations for $\text{CH}_3\text{CSSCH}_2\text{CH}_3$, $\text{CD}_3\text{CSSCH}_2\text{CH}_3$ and $\text{CH}_3\text{-CSSCD}_2\text{CH}_3$ are compared with the experimental results, taken from TEIXEIRA-DIAS *et al.* [3], in Table 1. In Table 1 the molecules are taken to be in the *s-cis*, planar zig-zag conformation, i. e., with the C(2)S(4)C(5)C(6) torsional angle = 180°. Although little significance is attached to small frequency shifts, the comparison indicates that the force field developed for $\text{CH}_3\text{CSSCH}_3$ adequately reproduces the experimental results and trends for the three analogues of $\text{CH}_3\text{CSSC}_2\text{H}_5$. The most intense features in the RR spectra [3] are accounted for thus; the intense peak near 1190 cm^{-1} is due to a mode made up of contributions from $\nu_{\text{C}=\text{S}}$ (~43 % PED) and $\nu_{\text{C}-\text{C}}$ (~31 % PED), the peak near 1100 cm^{-1} has important contributions from $\nu_{\text{C}-\text{S}}$ and C(1)-C(2) stretching, the 870 cm^{-1} mode has a high degree of C(1)H₃ rocking character, the peak near 680 cm^{-1} is a fairly pure $\nu_{\text{S}-\text{C}}$ (~71 % PED) and the peak near 580 cm^{-1} largely consists of equal contributions from $\nu_{\text{C}=\text{S}}$, $\nu_{\text{C}-\text{S}}$ and $\nu_{\text{C}(1)-\text{C}(2)}$.

Since we are interested in the way in which the vibrational signatures, especially the RR peaks, vary with conformation we investigated the effect of varying the C(2)S(4)C(5)C(6) torsional angle. X-ray crystallographic data on more complex dithioesters show that preferred values for this angle lie in the regions near 180° and 90° [8]. The results of the normal coordinate calculations are summarised in Table 2 for those modes which are known to be prominent in the RR spectrum. A major conclusion from Table 2 is that the character of the normal modes, defined on the basis of the PEDs, is little changed among the rotamers. We can now compare the experimental results for different

Table 1

Observed and calculated frequencies (cm^{-1}) and approximate assignments for $\text{CH}_3\text{CSSCH}_2\text{CH}_3$, $\text{CD}_3\text{CSSCH}_2\text{CH}_3$ and $\text{CH}_3\text{CSSCD}_2\text{CH}_3$. The calculated values are for the s-cis, planar zig-zag conformation.

$\text{CH}_3\text{CSSCH}_2\text{CH}_3$		$\text{CD}_3\text{CSSCH}_2\text{CH}_3$		$\text{CH}_3\text{CSSCD}_2\text{CH}_3$		Approximate assignments
ν_{obs}	ν_{calc}	ν_{obs}	ν_{calc}	ν_{obs}	ν_{calc}	
	2991		2991	2228	2234	as CH_2
	2975	2169	2221		2975	as CH_3^-
	2973	2100	2217		2973	as CH_3^-
	2960	2962	2960	2965	2960	as $-\text{CH}_3$
	2960		2960	2927	2960	as $-\text{CH}_3$
	2916	2924	2916	2123	2132	ss CH_2
	2911	2039	2095	2907	2911	ss CH_3^-
	2882	2872	2882	2867	2882	ss $-\text{CH}_3$
	1495		1494		1495	ad $-\text{CH}_3$
1449	1467	1452	1467	1448	1465	ad $-\text{CH}_3$
1426	1433	1038	1037	1448	1433	ad CH_3^-
1403	1409	1403	1409	990	962	s CH_2
	1400		1010		1400	ad CH_3^-
1374	1377		1377		1373	sd $-\text{CH}_3$
1360	1345		1017	1357	1345	sd CH_3^-
1271	1276		1275	840	845	w CH_2
	1210		1210		850	t CH_2
1188	1183	1192	1178	1195	1192	C = S + C_1-C_2
1102	1093	1085	1084	1105	1093	C - S + C_1-C_2
	1048		1048		1055	r $-\text{CH}_3$
	1028	971	1028		1091	r $-\text{CH}_3$
1052	1006	1051	1006	1077	1138	C_5-C_6 (ethyl)
922	916			908	916	r CH_3^-
866	864	738	679	863	864	r CH_3^-
753	819	834	820	632	668	r CH_2
682	720	680	718	665,676	686	S-C
583	599	567	575	568	598	C_1-C_2 + C = S + C-S

plus skeleton def.^a, out-of-plane wag = S, and torsions.

* as, ss = antisymmetric, symmetric stretching; ad, sd = antisymmetric, symmetric deformation, s = scissoring; w = wagging; t = twisting; r = rocking. Notation on molecular groups refers to molecule as viewed in Fig. 1 from left to right. Examples: CH_3^- refers to $\text{CH}_3-(\text{C}=\text{S})$; $-\text{CH}_3$ refers to $(\text{CH}_2-)\text{CH}_3$.

rotamers with those calculated in Table 2. The Raman spectrum of $\text{CH}_3\text{CSSC}_2\text{H}_5$ shows clear evidence for the presence of more than one rotamer; at room temperature there are peaks at 697, 681 cm^{-1} and at 589, 579 cm^{-1} whereas at -132°C only the peaks at 682 and 583 cm^{-1} remain [4, 6]. The X-ray crystallographic results for two *N*-benzoylglycine ethyl dithioesters [reference 8; and listed in Table 4] show that the ethyl group has two conformational preferences with the CH_3 in

the plane (crystalline *N*-benzoylglycine ethyl dithioester), or orthogonal to (crystalline *N*-(pClbenzoyl)glycine ethyl dithioester), the plane of the $\text{C}(=\text{S})-\text{S}-\text{C}$ skeleton. In the 550-700 cm^{-1} region the planar analog has peaks at 599 and 698 cm^{-1} while the other form has bands at 587 and 681 cm^{-1} (Table 4). The trend seen in the crystalline dithioesters for the mode near 700 cm^{-1} is reproduced in the calculations. For ethyl dithioacetate in the planar form $\text{C}(2)\text{S}(4)\text{C}(5)\text{C}(6) = 180^\circ$

Table 2

Calculated normal modes of ethyl dithioacetate known to be prominent in the RR spectrum. β is the $C_{(2)}S_{(4)}-C_{(5)}C_{(6)}$ torsional angle

s-cis, $\beta = 180^\circ$	
ν_{calc}	PED
1183	C = S(43) + C_1-C_2 (31)
1093	C - S(53) + C_1-C_2 (28)
720	S - C(71)
599	C = S(31) + C_1-C_2 (26) + C - S(22)
s-cis, $\beta = 90^\circ$	
ν_{calc}	PED
1200	C = S(32) + C_1-C_2 (23)
1165	C = S(13) + C_1-C_2 (12)
1092	C - S(52) + C_1-C_2 (28)
706	S - C(74)
600	C = S(27) + C_1-C_2 (18) + C - S(18)
s-cis, $\beta = 60^\circ$	
ν_{calc}	PED
1190	C = S(44) + C_1-C_2 (33)
1093	C - S(52) + C_1-C_2 (29)
692	S - C(72)
578	C = S(26) + C - S(25) + C_1-C_2 (24)
s-cis, $\beta = 0^\circ$	
ν_{calc}	PED
1190	C = S(45) + C_1-C_2 (33)
1095	C - S(51) + C_1-C_2 (27)
686	S - C(72)
581	C = S(27) + C - S(25) + C_1-C_2 (20)
s-trans	
ν_{calc}	PED
1208	C = S(42) + C_1-C_2 (29)
1090	C - S(55) + C_1-C_2 (25)
708	S - C(66) + C_1-C_2 (15)
615	C = S(24) + C_1-C_2 (30) + C - S(19)

ν_{S-C} is found at 720 cm^{-1} , while when this torsional angle $= 90^\circ$, ν_{S-C} is found at 706 cm^{-1} . Returning to $\text{CH}_3\text{CSSC}_2\text{H}_5$ in the liquid state, it is seen that the calculations also account for the differences in frequencies of the bands near 680 cm^{-1} in terms of the different

rotamer populations. In this case, however, there is a problem associated with assignment. In the paper by VERMA *et al.* [6] the low frequency band in the $697, 681\text{ cm}^{-1}$ pair was associated with the planar form on the basis of depolarisation measurements. This is in the reverse order suggested by the calculations. Since neither the assignment based on depolarisation measurements, nor the calculations provide a definitive solution, we are unable to decide between the two. However, the X-ray results on the complex dithioesters cannot be in question and the agreement of the calculation with the Raman results on the complex dithioester crystals gives strong support to the trends seen in the calculations.

In order to interpret the RR spectra of complex species it is necessary to investigate the effect on the vibrational spectrum of going to a *s-trans* conformation. Therefore, calculations were performed on ethyl dithioacetate in its *s-trans* form (with the $\text{H}_3\text{CC-SCH}_2$ torsional angle equal to 0°) and the results are given in Table 2. There are marked frequency differences between the *s-cis* and *s-trans* forms but it is apparent that a major reorganisation of the normal mode structure does not occur.



The results from the normal coordinate calculations for four rotamers of methyl dithiopropionate are summarized in Table 3. The Table includes only those modes containing a significant contribution from a stretching motion involving the CSSC group since these are the modes which are expected to be prominent in the RR spectrum. The rotamers chosen are the planar forms 'A' and 'B', which are analogous to the geometries found for *N*-acylglycine dithioesters [7], and two forms with a non-planar heavy atom skeleton with the torsional angle C-C-C (=S) 60° and 120° . There are considerable changes in the normal mode pattern compared to $\text{CH}_3\text{CSSCH}_3$ [3] or $\text{CH}_3\text{CSSC}_2\text{H}_5$. In the

Table 3

Calculated normal modes of methyl dithiopropionate known to be prominent in the RR spectrum. β is the $C_{(1)}S_{(2)}-C_{(3)}C_{(5)}$ torsional angle

$\beta = 0^\circ$ (form "A")	
ν_{calc}	PED
1211	$C = S(40) + C_2C_3(29)$
1090	$C - S(51) + C_2C_3(14) + C = S(10)$
728	$S - C(88)$
604	$C = S(27) + C_2C_3(23) + C - S(10)$
$\beta = 180^\circ$ (form "B")	
ν_{calc}	PED
1175	$C = S(28) + C_2C_3(28)$
1115	$C - S(46) + C_2C_3(13) + C = S(25)$
729	$S - C(88)$
586	$C = S(16) + C_2C_3(22) + C - S(28)$
$\beta = 60^\circ$	
ν_{calc}	PED
1184	$C = S(17) + C_2C_3(27) + \text{others}$
1105	$C - S(26) + C_2C_3(10) + \text{others}$
728	$S - C(86)$
633	$C = S(14) + C_2C_3(14) + \dots$
524	$C = S(16) + C_2C_3(9) + C - S(19) + \dots$
$\beta = 120^\circ$	
ν_{calc}	PED
1174	$C = S(17) + C_2C_3(31) + \text{others}$
1104	$C - S(29) + C = S(12) + \text{others}$
730	$S - C(86)$
621	$C_2C_3(12) + C - S(16) + \dots$
524	$C = S(23) + C_2C_3(10) + C - S(12) + \dots$

1000 cm^{-1} region significant C=S stretching character is shared among two or more modes. However, S-C stretch remains a highly localised mode with a PED of $\sim 88\%$ for ν_{S-C} at 730 cm^{-1} . Interestingly, the mode seen for both the planar forms near 590 cm^{-1} , containing $\nu_{C_1C_2}$, $\nu_{C=S}$, and ν_{C-S} , appears to 'split' in the non-planar rotamers to give two features near 625 and 524 cm^{-1} . This provides a possible explanation for the intense RR band at 539 cm^{-1} , seen in room temperature but not low temperature spectra, of

$\text{CH}_3\text{CH}_2\text{CSSCH}_3$ [4, 6]. Thus, the calculations suggest that the 539 cm^{-1} feature originates from a non-planar rotamer.



Several studies have been carried out on the vibrational properties of *N*-acylglycine dithioesters [5, 7, 8, 15]. These dithioesters are treated as model compounds which provide a basis for understanding and interpreting the RR spectra of enzyme intermediates containing the dithioester group [16, 17]. The model work includes Raman, RR and FTIR [18] analysis of *N*-acylglycine dithioesters in solution and, importantly, combined Raman and X-ray crystallographic analyses of single crystals [7, 8]. The latter approach is used to set up precise Raman spectra-structure correlations. In addition, a body of vibrational data is available in which D, ^{15}N and ^{13}C replacements have been made in *N*-acylglycine dithioesters in solution and in the crystalline phase [15]. The normal coordinate calculations were carried out on the simplest glycine dithioester *N*-acetylglycine ethyl dithioester. For comparison, X-ray and Raman analyses of *N*-acetylglycine ethyl dithioester single crystals have been carried out [7, 5]. This molecule crystallises in a geometry known as conformer B shown in fig. 3. The other important preferred conformer for *N*-acylglycine dithioesters is known as conformer A. It differs from B by an $\sim 150^\circ$ rotation about the $\text{NHC}-\text{C}(=\text{S})$ bond and it is shown also in fig. 3. The geometry of form A was derived from crystals of *N*(*p*- NO_2 benzoyl)glycine ethyl dithioester and the calculations were carried out by replacing the *p*- NO_2 phenyl ring by a methyl group. Most of the isotopic replacements were carried out on *N*-benzoyl or *N*-phenylpropional glycine ethyl dithioesters [15] but our experience with *N*-acylglycine ethyl dithioesters in general is sufficiently extensive that we feel confident in correlating the results for the former compounds with the calculations on the *N*-acetyl derivative.

Table 4

Experimental and theoretical results for conformer B

Com- pound *	Spectrum, solvent	$\tilde{\nu}_{\text{obs}} / \text{cm}^{-1}$				Band type	$\tilde{\nu}_{\text{calc}} / \text{cm}^{-1}$				PED for non-isot.
		non-isot.	^{13}C	^{15}N	ND		non-isot.	^{13}C	^{15}N	ND	
3	R (crystal)	1141				II					
1	RR, CH_3CN	1124	1100	1123	1128	II					
1	R (crystal)	1120	1103	1119		II					
5	RR, CH_3CN	1132	1115/1079	1131	1132	II	1227	1203	1224	1222	C=S(28)+C—C(27)+N—C(14)
3	R (crystal)	1088				III					
5	RR, CH_3CN	1085	1068	1082	1097	III	1121	1105	1118	1116	C—S(28)+C=S(13)+N—C(13)
1	R (crystal)	1052				?					
1	RR, CH_3CN	1038	1035	1037	1038	?	1044	1028	1038	1033	C—S(24)+C—C(12)+others
5	RR, CH_3CN	1040	1037	1041	1042	?					
3	R (crystal)	698				ν (S-C)					
1	R (crystal)	698	696	696		ν (S-C)	737	736	734	735	S—C(27)+NCC(22)+others
5	R (crystal)	697				ν (S-C)					
7	R (crystal)	681				ν (S-C)	703	702	700	698	S—C(44)+SCC(14)+others
3	R (crystal)	617 584 502									
1	R (crystal)	599 538	596 548	597 533			532	531	529	526	skel.def.(35)+C=S(12)+others
5	R (crystal)	613 574 532					434	433	433	432	skel.def.(19)+C=S(17)+others
7	R (crystal)	587 549									

* 1 = $\text{PhC}(=\text{O})\text{NHCH}_2\overset{\text{S}}{\underset{\text{||}}{\text{C}}}\text{SC}_2\text{H}_5$; 3 = $\text{CH}_3\text{C}(=\text{O})\text{NHCH}_2\overset{\text{S}}{\underset{\text{||}}{\text{C}}}\text{SC}_2\text{H}_5$; 5 = $\text{PhCH}_2\text{CH}_2\text{C}(=\text{O})\text{NHCH}_2\overset{\text{S}}{\underset{\text{||}}{\text{C}}}\text{SC}_2\text{H}_5$; 7 = $p\text{ClPhC}(=\text{O})\text{NHCH}_2\overset{\text{S}}{\underset{\text{||}}{\text{C}}}\text{SC}_2\text{H}_5$.

The results of the calculations are compared with the experimental data for forms B and A in Tables 4 and 5, respectively. For conformer B the calculated mode at 1227 cm^{-1} with contributions from $\nu_{\text{C}=\text{S}}$, $\nu_{\text{C}-\text{C}}$ and $\nu_{\text{N}-\text{C}}$, likely corresponds to the experimental RR peak in the 1135 cm^{-1} region designated as Band II [16]. The mode at 1121 cm^{-1} , with $\nu_{\text{C}-\text{S}}$, $\nu_{\text{C}=\text{S}}$ and $\nu_{\text{N}-\text{C}}$ components, probably corresponds to the experimental peak near 1085 cm^{-1} , designated Band III [16]. The agreement in the shifts of Band II and III upon ^{13}C substitution in $\text{C}=\text{S}$

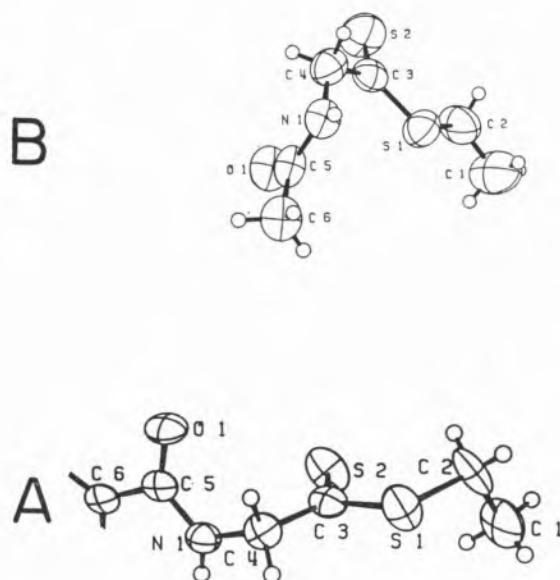


Fig. 3

Geometries of conformers A and B.

is particularly good. The agreement in shifts of the band near 1050 cm^{-1} on ^{13}C replacement is less satisfactory, the experimental peak shows a very small shift of $\approx 3\text{ cm}^{-1}$ in the ^{13}C compound whereas the calculation indicates a 16 cm^{-1} change. As in the case of the dialkyl dithioesters the calculation indicates that the S-C stretching motion makes a substantial contribution to modes in the 700 cm^{-1} region. However, for the conformer B *N*-acetyl analog there are two features with substantial $\nu_{\text{S}-\text{C}}$ in the PED, compared to one in the dialkyl calcula-

tions. In the experimental data, e. g. for $\text{PhC}(=\text{O})\text{NHCH}_2\text{C}(=\text{S})\text{SC}_2\text{H}_5$ in fig. 5 of reference [8], there is evidence for more than one peak in the 700 cm^{-1} region. In all likelihood the most intense peak in this range should be associated with the calculated mode having the highest $\nu_{\text{S}-\text{C}}$ PED contribution. Although some of the RR signatures in the $550\text{--}650\text{ cm}^{-1}$ region for conformer B have been established empirically [15] the agreement between experiment and calculations in Table 4 is poor.

The calculations for conformer A summarised in Table 5 make an interesting comparison to those for conformer B. The intense RR feature near 1165 cm^{-1} , designated Band I [5], probably corresponds to the calculated mode at 1251 cm^{-1} . There are two trends seen for the calculations which agree with experiment; Band I for conformer A is found at a higher frequency than Band II, the corresponding peak for conformer B, and the shift in Band I upon ^{13}C substitution is greater than for Band II. Also, while there is a suitable candidate for Band III in the conformer B calculations, an analogous mode is not found for conformer A, again in agreement with experiment.

For conformer A the contribution from $\nu_{\text{S}-\text{C}}$ is more localised than in conformer B with the calculated mode at 672 cm^{-1} containing a 60 % contribution from $\nu_{\text{S}-\text{C}}$ according to the PED. The results on Band I and the $\nu_{\text{S}-\text{C}}$ mode suggest that the modes for conformer A are, in some cases, more localised compared to those of the B conformer. As in the case of conformer B there is poor agreement between experiment and calculations regarding the $400\text{--}650\text{ cm}^{-1}$ region for conformer A.

At this point it is worth noting that the correlations between theory and experiment discussed above were obtained without any attempt to refine the force field beyond that used for the simple dialkyl dithioesters and *N*-methyl acetamide. The approximations accompanying this approach were outlined in the Introduction. Doubtless better agreement between calculations and experimental spec-

Table 5

Experimental and theoretical results for conformer A

Com- pound *	Spectrum, solvent	$\nu_{\text{obs}}/\text{cm}^{-1}$				Band type	$\nu_{\text{calc}}/\text{cm}^{-1}$				PED for non-isot.
		non-isot.	^{13}C	^{15}N	ND		non-isot.	^{13}C	^{15}N	ND	
1	RR, CH_3CN	1165	1134	1162	1163	I	1251	1222	1250	1249	C = S(36) + C-C(30)
5	RR, CH_3CN	1165	1136	1165	1165	I					
8	R (crystal)	1170				I					
1	RR, CH_3CN	~685 ~660	—	—	—	—	672	672	671	672	S-C(60)
5	RR, CH_3CN	~685 ~665	—	—	—	—					
8	R (crystal)	~680 ~660	—	—	—	—					

* 1 = $\text{PhC}(=\text{O})\text{NHCH}_2\overset{\text{S}}{\underset{\parallel}{\text{C}}}\text{SC}_2\text{H}_5$; 5 = $\text{PhCH}_2\text{CH}_2\text{C}(=\text{O})\text{NHCH}_2\overset{\text{S}}{\underset{\parallel}{\text{C}}}\text{SC}_2\text{H}_5$; 8 = $p\text{NO}_2\text{PhC}(=\text{O})\text{NHCH}_2\overset{\text{S}}{\underset{\parallel}{\text{C}}}\text{SC}_2\text{H}_5$.

tra would be achieved by, for example, introducing more off-diagonal force constants. However, given the paucity of the experimental data base, we feel that a refinement of the force field along these lines is physically unrealistic and could do nothing to improve our insight into the molecular vibrations. A more fruitful approach might be to develop a force field from molecular mechanics methods — the so-called consistent force field approach.

MOLECULAR ORBITAL CALCULATIONS

$\text{CH}_3\text{C}(=\text{X})\text{YCH}_3$ (X, Y = S, O)

The π -overlap populations for simple dimethyl dithioesters, thionoesters, thiolesters and dioxygen esters are compared in fig. 4. Sulfur d orbitals were included in the calculations since it has been shown that the $3d\pi$ orbitals contribute significantly to local molecular properties such as charge distri-

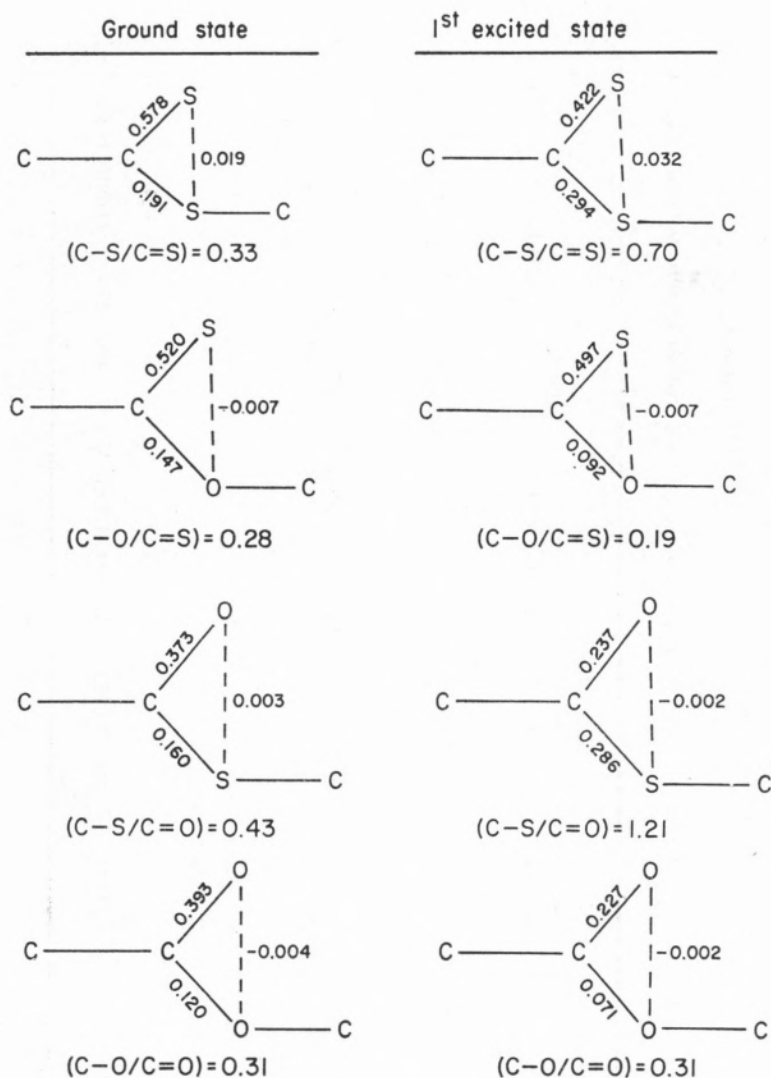


Fig. 4

Total π -overlap population ($q_{ij} = q_{ij}^{p\pi} + q_{ij}^{d\pi}$) for $\text{CH}_3\text{C}(=\text{X})\text{YCH}_3$, (X, Y = O, S).

bution [19]. The CNDO/2 calculations for the dithioesters show that there is significant π -overlap in both the formal C=S and C-S linkages and that the overlap changes markedly upon going from the ground to the first excited state. These results explain why

state, and when suitable excitation sources become available in the UV (thiol esters have an intense $\pi \rightarrow \pi^*$ transition in the 230 nm range) it will be worthwhile to compare the RR spectra of dithio and thiol esters. For the dithioesters it is noteworthy that there is

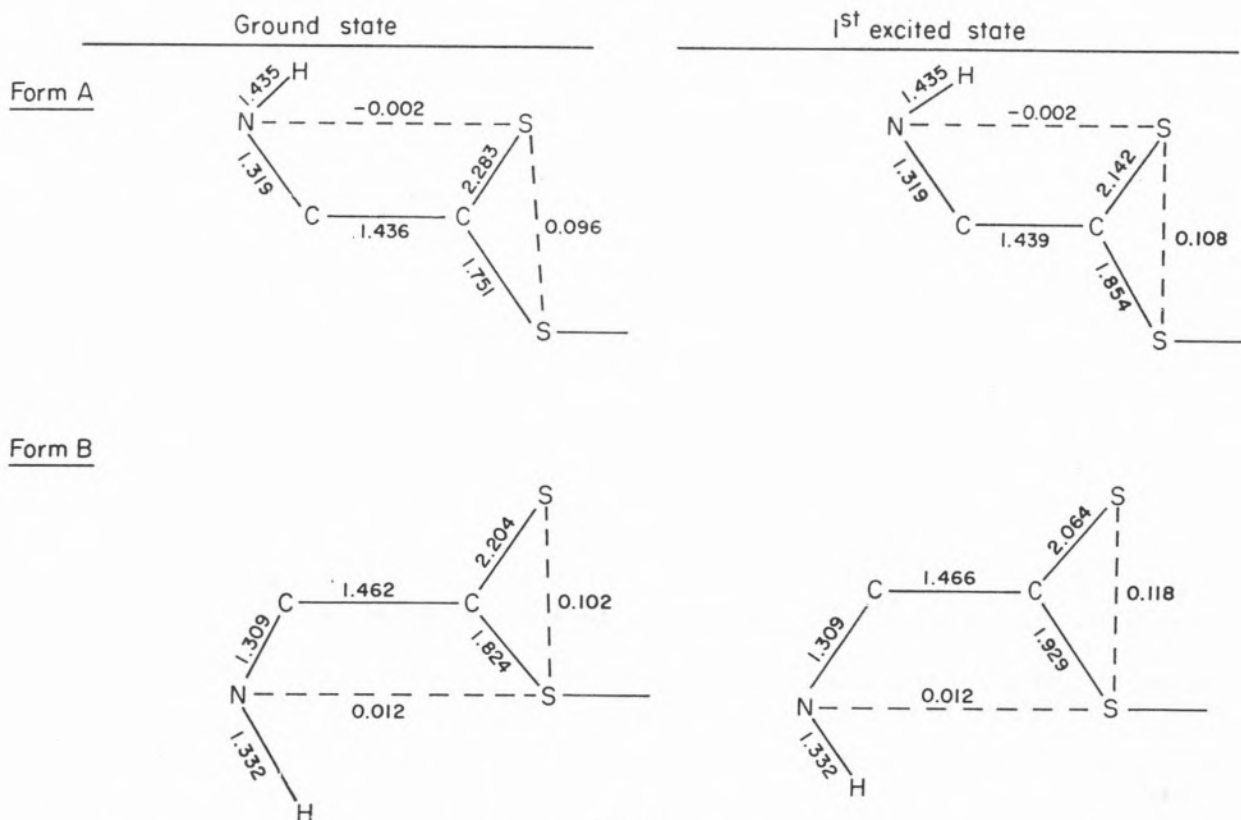


Fig. 5

Total overlap populations ($q_{AB} = \sum_{i \in A} \sum_{j \in B} q_{ij}$) of conformers A and B of $\text{CH}_3\text{C}(=\text{O})\text{NHCH}_2\text{C}(=\text{S})\text{SC}_2\text{H}_5$.

the thiol sulphur must be considered as part of the chromophore and why significant RR intensity enhancement is observed for modes involving the C-S linkage [3]. Overlap changes are taken as an indication that bond length changes will occur upon going to the excited state and it is known the RR enhancement is maximal for normal coordinates which distort the molecular geometry in the direction taken in going from the ground to the excited state [20]. Qualitatively similar π -overlap changes occur for thiol esters upon going to the first excited

state, and especially the first excited state.



The total overlap populations of conformers A and B of $\text{CH}_3\text{C}(=\text{O})\text{NHCH}_2\text{C}(=\text{S})\text{SCH}_2\text{CH}_3$ are shown in fig. 5. For both conformers significant changes occur in the overlap populations of the C=S and C-S bonds upon going to the excited state accounting, as in the case of simple dithioesters, for the delocalised nature of the RR and electronic

chromophore. The changes in overlap populations are similar for both conformers, suggesting that the RR intensity enhancement is similar in both cases.

The non-bonding N...S interaction is an important facet of conformer B. Evidence has been presented that this is an attractive LUMO-HOMO contact involving the lone pair on the nitrogen (HOMO) and the σ^* orbital of the S-C bond (LUMO) [8]. The CNDO/2 calculations support the notion that the interaction is attractive since there is a small positive overlap population of 0.012 units between the N and S for conformer B. In conformer A there is a very small negative value between the N and thiono S atom indicating that there is not an attractive interaction in this case.

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RESUMO

Cálculos de coordenadas normais em isômeros rotacionais do ditioacetato de etilo, ditiopropionato de metilo e ditioésteres de etilo da N-acetilglicina

Efectuam-se cálculos de coordenadas normais para diferentes isômeros rotacionais do ditioacetato de etilo, ditiopropionato de metilo, ditioésteres de etilo da N-acetilglicina e alguns derivados substituídos isotopicamente destas moléculas. Os resultados dos cálculos são comparados com os dados experimentais existentes. Além disso, realizam-se cálculos CNDO/2 em $\text{CH}_3\text{C}(=\text{X})\text{YCH}_3$ ($\text{X}, \text{Y} = \text{O}, \text{S}$) e nos confôrmeros A e B de $\text{CH}_3\text{C}(=\text{O})\text{NHCH}_2\text{C}(=\text{S})\text{SC}_2\text{H}_5$. As diferenças nas populações de sobreposição entre o estado fundamental e o primeiro estado excitado permitem uma explicação da existência de elevado número de picos intensos nos espectros de ressonância Raman destas moléculas. Os cálculos para a forma B de $\text{CH}_3\text{C}(=\text{O})\text{NHCH}_2\text{C}(=\text{S})\text{SC}_2\text{H}_5$ mostram que o contacto entre os átomos N e S (tiol), característico do confôrmero B, é de tipo atractivo.