Oxygen-by-sulfur substitutions in glycine: conformational and vibrational effects †

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Molecular geometries, energies, dipole moments and atomic charges of several conformations of glycine ($NH_2CH_2C(=O)OH$) and its oxygen-by-sulfur substituted analogues ($NH_2CH_2C(=O)SH$, $NH_2CH_2C(=S)OH$ and $NH_2CH_2C(=S)SH$) were determined by *ab initio* MO calculations at the MP2/6-31G** level, and vibrational frequencies, infrared and Raman intensities were evaluated within the harmonic approximation, at the HF/6-31G** level. Profiles for the potential energy and several geometric parameters as a function of the NC–C(=X) (X = O, S) dihedral angle (C–C internal rotation) were obtained using the 3-21G(N*) basis set. Conformational and vibrational effects of oxygen-by-sulfur substitutions are discussed. In particular, the occurrence of intramolecular close contacts between the NH_2CH_2– and –$C(=X)YH$ (X, Y = O or S) moieties of the molecule is considered, for some of the most stable conformations of each analogue. As a general trend, the results clearly point to the stabilisation of the *G/anti* forms (:NCC ≅ 60°, NCCX ≅ 180°), highlighting the importance of the N:···H(Y) and N:···S(H) interactions, *e.g.* in conformers *G/anti/s-trans* for the thione form (X = S) and *G/anti/s-cis* for the thiol one (Y = S), respectively.

Introduction

Glycine (NH_2CH_2COOH), the simplest amino acid and a prototype structural unit for other amino acids and proteins, has been the subject of numerous studies over the years.[1–29] Its conformational degrees of freedom are related to internal rotations about the N–C, C–C and C–O bonds, which can be described, respectively, by the :N–CC, NC–C(=O) and (O=)C–OH dihedral angles (: standing for the nitrogen lone pair). These angles can take the following typical values (Fig. 1): *i*) :N–CC—*A* (*anti*, 180°), *G* (*gauche*, ±60°) or *S* (*syn*, 0°); *ii*) NC–C(=O)—*anti* (180°), *skew* (±120°) or *syn* (0°); *iii*) (O=)C–OH—*s-cis* (0°) or *s-trans* (180°). A prime is used to denote a negative dihedral angle. Each particular conformation will then be described by the values of :N–CC, NC–C(=O) and (O=)C–OH, in this order: thus, *A/syn/s-cis*, for instance, refers to the geometry where :N–CC is *A*, NC–C(=O) is *syn* and (O=)C–OH is *s-cis*.

Previously reported microwave studies on glycine yielded *S/anti/s-trans* as the predominant form in the gas phase.[3,4,6] In this conformation, a hydrogen bond type interaction N···HO is formed, leading to the formation of a five-membered ring $N(H_2)$–$C(H_2)$–C–O–H. *Ab initio* MO calculations[1,2] as well as joint experimental–theoretical studies,[8] on the other hand, found *A/syn/s-cis* as the lowest energy conformer for glycine. In this form, a NH_2···O(=) interaction is formed, closing the five-membered ring H_2N–$C(H_2)$–C=O, with the nitrogen bonded H atoms standing above and below the ring plane.

A more recent study by electron diffraction techniques on gaseous glycine[19] has also found *A/syn/s-cis* as the most stable
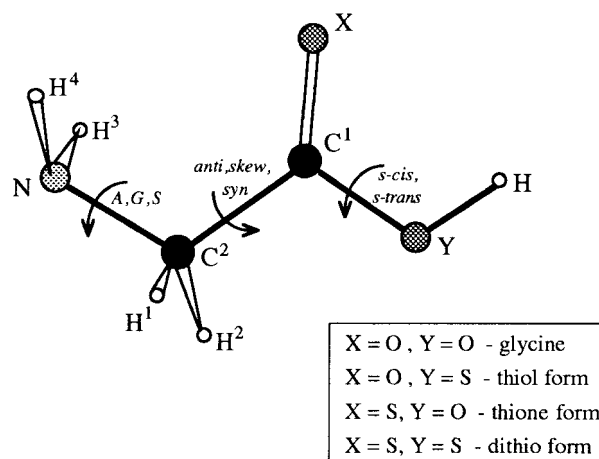

X = O , Y = O - glycine
X = O , Y = S - thiol form
X = S , Y = O - thione form
X = S , Y = S - dithio form

Fig. 1 Schematic representation of the glycine molecule and its sulfur analogues, $NH_2CH_2C(=X)YH$ (X, Y = O or S).

conformation, apart from a minor component probably consisting of a mixture of *S/anti/s-trans* and *A/anti/s-cis* structures. It should not be forgotten that the low electric dipole moment of *A/syn/s-cis* renders its detection by microwave spectroscopy more difficult, which can explain the reported contradictory results.[5,8] In turn, an infra-red study of glycine isolated in inert gas matrices[26] led to the detection of some of the conformations predicted by *ab initio* calculations, while experiments using a free-expansion jet microwave spectrometer[27,28] allowed the observation of higher energy conformers.

In a thorough *ab initio* conformational study performed for glycine[17] it was concluded that *S/anti/s-trans* and *A/anti/s-cis* forms have higher energies than their *gauche* counterparts *G/anti/s-trans* and *G/anti/s-cis*. However, sensitivity of the conformational energy differences to the basis set has to be taken into account. Thus, some recent theoretical works have been reported on the ground state potential energy surface of this

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Table 1 Conformational energies for the $NH_2CH_2C(=X)YH$ (X, Y = O or S) molecules

Molecule		Energy differences/kJ mol^{-1} [a]				Energy barriers/kJ mol^{-1}	
		3-21G(N*)	3-21G(N*,S*)	6-31G**	MP2/6-31G**		
$NH_2CH_2C(=O)OH$	A/anti/s-cis	7.58	—	8.00	6.95	A/syn/s-cis→	
	A/syn/s-trans	34.19	—	28.96	26.09	→A/anti/s-cis	19.10 [b]
	A/anti/s-trans	48.23	—	37.53	33.50	G/anti/s-trans→	
	G/syn/s-cis	11.88	—	8.57	8.52	→G'/anti/s-trans	0.99 [c]
	G/skew'/s-cis	15.07	—	13.02	12.82		
	G/syn/s-trans	—[d]	—	38.42	35.64		
	G/anti/s-trans	16.44	—	12.58	5.87		
$NH_2CH_2C(=O)SH$	A/anti/s-cis	1.96	2.68	4.16	0.78	A/syn/s-cis→	
	A/syn/s-trans	13.35	9.14	5.87	6.40	→A/anti/s-cis	14.13 [b]
	A/anti/s-trans	29.02	25.93	20.71	21.42	G/anti/s-trans→	
	G/syn/s-cis	12.38	11.92	9.00	8.87	→G'/anti/s-trans	2.87 [c]
	G/anti/s-cis	6.04	−0.15	4.38	1.92	G/anti/s-cis→	
	G/syn/s-trans	26.96	—[d]	16.70	17.48	→G'/anti/s-cis	2.19 [c]
	G/anti/s-trans	14.57	10.14	8.74	5.72		
$NH_2CH_2C(=S)OH$	A/anti/s-cis	7.21	6.86	7.40	7.91	A/syn/s-cis→	
	A/syn/s-trans	36.17	39.52	31.36	25.95	→A/anti/s-cis	15.51 [b]
	A/anti/s-trans	46.35	45.80	—[d]	31.92	G/anti/s-trans→	
	G/syn/s-cis	17.19	16.48	12.63	11.65	→G'/anti/s-trans	0.51 [c]
	G/skew'/s-cis	17.39	16.60	13.21	13.17		
	G/syn/s-trans	56.59	54.92	46.04	39.98		
	G/anti/s-trans	8.75	9.94	8.64	0.77		
$NH_2CH_2C(=S)SH$	A/anti/s-cis	4.19	3.25	4.80	3.43	A/syn/s-cis→	
	A/syn/s-trans	11.25	6.06	5.23	3.79	→A/anti/s-cis	10.98 [b]
	A/anti/s-trans	27.49	22.36	20.94	18.53	G/anti/s-trans→	
	G/syn/s-cis	17.56	17.47	12.45	11.69	→G'/anti/s-trans	3.76 [c]
	G/anti/s-cis	5.86	0.13	3.58	2.16	G/anti/s-cis→	
	G/syn/s-trans	30.68	25.69	20.58	18.82	→G'/anti/s-cis	3.26 [c]
	G/anti/s-trans	8.84	5.08	5.81	1.62		

[a] Relative to the most stable conformer *A/syn/s-cis*. [b] Calculated at the 3-21G(N*) level. [c] Calculated at the MP2/6-31G** level. [d] Does not converge with this basis set.

amino acid, exploring the effect of basis set improvement and better treatment of electron correlation, from the MP2, MP3 and MP4 optimizations of Császár,[24] to the studies of Hu *et al.* at the CISD/DZP level of theory,[25] and Nguyen *et al.* using density functional theory (DFT).[29]

The present work deals with conformational and vibrational effects of oxygen-by-sulfur substitutions in glycine. $NH_2CH_2C(=X)YH$ (X, Y = O or S) molecules ((O,O), (O,S), (S,O) and (S,S)) are studied by *ab initio* MO calculations, at the MP2/6-31G** level, and the C–C internal rotation is analysed using the 3-21G(N*) basis set. Characterisation of several intramolecular interactions, namely N:···Y, N:···HY, $(N)H_2···X=$ and $(N)H_2···Y$, and evaluation of their relative contributions are particularly important for understanding the conformational behaviour of α-amino substituted carbonylic and thiocarbonylic compounds. In particular, these interactions are of crucial importance in enzymatic processes involving this kind of molecule. The fact that oxygen-by-sulfur substitutions have been systematically used in Raman spectroscopic biochemical studies, with the aim of generating chromophores acting as resonance Raman probes in the active sites of enzyme–substrate complexes,[30,31] adds to the practical relevance of the study herein carried out.

Computational methods

Ab initio MO calculations were carried out using the GAUSSIAN 94[32] program, with the split valence basis sets 3-21G+d($\zeta_N = 0.8$) (abbreviated 3-21G(N*)), 3-21G+d($\zeta_N = 0.8$; $\zeta_S = 0.65$) (abbreviated 3-21G(N*,S*))[33,34] and 6-31G**,[35,36] at the Hartree–Fock (HF) level, and 6-31G** using second-order Möller–Plesset perturbation theory (MP2). Molecular geometries were fully optimized by the Berny algorithm using redundant internal coordinates:[37] the bond lengths to within

ca. 0.1 pm and the bond angles to within *ca.* 0.1°. The final root-mean-square (rms) gradients were always less than 3×10^{-4} hartree bohr^{-1} or hartree radian^{-1}.

In the compounds under study, the relevant dihedral angles (Fig. 1) should adopt values around 0°, ±60° or 180° for :N–CC; 0°, ±120° or 180° for NC–C(=X); and 0° or 180° for (X=C)–YH. In order to study the C–C internal rotation, the geometries were optimized for different fixed NC–C(=X) dihedral angles.

Calculation of the vibrational spectra was carried out at the HF/6-31G** level, as inclusion of electronic correlation was found not to pay for extra computing time and disk space requirements.

The graphical representation of the potential-energy and structural parameter variations were based on least-squares fitted Fourier-type functions of a torsional angle [eqn. (1)],

$$P = P_0 + \Sigma_{(n=1,3)} \tfrac{1}{2} P_n [1 - \cos(n\theta)] \qquad (1)$$

where θ is the NC–C(=X) (X = O or S) dihedral angle and P are functional values that may correspond to potential energy (V), bond distance or bond angle differences relative to a reference value (P_0 is the parameter corresponding to a NC–C(=X) angle of 0°).

Results and discussion

Stable conformations and intramolecular interactions

Table 1 lists the conformational energy differences of the distinct conformers of the $NH_2CH_2C(=X)YH$ molecules (X, Y = O or S) (Fig. 2), as well as the energy barriers corresponding to some of their elementary internal rotations. Conformational energy minima, not separated by more than 15 kJ mol^{-1} from the most stable conformer, *A/syn/s-cis*, are shown in Fig. 3.
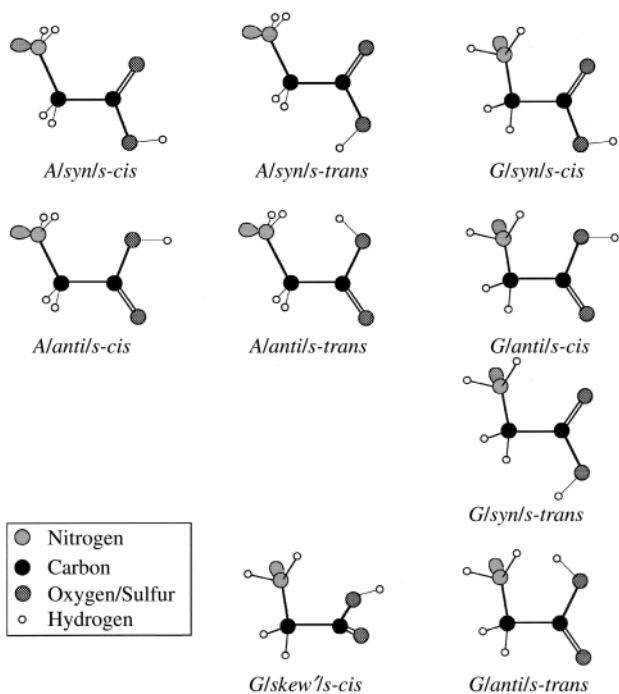
Fig. 2 Schematic representation of the different conformations found for the NH$_2$CH$_2$C(=X)YH (X, Y = O or S) molecules.
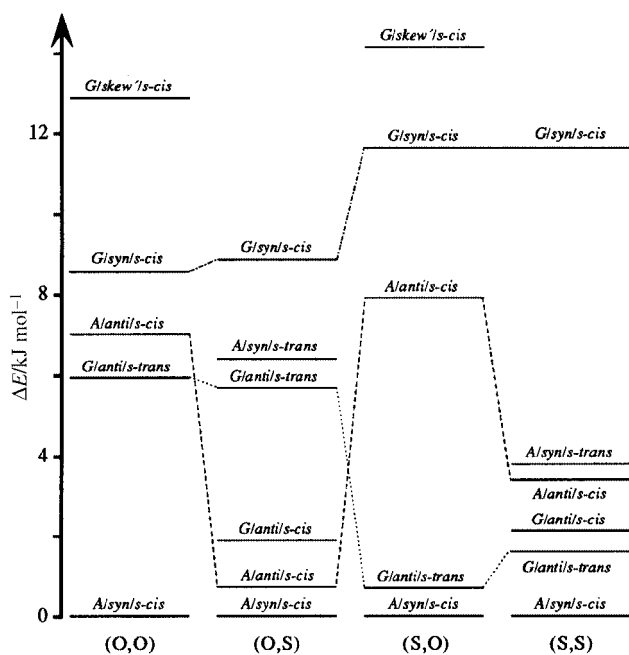
Fig. 3 Schematic representation of the relative energies of the most stable conformers of the NH$_2$CH$_2$C(=X)YH (X, Y = O or S) molecules (at the MP2/6-31G** level of calculation).

It was verified that all the **:**N–CC *syn* (S) conformations are first order saddle points. Tables 2 and 3 comprise the optimized geometries, as well as the Mulliken atomic charges and dipole moments calculated for the *A*/*syn*/*s-cis* conformers.

Oxygen-by-sulfur substitutions were found to cause shifts in the conformational energy levels of the molecules under study. In some cases, these shifts are sensitive to a particular type of substitution, either in the X or the Y atom. Thus, the energy difference between conformers *G*/*syn*/*s-cis* and *A*/*syn*/*s-cis*, *i.e.*, (*G* − *A*)/*syn*/*s-cis* — 8.5 kJ mol^{-1} for (O,O), 8.9 for (O,S), 11.7 for (S,O) and 11.7 for (S,S) (Table 1, Fig. 3) — is almost insensitive to the oxygen-by-sulfur substitution in the Y position, but it increases by *ca.* 3 kJ mol^{-1} due to the presence of a thione sulfur atom. In fact, for X = O there is evidence of a significant stabilising attractive =O · · · H(N) interaction (favoured by the

Table 2 Optimized geometries for the most stable conformer (*A*/*syn*/*s-cis*) of the NH$_2$CH$_2$C(=X)YH (X, Y = O or S) molecules[a]

	(O,O)	(O,S)	(S,O)	(S,S)
Bond lengths/pm				
C^1=X	121.8	121.8	162.9	162.8
C^1–C^2	151.7	152.6	151.7	153.0
C^1–Y	135.9	179.9	134.8	176.0
Y–H	97.1	133.2	97.2	133.2
C^2–H^1	109.1	109.2	109.3	109.3
C^2–H^2	109.1	109.2	109.3	109.3
N–C^2	145.0	144.8	144.5	144.4
N–H^3	101.5	101.4	101.4	101.5
N–H^4	101.5	101.4	101.4	101.5
Bond angles/°				
C^2–C^1=X	125.4	123.4	126.5	124.1
X=C^1–Y	123.3	123.0	124.2	124.9
C^1–Y–H	105.7	93.2	107.0	95.6
C^1–C^2–H^1	107.8	108.0	106.8	107.4
C^1–C^2–H^2	107.8	108.0	106.8	107.4
N–C^2–C^1	114.8	114.6	117.7	117.5
C^2–N–H^3	108.6	108.9	109.1	109.2
C^2–N–H^4	108.6	108.9	109.1	109.2
C^2–C^1–Y	111.3	113.6	109.3	111.0
Dihedral angles/°				
H^1–C^2–C^1=X	−122.9	−122.7	−123.5	−123.0
H^2–C^2–C^1=X	122.9	122.7	123.5	123.0
N–C^2–C^1=X	0.0	0.0	0.0	0.0
H^3–N–C^2–C^1	56.7	57.0	57.3	57.3
H^4–N–C^2–C^1	−56.7	−57.0	−57.3	−57.3
H–Y–C^1–C^2	180.0	180.0	180.0	180.0

[a] The atoms are numbered according to Fig. 1.

Table 3 Atomic charges and dipole moments (μ) for the most stable conformer (*A*/*syn*/*s-cis*) of the NH$_2$CH$_2$C(=X)YH (X, Y = O or S) molecules

	(O,O)	(O,S)	(S,O)	(S,S)
Atomic charge/e[a]				
C^1	0.727	0.320	0.250	−0.215
X(=C^1)	−0.579	−0.519	−0.228	−0.147
C^2	−0.120	−0.118	−0.071	−0.059
Y(–H)	−0.611	0.014	−0.562	0.109
H(–Y)	0.371	0.093	0.387	0.093
H^1	0.166	0.163	0.170	0.165
H^2	0.166	0.163	0.170	0.165
N	−0.675	−0.675	−0.680	−0.677
H^3	0.278	0.280	0.282	0.283
H^4	0.278	0.280	0.282	0.283
μ/D[d]	1.36	0.99	1.47	1.31

[a] e = 1.6021982 × 10^{-19} C. [b] 1 D = $\frac{1}{3}$ × 10^{-2} Cm.

large negative charge on the oxygen atom), leading to a rotation of the amine group and an approach between (N)H^3 and O= — H^{3}NC^{2}C^1 *ca.* −46°, NC^{2}C^1=O *ca.* 27°, H^3· · ·O= *ca.* 240 pm while the sum of the corresponding van der Waals radii is equal to 260 pm. For the (S,O) and (S,S) molecules, in turn, this conformational rearrangement is not as significant — H^{3}NC^{2}C^1 *ca.* −56°, H^3· · ·S= *ca.* 270 pm (sum of the van der Waals radii 305 pm).

Similarly, the (*G*/*anti*/*s-trans*) − (*A*/*syn*/*s-cis*) energy difference — 5.9 kJ mol^{-1} for (O,O), 5.7 for (O,S), 0.8 for (S,O) and 1.6 for (S,S) (Table 1, Fig. 3) — discriminates against oxygen-by-sulfur substitutions in the same way as in the previous case: (O,O), (O,S) *vs.* (S,O), (S,S). It was verified that this conformational energy difference is reduced by 4 to 5 kJ mol^{-1} when a thione sulfur atom is introduced in the molecule, for an *anti* NC–C(=X) dihedral angle. In fact, for X = S the steric repulsion

between N and X leads to a relative stabilisation of the *G*/*anti*/*s-trans* form, where these two atoms stand well apart (Fig. 2). Also, the effect of electronic correlation, detected by comparing the HF/6-31G** and MP2/6-31G** energy values (Table 1), is worth noticing, as introduction of correlation leads to a clear stabilisation of the X = S molecules, *i.e.*, distinguishes between (O,O) and (O,S) systems *vs.* (S,O) and (S,S).

On the other hand, conformation *A*/*syn*/*s-trans* is strongly stabilised by the introduction of a thiol atom. In fact, the corresponding energy differences from the most stable conformer, *A*/*syn*/*s-cis*, are: 26.1 kJ mol^{-1} for (O,O), 6.4 for (O,S), 26.0 for (S,O) and 3.8 for (S,S) (Table 1). These values highlight the fact that the energy difference for this *s-cis→s-trans* rearrangement is substantially lowered when Y is a sulfur atom, thus suggesting a reduction in the C–Y double bond character, *i.e.* a decrease of the mesomeric effect in the thiol analogues, due to the lower conjugating properties of the sulfur 3p orbitals relative to the oxygen 2p orbitals. This gives rise to a weaker S–H $\cdots$ X intramolecular hydrogen bond interaction as compared to the O–H $\cdots$ X one, and a smaller stabilisation of the *s-cis* conformations.

In contrast to the (O,S) and (S,S) systems, the *G*/*anti*/*s-cis* conformation was found not to be an energy minimum for the (O,O) and (S,O) molecules. Instead, the similar geometry *G*/*skew'*/*s-cis* was obtained as a conformer for the latter. In fact for Y = O there is both a N $\cdots$ Y repulsive interaction and an attractive (N)H^3 $\cdots$ Y one, reflected in the rotation of the C(=X)YH molecular fragment (leading to a *skew'* NCC=X angle), H^3 $\cdots$ Y being equal to 242 pm while the sum of the corresponding van der Waals radii is 260 pm. When Y = S a N $\cdots$ S close contact occurs (Fig. 2), which is responsible for the stabilisation of the *G*/*anti*/*s-cis* form. This approach between the nitrogen lone-pair and the Y sulfur atom in *G*/*anti*/*s-cis*, and between the H^3 and Y atoms (for Y = O), is evidenced by the values of the relevant dihedral angles: NCC(=O) = 164.6°, H^{3}NCC = −83.8° and H^{4}NCC = 156.6° for the (O,S) molecule *vs.* NCC(=O) = −136.5°, H^{3}NCC = −63.7° and H^{4}NCC = 179.8° for the (O,O) one; and NCC(=S) = 158.4°, H^{3}NCC = −80.8° and H^{4}NCC = 160.3° for the (S,S) compound *vs.* NCC(=S) = −131.2°, H^{3}NCC = −65.7° and H^{4}NCC = 177.9° for the (S,O) one. Furthermore, the presence of the N $\cdots$ S interaction is reflected by both an increase of the negative charge on the nitrogen and a slightly positive charge on the thiol sulfur atom, N $\cdots$ S being equal to *ca.* 280 pm *vs.* a sum of the van der Waals radii of 335 pm. The atoms N, S and H were not found to deviate significantly from a straight line in these systems (N $\cdots$ S–H *ca.* 152°), meeting the geometrical criterion of Rosenfield *et al.*[38] for a nucleophilic nitrogen approaching an electrophilic sulfur. Consideration of electron correlation was found to be essential for a correct mimetization of this N $\cdots$ S intramolecular interaction (Table 1). This particular nonbonding close contact was previously found by Carey and coworkers[39] to have a significant stabilising role in acyl-thioproteases.

The energy difference between the most stable conformation, *A*/*syn*/*s-cis*, and each one of those conformers — *G*/*skew'*/*s-cis* for (O,O) and (S,O), and *G*/*anti*/*s-cis* for (O,S) and (S,S) — takes the following values: 12.8 kJ mol^{-1} for (O,O), 1.9 for (O,S), 13.2 for (S,O) and 2.2 for (S,S) (Table 1). Sensitivity to the position of the oxygen-by-sulfur substitution is then clearly evidenced as, while almost insensitive to introduction of a thione atom, these values decrease by *ca.* 11 kJ mol^{-1} when Y = S.

Oxygen-by-sulfur substitutions also discriminate against amine $\cdots$ Y close contact intramolecular interactions occurring in the *A*/*anti*/*s-cis* conformation (Fig. 3), where the (N)H$_2$ atoms stand above and below the NCCY ring plane (Fig. 2). This *A*/*anti*/*s-cis* form results from the most stable one, *A*/*syn*/*s-cis*, by a 180° rotation around the C–C central bond. In fact, for all the molecules studied, both *A*/*syn*/*s-cis* and *A*/*anti*/*s-cis* correspond to minima in the potential-energy
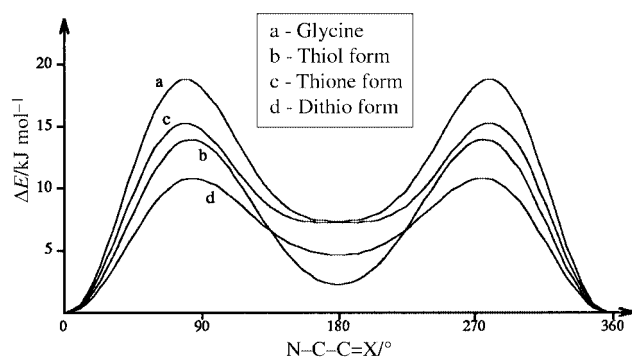

Fig. 4 Potential-energy profile for the internal rotation around the C–C bond of the NH$_2$CH$_2$C(=X)YH (X, Y = O or S) molecules, at the 3-21G(N*) level of calculation. (*Anti* and *s-cis* orientations were considered for the nitrogen electron lone pair and the C(=X)YH group respectively. Fourier coefficients (see computational methods) are: V_1 = 2.1, 0.0, 2.7 and 2.5; V_2 = 14.7, 12.8, 11.3 and 8.5; V_3 = 5.3, 2.3, 4.6 and 2.1, for the (O,O), (O,S), (S,O) and (S,S) molecules, respectively).

profile for the internal rotation around the C–C bond (Fig. 4): at 0° — for *A*/*syn*/*s-cis*, the lowest energy conformer — and 180° — for *A*/*anti*/*s-cis*.

In fact, the *A*/(*anti* − *syn*)/*s-cis* energy difference takes the following values: 7.0 kJ mol^{-1} for (O,O), 0.8 for (O,S), 7.9 for (S,O) and 3.4 for (S,S) (Table 1). In turn, the energy barriers for the corresponding *A*/*syn*/*s-cis→A*/*anti*/*s-cis* interconversion are (at the 3-21G(N*) level): 19.1 kJ mol^{-1} for (O,O), 14.1 for (O,S), 15.5 for (S,O) and 11.0 for (S,S) (Table 1). Interestingly enough, these values, as well as the potential-energy deconvolution profiles obtained for these systems (Fig. 4), seem to suggest that the oxygen-by-sulfur substitution in the Y position favours those conformations where the C–Y bond is eclipsed with either C–N or C–H (NCCY = 0° or ±120°, *i.e.* C=X staggered) — V_3 being lower for Y = S (2.3 and 2.1, relative to 5.3 and 4.6 for Y = O). This occurs especially when X is an oxygen, which is evidenced by the smaller V_1 values obtained for the (O,O) and (O,S) systems (Fig. 4). Moreover, the decrease of that energy barrier is almost additive with respect to oxygen-by-sulfur substitutions in both the thiol and the thione positions, V_2 displaying a steady decrease when going from (O,O) to (S,O), (O,S) and (S,S) molecules — 14.7, 12.8, 11.3 and 8.5, respectively.

The graphical representation of the dependence of the N–C bond length on the NCCX dihedral angle (Fig. 5(a)) presents minima, *i.e.* shorter N–C values, at 0° (*syn*) and 180° (*anti*), and a maximum at *ca.* 90°, with a highest overall variation of approximately 2 pm attained for the thiol compound. The NCC bond angle, in turn, displays an opposite behaviour (Fig. 5(b)), with maxima at 0° (*syn*) and 180° (*anti*), and a minimum at *ca.* 90°. This minimum is lowest for X = S, due to the high sensitivity of the NCC angle to repulsive steric interactions, namely between –C=S and –CH$_2$NH$_2$ molecular fragments. Moreover, a conformation displaying eclipsed C–N and C–SH bonds corresponds to maximal variations of NCC (*ca.* 6°), on account of both steric and electrostatic repulsions (the charge on both the S thiol and the (N)H hydrogen atoms being slightly positive).

The plot of the dependence of the C–Y bond length on the NCC(=X) dihedral angle (Fig. 6(a)) displays minima at *ca.* ±60° (*gauche*) and 180° (*anti*), and a peak at *ca.* ±120°, with a maximum overall variation of more than 1.5 pm for the thiol molecule. As for the CCY bond angle (Fig. 6(b)), whose maximum variation exceeds 2°, the opposite behaviour was observed, with minima at 0° (*syn*) and *ca.* ±120° (*skew*), and maxima at *ca.* ±60° (*gauche*) and 180° (*anti*).

The plot of the C=X bond length as a function of the NCCX dihedral angle, in turn, shows maxima at *ca.* ±60° (*gauche*) and 180° (*anti*) and minima at 0° (*syn*) and *ca.* ±120° (*skew*)
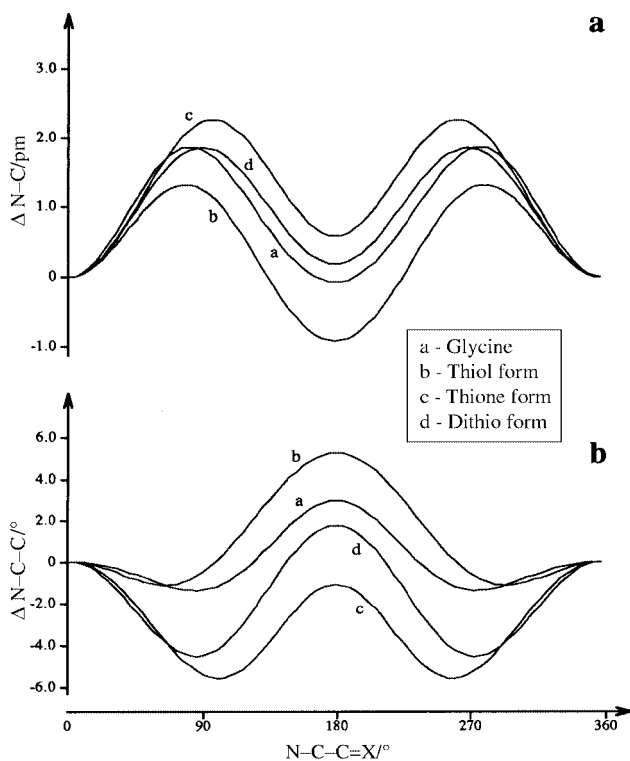
Fig. 5 Graphical representation of the dependence of (a) the N–C bond length and (b) the N–C–C bond angle as a function of the N–C–C=X dihedral angle, for the $NH_2CH_2C(=X)YH$ (X, Y = O or S) molecules.

Fig. 6 Graphical representation of the dependence of (a) the C–Y bond length and (b) the C–C–Y bond angle as a function of the N–C–C=X dihedral angle, for the $NH_2CH_2C(=X)YH$ (X, Y = O or S) molecules.

(Fig. 7(a)). In addition, the variation of the CC=X bond angle (Fig. 7(b)) exhibits maxima at 0° (*syn*) and *ca.* 120° (*skew*) and minima at *ca.* 60° (*gauche*) and 180° (*anti*). Maximum values of this bond angle suggest the occurrence of steric repulsions between the –CH$_2$NH$_2$ and –C(=X)YH (X, Y = O or S) moieties
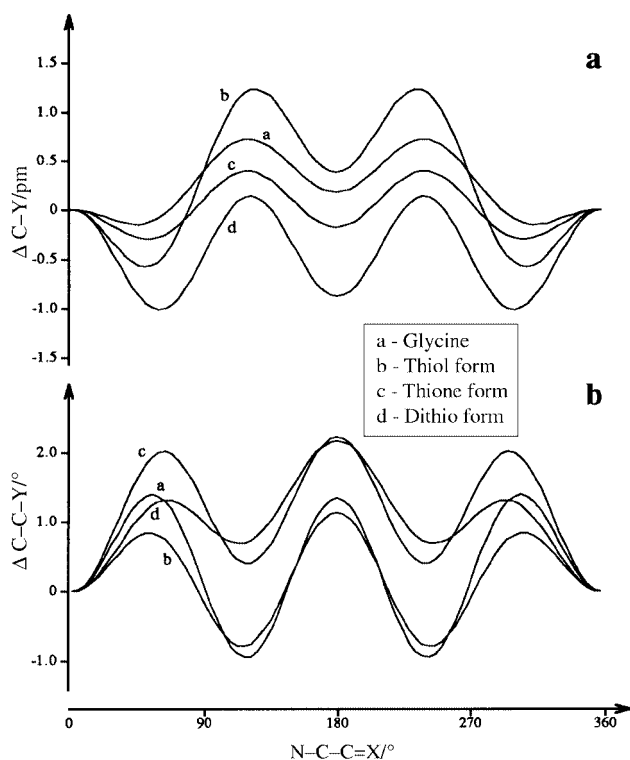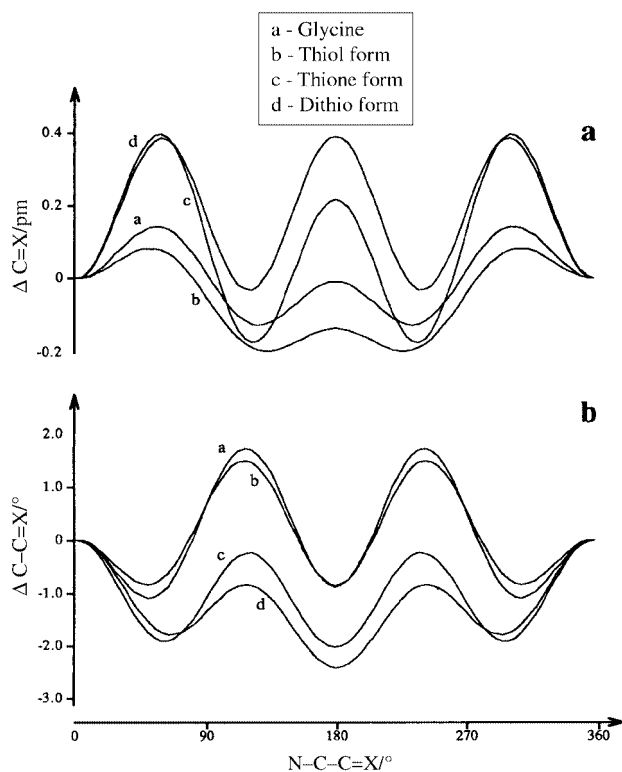

Fig. 7 Graphical representation of the dependence of (a) the C=X bond length and (b) the C–C=X bond angle as a function of the N–C–C=X dihedral angle, for the $NH_2CH_2C(=X)YH$ (X, Y = O or S) molecules.

of the molecules, inasmuch as they are reduced by the opening of those angles.

In summary, the NCC bond angle presents maxima at both 0° (*syn*) and 180° (*anti*) — when the N–C bond is eclipsed by C=X or C–Y — whereas CCY exhibits maxima at *ca.* ±60° (*gauche*) and 180° (*anti*) — when C–Y is eclipsed by C–H or C–N. The CCX bond angle, in turn, displays maxima at 0° (*syn*) and ±120° (*skew*) — for a C–Y bond eclipsed by C–H or C–N. Thus, this skeletal angle variation is mainly determined by the steric hindrances occurring within these molecules.

The *G/anti/s-trans* form, which is stabilised by an intra-molecular N · · · H–Y interaction, was found to be the second lowest energy conformer for all the molecules studied, except for the (O,S) system (Table 1). However, the *A/syn/s-cis→ G/anti/s-trans* interconversion is not an elementary process — as it requires intramolecular rotations around more than one bond, namely N–C, C–C and C–Y — and the corresponding energy barrier was not directly evaluated, neither can it be indirectly determined since not enough intermediate confor-mational states were studied.

When compared to the similar systems propionic acid and its oxygen-by-sulfur substituted derivatives — $CH_3CH_2C(=X)YH$ (X, Y = O or S) — glycine and its thiol and thione analogues — $NH_2CH_2C(=X)YH$ (X, Y = O or S) — display a slightly different conformational behaviour. In fact, when considering the C–C intramolecular rotation, the latter present energy minima at 0° and 180°, while propionic acid and its derivatives display minima at 0° and 120°.[40] Moreover, the $NH_2CH_2C(=X)YH$ molecules have lowest minima at 0°, irrespective of X and Y being either O or S, as opposed to the $CH_3CH_2C(=X)YH$ systems, for which the most stable conformers for X = S occur for a central dihedral angle of 120°. This particular confor-mational behaviour of glycine and its analogues is due to the presence of the nitrogen atom, that allows the formation of relevant stabilising intramolecular close contacts — namely in the thiol compounds, where a N: · · · S(H) interaction occurs.

Table 4 Calculated vibrational frequencies (IR; Raman intensities) for the most stable conformers of the NH₂CH₂C(=X)YH (X, Y = O or S) molecules

NH₂CH₂C(=O)OH		NH₂CH₂C(=O)SH			NH₂CH₂C(=S)OH		NH₂CH₂C(=S)SH		
Alsynls-cis C_s^a (>80%)	Glantils-trans C_1 (≅16%)	Alsynls-cis C_s (≅35%)	Alantils-cis C_s (≅25%)	Glantils-cis C_1 (≅33%)	Alsynls-cis C_s (≅40%)	Glantils-trans C_1 (≅58%)	Alsynls-cis C_s (≅30%)	Glantils-cis C_1 (≅25%)	Glantils-trans C_1 (≅31%)
86[b] (7;0) A″	102 (5;0)	64 (1;0) A″	56 (1;0) A″	84 (9;1)	95 (2;0) A″	57 (3;1)	71 (0;0) A″	80 (7;2)	83 (8;2)
238 (53;4) A″	269 (17;2)	218 (6;0) A′	222 (1;0) A′	221 (3;0)	230 (5;2) A′	271 (15;2)	230 (2;1) A′	233 (3;1)	252 (6;2)
252 (9;0) A′	333 (23;0)	234 (52;8) A″	337 (0;21) A″	240 (67;5)	297 (51;4) A″	304 (15;4)	294 (7;5) A′	256 (73;4)	269 (28;2)
462 (38;3) A″	497 (4;4)	292 (66;16) A″	384 (112;1) A″	415 (8;11)	419 (19;3) A′	408 (8;3)	303 (36;8) A″	311 (4;7)	297 (6;5)
515 (69;4) A″	560 (11;2)	334 (47;7) A′	403 (3;12) A′	424 (15;18)	483 (19;5) A″	477 (1;5)	340 (60;11) A″	417 (6;5)	414 (6;6)
641 (20;6) A′	652 (9;1)	416 (4;24) A′	466 (74;6) A′	451 (30;1)	526 (12;5) A′	502 (1;6)	407 (13;12) A′	462 (19;16)	445 (70;10)
642 (161;2) A″	760 (202;3)	514 (1;0) A″	510 (2;0) A″	549 (37;8)	644 (22;11) A′	773 (12;8)	448 (10;2) A″	462 (1;8)	484 (5;10)
827 (43;9) A′	821 (2;8)	741 (23;15) A′	535 (43;23) A′	566 (24;16)	679 (192;3) A″	886 (60;1)	616 (9;13) A′	554 (19;7)	567 (6;5)
942 (8;0) A″	925 (44;2)	794 (104;16) A′	841 (150;14) A′	875 (119;7)	902 (0;2) A″	915 (137;4)	828 (67;9) A′	877 (2;3)	839 (5;31)
1009 (196;2) A′	1027 (123;5)	910 (1;0) A″	895 (2;0) A″	886 (46;4)	978 (304;2) A′	983 (32;3)	880 (0;2) A″	896 (131;2)	880 (11;7)
1134 (194;3) A′	1073 (16;7)	966 (388;8) A′	930 (226;6) A′	981 (111;12)	1056 (8;4) A′	1007 (168;7)	936 (126;19) A′	945 (237;21)	934 (322;17)
1164 (141;3) A′	1225 (4;5)	1020 (24;5) A′	1038 (113;4) A′	1064 (51;9)	1167 (29;4) A′	1101 (67;9)	984 (226;1) A′	1052 (1;8)	1049 (8;6)
1239 (3;2) A″	1235 (8;2)	1153 (67;6) A′	1148 (7;3) A′	1136 (27;3)	1233 (0;2) A‴	1230 (5;2)	1159 (33;6) A′	1096 (50;2)	1115 (40;4)
1350 (18;5) A′	1342 (301;10)	1234 (0;1) A″	1230 (1;1) A″	1232 (1;3)	1257 (449;1) A′	1298 (415;6)	1175 (88;5) A′	1174 (33;4)	1157 (77;13)
1421 (29;1) A′	1373 (245;5)	1398 (6;3) A′	1390 (15;3) A′	1364 (16;9)	1392 (63;3) A′	1381 (44;10)	1239 (1;1) A″	1229 (4;3)	1225 (11;3)
1426 (0;13) A″	1425 (2;4)	1428 (2;12) A″	1420 (1;12) A″	1436 (2;6)	1414 (104;2) A′	1411 (102;1)	1414 (13;3) A′	1384 (8;7)	1384 (14;6)
1524 (21;18) A′	1533 (6;14)	1516 (23;19) A′	1509 (4;14) A′	1527 (4;16)	1426 (1;11) A″	1486 (204;7)	1435 (2;12) A′	1440 (6;6)	1436 (6;7)
1729 (19;6) A′	1715 (35;8)	1728 (22;6) A′	1720 (23;5) A′	1720 (31;9)	1513 (1;25) A′	1518 (74;11)	1514 (6;21) A′	1528 (6;13)	1533 (6;13)
1840 (263;4) A′	1874 (322;8)	1809 (248;11) A′	1800 (275;13) A′	1797 (251;13)	1727 (26;4) A′	1711 (32;10)	1725 (22;4) A′	1718 (26;10)	1714 (28;10)
3023 (11;98) A′	3017 (10;81)	2485 (4;163) A′	2488 (5;170) A′	2460 (20;185)	3002 (9;143) A′	3033 (3;69)	2484 (1;115) A′	2462 (9;129)	2432 (23;155)
3057 (7;73) A″	3057 (12;60)	3015 (5;83) A′	3010 (11;118) A′	2986 (25;113)	3032 (5;97) A″	3078 (2;43)	2992 (8;128) A″	2993 (9;98)	2994 (6;95)
3394 (2;75) A′	3411 (6;92)	3050 (4;60) A″	3046 (5;86) A″	3028 (11;77)	3400 (2;58) A′	3341 (443;88)	3022 (4;87) A″	3028 (11;65)	3040 (9;60)
3451 (1;51) A″	3480 (8;75)	3397 (3;80) A′	3414 (2;61) A′	3416 (4;99)	3463 (4;35) A″	3427 (6;101)	3400 (3;59) A′	3409 (3;117)	3403 (44;113)
3623 (69;125) A′	3537 (197;41)	3456 (2;54) A″	3488 (7;37) A″	3488 (5;85)	3600 (108;99) A′	3497 (15;81)	3464 (4;35) A″	3480 (4;101)	3473 (5;99)

[a] Symmetry point group and population at 25 °C. [b] Frequencies (scaled by 0.9370[44]) are in cm⁻¹, IR intensities in km mol⁻¹ and Raman scattering activities in Å⁴ amu⁻¹.

Vibrational spectra

The effect of oxygen-by-sulfur substitutions on both conformational energy differences and intramolecular interactions have been analysed above. The way they affect vibrational spectra will now be considered.

Table 4 lists the vibrational frequencies, as well as the infrared and Raman intensities, obtained within the harmonic approximation at the HF/6-31G** level, for several conformers of the $NH_2CH_2C(=X)YH$ (X, Y = O or S) molecules.

For glycine (X = O, Y = O), only two conformational levels were found to be appreciably populated, namely: *A/syn/s-cis* — statistical weight, $w = 1$; energy difference to the most stable form, $\Delta E = 0.0$ kJ mol^{-1}; Boltzmann population, $\rho > 80\%$ — and *G/anti/s-trans* — $w = 2$; $\Delta E = 5.9$ kJ mol^{-1}; $\rho \approx 16\%$ (Table 1). As referred to previously, *A/syn/s-cis* and *G/anti/s-trans* display intramolecular $NH_2 \cdots O=C$ and $N\colon \cdots HO$ close contacts, respectively (Fig. 2). The OH stretching frequency of *G/anti/s-trans* (3537 cm^{-1}) is shifted to a lower value by more than 80 cm^{-1} relative to the most stable form (Table 4). In addition, its infrared intensity increases almost threefold, while its Raman intensity decreases to approximately one third. These facts seem to suggest that the $N \cdots HO$ close contact in the *G/anti/s-trans* conformation might correspond, for the (O,O) molecule, to a hydrogen bond type of interaction. Concurrently with the changes detected in the OH stretching vibrational mode, this intramolecular interaction is proposed to be also responsible for a blue shift of both the carbonyl stretching band at 1840 cm^{-1} (by 34 cm^{-1}) and (by 18 cm^{-1}) of the mode herein tentatively ascribed to the NH_2 wagging motion (a very strong infrared mode, whose frequency for the *A/syn/s-cis* conformer was now calculated to be 1009 cm^{-1}).

Regarding the (O,S) molecule, the three most stable conformations, namely, *A/syn/s-cis* ($w = 1$; $\Delta E = 0.0$ kJ mol^{-1}; $\rho \approx 35\%$), *A/anti/s-cis* ($w = 1$; $\Delta E = 0.8$ kJ mol^{-1}; $\rho \approx 25\%$) and *G/anti/s-cis* ($w = 2$; $\Delta E = 1.9$ kJ mol^{-1}; $\rho \approx 33\%$) (Table 1), gather *ca.* 90% of the total Boltzmann population (assuming that the four most stable levels correspond to 100%). As *A/anti/s-cis* and *G/anti/s-cis* are stabilised by $NH_2 \cdots S(H)$ and $N\colon \cdots S(H)$ intramolecular close contacts, respectively, the corresponding S–H stretching frequency displays a downward shift (relative to *A/syn/s-cis* at 2485 cm^{-1}) of 25 cm^{-1} for the latter, while it is almost unchanged for the former (2488 cm^{-1}).

The pattern of vibrational changes exhibited by both $\nu_{as}(NH_2)$ (asymmetric NH_2 stretching) and $\nu_s(NH_2)$ (symmetric NH_2 stretching) in these two relevant excited conformational levels of the (O,S) molecule is worth mentioning. In fact, these vibrational modes, upward shifted relative to the most stable form (3456 and 3397 cm^{-1}), by 32 and 17 cm^{-1}, respectively, display very close frequencies for the two conformers (*A/anti/s-cis* and *G/anti/s-cis*). In turn, both $\nu_{as}(CH_2)$ (asymmetric CH_2 stretching) and $\nu_s(CH_2)$ (symmetric CH_2 stretching) are only slightly shifted in the *A/anti/s-cis* conformation (3010 and 3046 cm^{-1}) and appreciably downward shifted in *G/anti/s-cis*, by 29 and 22 cm^{-1}, respectively. These facts seem to suggest that, for the (O,S) molecule, $\nu_s(CH_2)$ and $\nu_{as}(CH_2)$ modes act as probes for the $\colon N$–CC dihedral angle, whereas $\nu_s(NH_2)$ and $\nu_{as}(NH_2)$ are more sensitive to the value of NC–C(=O). Moreover, the band occurring at 966 cm^{-1} for *A/syn/s-cis*, herein ascribed to the NH_2 wagging mode, is downward shifted by 36 cm^{-1} in the *A/anti/s-cis* conformation and upward shifted by 15 cm^{-1} in the *G/anti/s-cis* form, thus suggesting a specific sensitivity of this vibrational mode to intramolecular interactions involving the nitrogen atom.

For the (S,O) molecule there are only two relevant conformational levels, namely, *A/syn/s-cis* ($w = 1$; $\Delta E = 0.0$ kJ mol^{-1}; $\rho \approx 40\%$), and *G/anti/s-trans* ($w = 2$; $\Delta E = 0.8$ kJ mol^{-1}; $\rho \approx 58\%$) (Table 1), gathering *ca.* 98% of the total Boltzmann population (all the populations being normalized for the three most stable conformers). From Table 4 it can be seen that the OH stretching band of *G/anti/s-trans* (3497 cm^{-1}) is shifted to lower frequencies by 103 cm^{-1}, relative to the corresponding value of the most stable conformer (*A/syn/s-cis*). In contrast to the (O,O) compound, the infrared intensity of this vibrational mode decreases substantially, suggesting that the oxygen-by-sulfur substitution in the X position might lead to a decrease in the extent of the mesomeric effect in the molecule. Both $\nu_{as}(NH_2)$ (3427 cm^{-1}) and $\nu_s(NH_2)$ (3341 cm^{-1}) vibrational modes of the *G/anti/s-trans* conformer are downward shifted by 36 and 59 cm^{-1}, respectively, relative to the corresponding frequencies of the most stable form. $\nu_{as}(CH_2)$ (3078 cm^{-1}) and $\nu_s(CH_2)$ (3033 cm^{-1}), in turn, are upward shifted by 46 and 31 cm^{-1}. In this case, clear-cut patterns of conformationally induced vibrational changes are difficult to discern, since all the relevant dihedral angles change from *A/syn/s-cis* to *G/anti/s-trans* conformations. Similarly to the (O,O) and (O,S) molecules, the band occurring at 978 cm^{-1} for *A/syn/s-cis* in the (S,O) molecule, herein tentatively ascribed to the NH_2 wagging mode, is upward shifted by 29 cm^{-1} in the *G/anti/s-trans* form.

As for the (S,S) molecule, three appreciably populated conformational levels occur, namely, *A/syn/s-cis* ($w = 1$; $\Delta E = 0.0$ kJ mol^{-1}; $\rho \approx 30\%$), *G/anti/s-trans* ($w = 2$; $\Delta E = 1.6$ kJ mol^{-1}; $\rho \approx 31\%$) and *G/anti/s-cis* ($w = 2$; $\Delta E = 2.2$ kJ mol^{-1}; $\rho \approx 25\%$) (Table 1) (the populations being normalized for the five most stable conformers). For the two *G/anti* conformers, the Raman intensities of both $\nu_{as}(NH_2)$ (*ca.* 3476 cm^{-1}) and $\nu_s(NH_2)$ (*ca.* 3406 cm^{-1}) modes increase appreciably with respect to the corresponding values for the most stable form, *A/syn/s-cis* (Table 4). In addition, $\nu(SH)$ is downward shifted by 52 cm^{-1} (2432 cm^{-1}) and 22 cm^{-1} (2462 cm^{-1}) for *G/anti/s-trans* and *G/anti/s-cis*, respectively. The relative magnitudes of these shifts are consonant with the nature of the intramolecular interactions occurring in these conformers.

Conclusion

The conformational preferences of both glycine and its sulfur analogues were found to be significantly sensitive to oxygen-by-sulfur substitutions, either in the X or in the Y position (or in both), the conformers obtained being mainly determined by the interplay of distinct intramolecular close contacts. Among these, $N\colon \cdots H(S)$ and $N\colon \cdots S(H)$ are particularly interesting, the latter opposing the unfavourable $N\colon \cdots O(H)$ interactions (in accordance with previous theoretical studies on glycine [29]). It is worth noticing that while the $N\colon \cdots H(S)$ close contact is weaker than the $N\colon \cdots H(O)$ one, $N\colon \cdots S(H)$ is a stabilising interaction in contrast to the $N\colon \cdots O(H)$ one. A direct consequence of this kind of energetically favourable close contact is the stabilisation of the *G/anti* conformations for X = S and/or Y = S.

Acknowledgements

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