Effect of Hydrogen Bonding on the Methyl Conformation of Thioacetamide: an *ab initio* Study

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The methyl rotational barrier height of thioacetamide was studied by *ab initio* molecular orbital calculations including electron correlation corrections up to the MP4/6-311+G**//MP2/6-31G* level. The calculations indicate that the methyl group of isolated thioacetamide shows a slight tendency to eclipse the C=S bond. This result was also found for the thiocarbonyl compounds thioacetone and thioacetaldehyde which are included in this work. Centrosymmetrical dimers and hexamers of thioacetamide are proposed as a simple simulation of the crystal field and *ab initio* calculations were carried out to investigate the effects of hydrogen bonding on the methyl conformation and on the molecular structure of thioacetamide. The oligomer models are capable of reproducing the changes in the π-character of the C=S and C–N bonds, the variations in the valence angles and the rotation of the methyl group observed by comparing the geometry of the isolated molecule with that of the crystal molecules. The structural perturbations due to self-association have been rationalized supposing that the contribution of the polar canonical form where the sulfur atom is negatively charged increases progressively in going from the monomer to the dimer and hexamer of thioacetamide molecule.

A crystal field is known to cause appreciable effects on molecular geometry. A wide number of accurate structural investigations of gas-phase and solid state molecules reveal that the bond lengths, bond angles and torsion angles found in the crystal may differ appreciably from those determined for the isolated molecule.[1] The geometrical parameters most likely affected by crystal forces are the torsion angles about single bonds. This is quite common for molecules involved in strong hydrogen bonding interactions so that the solid-state conformation may be significantly different from that of the gaseous phase.[2,3] Conformational differences were also found for some rotating groups not involved directly in hydrogen bonding interactions as for the methyl group of acetamide [CH_3–C(=O)–NH_2].[4] The crystal structure of acetamide, determined from neutron diffraction at 23 K for accurate location of hydrogen atom positions, showed that the methyl group is oriented with one C–H bond normal to the plane of the carbonyl group.[4] On the other hand, gas-phase electron diffraction[5] revealed that acetamide has C_S symmetry with one C–H bond eclipsed to the carbonyl group and *ab initio* calculations at the HF/3-21G*,[4] HF/6-31G**[6] and MP2/6-31G* levels[6] confirmed the tendency of the methyl group to eclipse the C=O bond. More recently, theoretical models of the solid state acetamide allowed Popelier *et al.* to conclude that the methyl conformation adopted in the crystal is due to electrostatic lattice forces.[7]

Conformational changes were also predicted for the methyl group of thioacetamide [CH_3–C(=S)–NH_2].[8] As for acetamide, the methyl conformation of isolated thioacetamide is different from that determined for the crystal molecule[8] and this fact suggests that intermolecular hydrogen bonding in the solid state causes the rotation of the methyl group. However, in contrast to acetamide, the experimental geometry of the gas-phase molecule has not yet been reported and information on the structural features of the isolated molecule arises exclusively from *ab initio* HF/3-21G and HF/3-21G* calculations.[8] Moreover, the energy differences between the rotamers of free thioacetamide were found to be negligible so that the molecule was destabilized by only 1 kJ mol^{-1} when the methyl group was constrained to the conformation observed in the crystal.[8] Bearing in mind the very small barrier to rotation of the methyl group and the lack of any accurate experimental geometry of gas-phase thioacetamide, it is worthwhile reconsidering the structural features of isolated thioacetamide by higher levels of the *ab initio* theory. In addition, it is interesting to evaluate the role of hydrogen bonding in determining the methyl conformation of the solid-state molecule. Recently, the structural modifications due to intermolecular association have received considerable attention[1] and reliable information has been provided from *ab initio* studies carried out on simple molecular models simulating intermolecular hydrogen bonding of imidazole,[9] diacetamide[10] and phenol[11] crystals.

The primary objective of the present work is the reinvestigation of the structural features of isolated thioacetamide by considering the effects of electron correlation. Particular emphasis has been given therefore to the calculation of the rotation barrier height of the methyl group using the Møller–Plesset perturbation theory[12] through MP2/6-31G* geometry optimizations and MP4/6-311+G**//MP2/6-31G* single point energy computations. Secondly, suitable molecular models of dimers and hexamers of thioacetamide have been studied by *ab initio* methods to describe some C=S ··· H–N hydrogen bonding interactions. The structures of such complexes offer the opportunity to investigate the effects of intermolecular hydrogen bonding on the geometry and, in particular, on the methyl rotational conformation of thioacetamide.

Computational Methods

The geometries of thioacetamide monomer and dimer were optimized at the Hartree-Fock (HF) level and at the second order of the Møller–Plesset perturbation theory (MP2) with all the orbitals active by analytical gradient based technique employing the split valence basis set 6-31G*.[13] Vibrational frequencies were calculated at the respective optimized geometries to characterize each stationary point on the potential energy surface. The split valence basis set 3-21G*,[13] including d-functions only on the sulfur atom, was employed for geometry optimizations of the thioacetamide hexamer.

Single point MCSCF calculations on the stable structures of monomer and dimer were then performed at the MP2/6-31G*

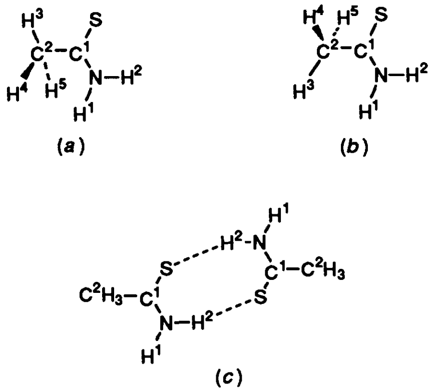

Fig. 1 Numbering of atoms in the monomer, eclipsed (*a*) and staggered (*b*) conformations, and dimer (*c*) of thioacetamide

optimized geometries employing the Complete Active Space SCF (CASSCF) method with the 4-31G* basis set.[13]

The relative stability between the methyl rotamers of the free molecule was evaluated by single-point calculations using the frozen core approximation (fc) up to the fourth order of the Møller–Plesset perturbation theory by including single, double, triple and quadruple excitations and using the 6-311G** and 6-311+G** basis sets.[13] The designation of these calculations is MP4(SDTQ)(fc)/6-311G**//MP2/6-31G* where // means 'at the geometry of'. Henceforth the term SDTQ(fc) will be omitted. The energy difference between the staggered and eclipsed conformers of the dimer molecule was investigated by MP2/6-311+G**//MP2/6-31G** single point calculations and that of the thioacetamide hexamer was evaluated by HF/6-31G* calculations at the HF/3-21G* optimized geometries. All computations were carried out using the Unix version of the GAUSSIAN 92/DFT package[14] running on an Alpha AXP-3000/500 cluster at the University of Rome.

Results and Discussion

Isolated Molecule.—The previous theoretical study[8] focused attention on the rotational isomerism of the methyl group of thioacetamide and HF/3-21G and HF/3-21G* geometry optimizations indicated that the lowest energy conformation of the isolated molecule has C_S symmetry with a CH bond lying in the plane of the thiocarbonyl group and eclipsing the C=S bond. However, it is well known that the structural features of molecules containing the amino group can be obtained reliably by *ab initio* methods only if polarization functions are included on all the non-hydrogen atoms of the molecule.[15] For instance, the HF/6-31G** and MP2/6-31G* geometries show that the amino group of acetamide is actually non-planar in the minimum energy conformer although the energy difference calculated with respect to the planar conformer is very small (less than 0.4 kJ mol^{-1}).[6] On the grounds of the theoretical results of acetamide, we have investigated the molecular structure of thioacetamide without any symmetry constraint by HF geometry optimizations using the 6-31G* basis set. Distinct orientations of the methyl group were considered and three stationary points were localized on the potential energy surface. Each critical point was then characterized by frequency calculations. In agreement with the HF/3-21G* results,[8] the HF/6-31G* level predicts the lowest energy structure of thioacetamide, the true minimum, to be planar at nitrogen and, in contrast with the previous study, to adopt an asymmetric orientation for the methyl group having the torsion angle H–C–C=S (φ) equal to 165.5°. The remaining structures, identified as first-order saddle-points by the presence of one imaginary frequency related to the C–C torsional mode, show once again a planar configuration at nitrogen. Such structures correspond to methyl orientations where a C–H bond is coplanar with the thiocarbonyl group and the remaining hydrogen atoms are located symmetrically on opposite sides of the plane of the thiocarbonyl group. The structure reproduced in Fig. 1(*a*) shows a C–H bond eclipsed to the C=S bond and henceforth it will be indicated as the eclipsed conformer; the second stationary point corresponds to a structure where a C–H bond eclipses the C–N bond [Fig. 1(*b*)] and it will be reported in the work as the staggered conformer. Nevertheless, the energy differences between the rotational conformers were found to be neglible (lower than 0.1 kJ mol^{-1}) and therefore no particular orientation for the methyl group seems to be preferred at this level of calculation for the isolated molecule. Moreover, the potential energy surface was found to change appreciably when electron correlation corrections were included. MP2/6-31G* geometry optimizations indicated the eclipsed conformer as the stable structure of thioacetamide, while the staggered conformation was characterized as the transition state between two equivalent eclipsed rotamers.

In order to obtain more accurate information about the equilibrium conformation of isolated thioacetamide, the methyl torsion barrier height was investigated including electron correlation at higher level of the Møller–Plesset perturbation theory and using the more extended 6-311G** and 6-311+G** basis sets. Consistent with the MP2/6-31G* results, the MP4/6-311G** and MP4/6-311+G** energy calculations at the MP2/6-31G* geometries confirmed that the eclipsed conformer of thioacetamide is the lowest energy structure. Although the barrier to rotation of the methyl group is once again very small (about 1 kJ mol^{-1}), one may conclude that the methyl group of isolated thioacetamide shows a slight tendency to eclipse the C=S bond.

As a matter of fact, this result is not a peculiarity of thioacetamide but it was demonstrated by *ab initio* studies[16] to be a property of methyl groups bonded to thiocarbonyl carbon atoms. Table 1 reports two examples of methyl thiocarbonyl molecules, thioacetone and thioacetaldehyde. In order to uniformly compare such molecules with thioacetamide, geometry optimizations were carried out at the MP2/6-31G* level and the methyl rotation barrier heights were evaluated by MP3/6-311G**//MP2/6-31G* and MP4/6-311G**//MP2/6-31G* single point energy calculations. As expected,[16] the eclipsed rotamer is the lowest energy structure for the three molecules. In addition, our calculations indicate that the barrier to torsion of the methyl group is significantly affected by the nature of the group bonded to the carbon atom. In particular, the results listed in Table 1 show that the torsion potential barrier progressively decreases in going from thioacetaldehyde (6 kJ mol^{-1}) to thioacetamide (1 kJ mol^{-1}). Since the π-character of the C=S bond decreases from thioacetaldehyde to thioacetamide, as suggested by the C=S bond distances (1.620 Å for thioacetaldehyde, 1.627 Å for thioacetone and 1.644 Å for thioacetamide), we can assert that the staggered orientation of the methyl group is stabilized with respect to the eclipsed orientation by increasing polarization of the C=S bond. In terms of valence bond theory, this means that the polar canonical form C^+–S^-, the contribution of which increases in going from thioacetaldehyde to thioacetamide, tends to stabilize staggered orientations of the methyl group.

The HF/6-31G* and MP2/6-31G* optimized geometries reported in Table 2 show that the absolute values of some geometrical parameters depend on the level of calculation. As it can be seen, inclusion of electron correlation causes a general lengthening of the bond distances, with the exception of the C=S bond which shortens at the MP2/6-31G* level by 0.01 Å. On the other hand, the differences between the geometrical parameters of the eclipsed and staggered conformations are substantially

Table 1 Selected MP2/6-31G* bond distances of thioacetaldehyde [CH_3–C(=S)–H], thioacetone [CH_3–C(=S)–CH_3] and thioacetamide [CH_3–C(=S)–NH_2] and relative energies, ΔE, of the eclipsed and staggered methyl rotamers.

	CH_3–C(=S)–H		CH_3–C(=S)–CH_3		CH_3–C(=S)–NH_2	
	Eclipsed	Staggered	Eclipsed	Staggered	Eclipsed	Staggered
Bond length/Å						
C=S	1.620	1.621	1.627	1.627	1.644	1.646
C–C	1.495	1.502	1.503	1.502	1.508	1.509
C–H	1.096	1.094	1.096	1.093	1.095	1.091
C–H′[b]	1.090	1.092	1.093	1.093	1.088	1.094
Bond angle (°)						
C–C–H	109.9	110.2	109.9	111.6	110.3	109.3
C–C–H′[b]	111.1	111.5	111.5	112.0	110.1	112.8
ΔE/(kJ mol^{-1})						
MP2/6-31G*	0	6.5	0	5.5	0	1.3
MP2/6-311G**[c]	0	6.0	0	4.5	0	0.8
MP3/6-311G**[c]	0	6.0	0	4.7	0	0.9
MP4/6-311G**[c]	0	5.6	0	4.3	0	0.8

[a] The second methyl group is assumed to have eclipsed orientation so that the equilibrium structure of thioacetone corresponds to the eclipsed-eclipsed methyl conformation. [b] H′ is distinguishable from H. [c] Short for MP2(fc)/6-311G**//MP2/6-31G*, MP3(fc)/6-311G**//MP2/6-31G* and MP4(fc)/6-311G**//MP2/6-31G*.

the same at each theoretical level and compare well with those obtained at the HF/3-21G*.[8] The geometry of thioacetamide is slightly affected by the orientation of the CH_3 group and the more appreciable differences between the rotameric structures regard the methyl group itself which shows small deviations from the C_3 symmetric internal top. As regards the eclipsed conformer, the distortions of the methyl group concern primarily the C–H bond lengths whereas, as regards the staggered conformer, the methyl asymmetry is particularly outstanding in the H–C–C bond angles. As can be seen from Table 1, the length of the C–H bond is shorter by about 0.006 Å when the C–H bond eclipses the C=S bond and such a structural feature is quite common when the methyl group is proximate to thiocarbonyl and carbonyl groups.[16] As far as the valence angles are concerned, it is worth observing that the H–C–C bond angle reaches the maximum value when the C–H bond eclipses the C–N bond, suggesting thus the tendency to tilt the methyl group towards the C=S group when the molecule adopts a staggered orientation. The angular deformations of CH_3, as well as the fact that the S=C–C bond angle opens by 1.0° in going from the eclipsed to the staggered conformations, can be perceived as being caused primarily by steric hindrance between the (N)H1 and H3(C) atoms. Such a consideration is suggested by the fact that the H1 ··· H3 intramolecular separation in the staggered conformer reaches a small value (2.209 Å) which should be compared with twice the van der Waals radius of hydrogen (2.4 Å).[17]

Oligomers.—The crystal structure of thioacetamide has been determined using single-crystal neutron diffraction at 15 K.[8] The crystal contains layers of molecules consisting of C=S ··· H–N hydrogen bonded ring dimers linked laterally to form buckled layers, as described in ref. 8 and schematically reproduced in Fig. 2(*a*). The crystal contains two crystallographically independent molecules having no significant differences in bond length and valence angle values. The two symmetry independent molecules are two CH_3 rotamers of thioacetamide having S=C–C–H torsional angles (φ) equal to 178.8° (molecule A) and 165.5° (molecule B). Within the proper crystalline symmetry, some simple models of dimers and hexamers were constructed with the aim of reproducing neighbouring intermolecular associations by *ab initio* calculations. The structural features of the oligomers proposed in this paper and discussed in the following sections, allow the investigation of the influence of hydrogen bonding on the molecular geometry and methyl rotational barrier of thioacetamide.

Dimer. The centrosymmetric dimer reproduced in Fig. 2(*b*) is the simplest model describing self-association of thioacetamide. In such a complex, two molecules are hydrogen bonded pairwise by two C=S ··· H–N bonds. On the ground of the monomer structure already discussed, the eclipsed ($\varphi = 0°$) and staggered ($\varphi = 180°$) orientations of the methyl group were investigated and geometry optimizations were carried out at the HF/6-31G* level imposing the C_{2h} symmetry constraint. Within this assumption, the monomer molecules share the same symmetry plane and the orientation of the methyl groups is equivalent in both the monomers. The correctness of the C_{2h} assumption was substantiated when frequency calculations were carried out for both the rotamers. The dimeric structure having both the methyl groups oriented in a staggered manner, henceforth indicated simply as staggered conformer, was characterized as a true minimum, whereas the eclipsed-eclipsed methyl dimeric rotamer, indicated simply as eclipsed conformer, shows two imaginary frequencies, corresponding to the A_g and B_u symmetry C–C torsional modes. These results suggest at once that self-association of thioacetamide produces conformational changes with respect to the free molecule. Such a tendency is confirmed by comparing the relative stability of the staggered and eclipsed conformations of the dimer with the corresponding value of the monomer. In contrast with the free molecule, for which the HF/6-31G* methyl torsion barrier height is extremely small (0.1 kJ mol^{-1}), the staggered conformer of the dimer is predicted to be more stable with respect to the eclipsed rotamer by about 2 kJ mol^{-1} (HF/6-31G* and HF/6-311+G**//HF/6-31G*). Such a value is clearly very small to provide certain conclusions about the effect of hydrogen bonding on the methyl rotational potential. However, the tendency to stabilize the staggered conformation of the thioacetamide dimer was confirmed when electron correlation corrections were included by MP2/6-31G* geometry optimizations and MP2/6-311G** and MP2/6-311+G** single point energy calculations (see Table 3).

The optimized geometries of the dimeric structures are reported in Table 2, along with the monomeric ones. The salient

Table 2 Geometrical parameters of thioacetamide monomer and ring dimer[a]

	Monomer[b]		Dimer	
Method	Eclipsed	Staggered	Eclipsed	Staggered
HF/6-31G* Bond length/Å[c]				
C1–C2	1.509_8	1.509_0	1.510_2	1.508_6
C1=S	1.654_3	1.658_8	1.670_6	1.676_1
C1–N	1.329_4	1.325_4	1.315_8	1.311_8
C2–H3	1.077_4	1.084_9	1.077_4	1.084_6
C2–H4	1.086_3	1.082_0	1.086_0	1.082_1
N–H1	0.995_2	0.994_7	0.996_2	0.995_6
N–H2	0.995_7	0.996_1	1.003_1	1.003_8
Bond angle (°)[c]				
C2–C1=S	123.1_8	122.0_3	121.7_1	120.4_8
N–C1=S	122.6_2	122.6_1	123.4_5	123.4_8
C2–C1–N	114.2_0	115.3_6	114.8_4	116.0_4
C1–C2–H3	110.5_5	112.6_9	110.7_2	112.5_2
C1–C2–H4	109.8_1	109.0_4	109.6_9	109.0_4
H4–C2–H5	108.0_8	107.6_1	108.1_2	107.6_2
H3–C2–H4	109.2_8	109.1_7	109.2_9	109.2_5
C1–N–H1	122.0_5	122.2_4	121.0_9	121.2_4
C1–N–H2	119.6_2	119.4_3	121.7_0	121.5_9
H1–N–H2	118.3_3	118.3_3	117.2_1	117.1_7
MP2/6-31G* Bond length/Å[c]				
C1–C2	1.508_0	1.509_2	1.508_5	1.508_1
C1=S	1.644_4	1.645_8	1.659_2	1.662_1
C1–N	1.351_0	1.348_6	1.335_8	1.333_0
C2–H3	1.087_6	1.094_1	1.087_7	1.093_9
C2–H4	1.095_2	1.091_3	1.094_9	1.091_4
N–H1	1.011_0	1.010_5	1.012_8	1.012_4
N–H2	1.011_8	1.012_4	1.024_2	1.025_3
Bond angle (°)[c]				
C2–C1=S	123.6_8	122.6_8	121.7_6	120.6_6
N–C1=S	122.8_2	122.9_0	123.9_8	124.0_8
C2–C1–N	113.5_0	114.4_2	114.2_6	115.2_6
C1–C2–H3	110.0_9	112.8_2	110.3_1	112.5_9
C2–C1–H4	110.2_9	109.3_3	110.1_2	109.3_3
H4–C2–H5	108.0_3	107.4_6	108.0_9	107.4_8
H3–C2–H4	109.0_5	108.8_8	109.0_7	108.9_9
C1–N–H1	122.1_0	122.2_7	120.5_3	120.7_0
C1–N–H2	119.3_2	119.1_3	122.2_2	122.0_6
H1–N–H2	118.5_8	118.6_0	117.2_5	117.2_4

[a] For atomic numbering see Fig. 1. [b] The minimum structure shows an asymmetric orientation of the CH_3 group with the following geometry: bond lengths (Å): C1–C2 = 1.509, C1=S = 1.658, C1–N = 1.326, C2–H3 = 1.085,C2–H4 = 1.080, C2–H5 = 1.084, N–H1 = 0.995, N–H2 = 0.996; bond angles (°): C2–C1=S = 122.2, N–C1=S = 122.6, C2–C1–N = 115.2, C1–C2–H3 = 112.5, C1–C2–H4 = 109.7, C1–C2–H5 = 108.5, H4–C2–H5 = 107.8, H3–C2–H4 = 109.5, H3–C2–H5 = 108.8, C1–N–H1 = 122.2, C1–N–H2 = 119.5, H1–N–H2 = 118.3; torsion angles (°): S=C1–C2–H3 = 165.5, S=C1–C2–H4 = 43.4, S=C1–C2–H5 = −74.2, S=C1–N–H1 = 179.8, S=C1–N–H2 = 0.4, C2–C1–N–H2 = −178.3, N–C1–C2–H3 = −15.9. [c] The bond distances and valence angles not reported can be found from the C_S local symmetry of each molecule.

result emerging from the HF/6-31G* as well as MP2/6-31G* structures is that dimerization causes appreciable geometrical changes, the most conspicuous of which are the lengthening of the C=S bond and the simultaneous shortening of the C–N bond. Changes also occur in the N–H bond participating in the hydrogen bonding which increases by 0.008 Å (HF) and 0.013 Å (MP2). As regards the hydrogen bond geometry, the MP2/6-31G* calculated H···S separation differs largely from the SCF value and, in particular, electron correlation causes a drastic shortening of the H···S hydrogen bond distance from 2.603 Å (HF/6-31G*) to 2.405 Å (MP2/6-31G*).

The structural modifications occurring upon self-association are consistent with those induced by the intermolecular C=O··· H–N interactions of amides[4] and reveal changes in the π-character for the C=S and C–N bonds. This suggests that the contribution of the polar canonical form shown in Fig. 3 as a resonance structure of thioacetamide increases upon dimerization. Consistent with such a consideration are the changes of the atomic charges and, in particular, the π-charges, on the thioamide group. The variations in the HF/6-311+G** π-gross orbital population occurring upon dimerization indicate in fact that the sulfur atom gains 0.10 esu whereas the nitrogen and carbon atoms lose 0.06 and 0.03 esu, respectively. To investigate quantitatively the contribution of low lying excited configurations to the ground state wave function of thioacetamide, we performed a CASSCF/4-31G* calculation on the stable structures of monomer and dimer using the MP2/6-31G* optimized geometries. In the isolated molecule, all excitations were allowed from the three *a″* highest occupied orbitals, the σ_{CH} (13 *a″*), the π_{CS} (19 *a″*) and the 17 *a″* orbital, localized prominently on the nitrogen atom, to the two *a″* lowest

Table 3 Relative energies (kJ mol^{-1}) of eclipsed and staggered conformations of the CH_3 group in the monomer, dimer and hexamer of thioacetamide

	Monomer		Dimer		Hexamer	
	Eclipsed	Staggered	Eclipsed	Staggered	Eclipsed	Staggered
HF/3-21G*	0	1.4[a]	0	1.0	3.4	0
HF/6-31G*//HF/3-21G*	0.1	0	2.1	0	4.7	0
HF/6-31G*	0.1	0	2.2	0	—	—
HF/6-311+G**//HF/6-31G*	0	0.1	1.8	0	—	—
MP2/6-31G*	0	1.3	0	0.6	—	—
MP2/6-311G**//MP2/6-31G*	0	0.8	0.3	0	—	—
MP2/6-311+G**//MP2/6-31G*	0	1.1	0.6	0	—	—
MP4/6-311+G**//MP2/6-31G*	0	1.0	—	—	—	—

[a] Ref. 8.

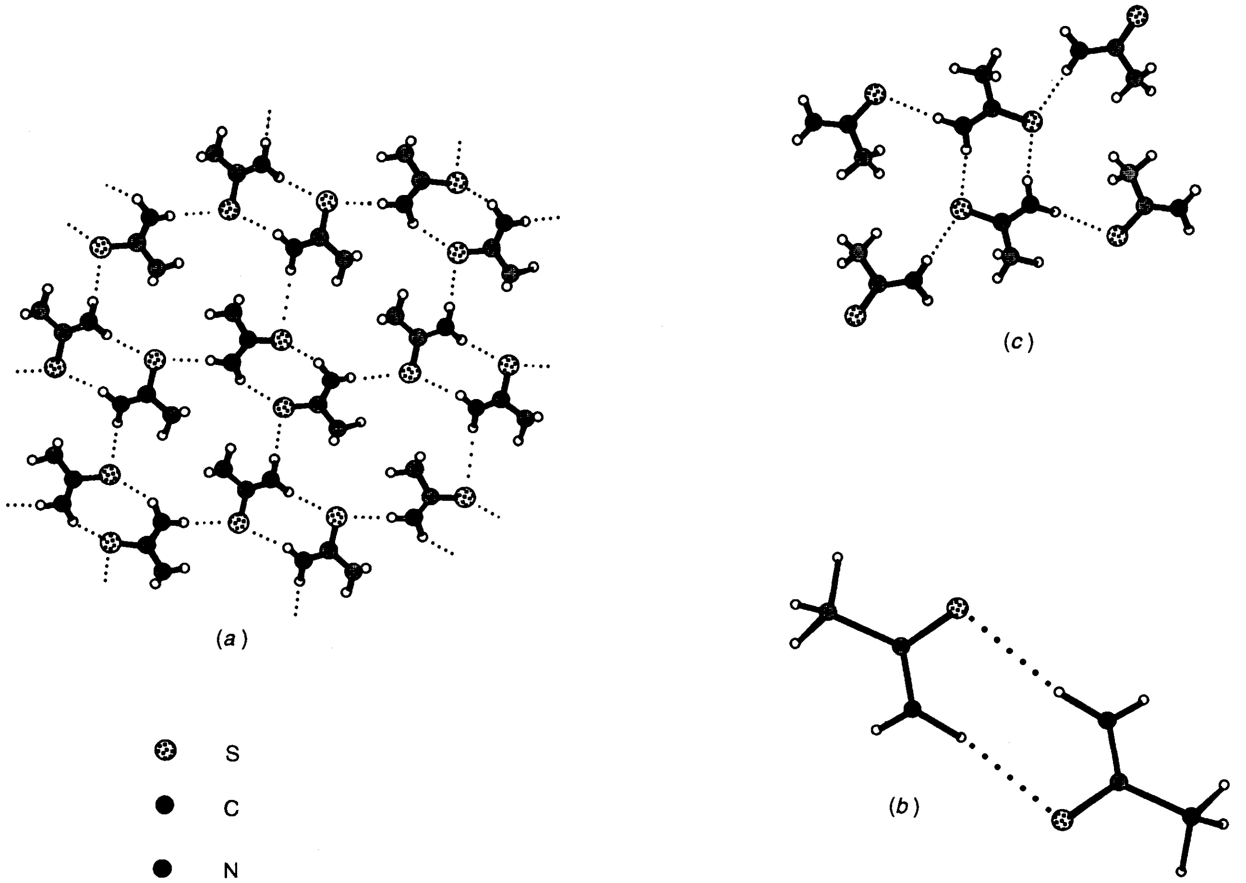

Fig. 2 Schematic representation of the crystal structure of thioacetamide (*a*). Centrosymmetrical dimer (*b*) and hexamer (*c*) models used to simulate the crystal field.

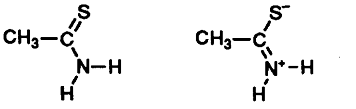

Fig. 3 Canonical forms for thioacetamide

unoccupied π^*_{CS} (21 a'') and σ^*_{CH} (13 a'') molecular orbitals. The resulting multiconfigurational wavefunction is referred to as a 6 × 5 CASSCF. The π_{CS} (38 a_g and 39 b_u) and π^*_{CS} (41 a_g and 42 b_u) orbitals along with the two orbitals (32 a_g and 33 b_u) with a prevalent contribution from the nitrogen atom were considered for the CASSCF calculations on the dimer (8 × 6 CASSCF) yielding a total of 105 electron configurations. Not surprisingly, the SCF configurations are dominant in the CAS wavefunction of the monomer as well as dimer. Significant contributions, other than the SCF configuration, also come from the $(\pi)^2_{CS} \rightarrow (\pi^*)^2_{CS}$ excitations. In addition, the CAS wavefunction of the dimer shows a further appreciable coefficient from the electron configuration $(38a_g)^1(39b_u)^1(41a_g)^1(42b_u)^1$ corresponding to two single excitations $(\pi)_{CS} \rightarrow (\pi^*)_{CS}$. Based on such results, the contribution from the π^*_{CS} orbital to the ground state of the molecule is increased upon hydrogen bonding and as a consequence the C═S bond distance lengthens upon dimerization.

In addition, the polarization of the C═S bond might be responsible for the slight stabilization of the staggered conformer calculated upon hydrogen bond formation. Such a conclusion is supported by the following results. First, the calculations previously reported for the thiocarbonyl compounds revealed that variations in the π-character of the C═S bond affect the rotational freedom of the methyl group. Secondly, the π-electron distribution on the thioamide group slightly depends on the methyl orientation. In particular, the rotation of the methyl group from the eclipsed to staggered

Table 4 *Ab initio* (HF/3-21G*) and experimental geometrical parameters of thioacetamide

	Monomer		Dimer		Hexamer[a]		Experimental[b]	
	Eclipsed	Staggered	Eclipsed	Staggered	Eclipsed	Staggered	Molecule A	Molecule B
Bond length/Å								
C1–C2	1.518	1.519	1.519	1.518	1.517	1.517	1.5044(10)	1.5021(9)
C1=S	1.652	1.656	1.668	1.674	1.684	1.691	1.6863(16)	1.6908(16)
C1–N	1.335	1.331	1.320	1.315	1.309	1.305	1.3178(8)	1.3167(8)
C2–H3	1.076	1.083	1.076	1.083	1.076	1.081	1.0903(17)	1.0880(17)
C2–H4	1.086	1.082	1.085	1.082	1.084	1.082	1.0903(16)	1.0855(16)
C2–H5	1.086	1.082	1.085	1.082	1.084	1.082	1.0887(16)	1.0832(16)
N–H1	0.998	0.998	1.000	0.999	1.006	1.007	1.0256(14)	1.0263(14)
N–H2	0.999	1.000	1.007	1.008	1.007	1.007	1.0246(15)	1.0231(14)
Bond angle (°)								
C2–C1=S	122.7	121.5	121.1	119.8	121.5	119.9	120.76(7)	121.27(6)
N–C1=S	123.1	123.0	124.0	124.0	123.5	123.6	122.73(6)	122.44(6)
C2–C1–N	114.2	115.5	114.9	116.2	115.0	116.4	116.51(5)	116.29(5)
C1–C2–H3	110.2	112.6	110.4	112.4	110.9	112.1	111.75(10)	111.33(10)
C1–C2–H4	109.7	108.9	110.0	108.9	109.4	108.9	109.05(10)	108.71(10)
C1–C2–H5	109.7	108.9	110.0	108.9	109.4	108.9	109.95(10)	110.91(10)
C1–N–H1	122.1	122.3	121.2	121.5	121.1	121.3	120.60(9)	120.20(9)
C1–N–H2	119.5	119.3	121.6	121.5	121.4	121.5	121.04(9)	120.92(9)
H1–N–H2	118.4	118.4	117.2	117.0	117.5	117.2	118.37(12)	118.81(12)
Torsion angle (°)								
S=C1–C2–H3	0[c]	180[c]	0[c]	180[c]	0[c]	180[c]	−177.7(1)	−165.0(1)
S=C1–C2–H4	+120.5	+58.6	+120.6	+58.4	+120.9	+58.9	+61.1(1)	+75.2(1)
S=C1–C2–H5	−120.5	−58.6	−120.6	−58.4	−120.9	−58.9	−56.2(1)	−43.2(1)
S=C1–N–H1	180[c]	180[c]	180[c]	180[c]	180[c]	180[c]	+178.2(1)	+179.9(1)
S=C1–N–H2	0[c]	0[c]	0[c]	0[c]	0[c]	0[c]	−1.8(1)	+3.1(1)
C2–C1–N–H2	180[c]	180[c]	180[c]	180[c]	180[c]	180[c]	+178.2(1)	−177.6(1)
N–C1–C2–H3	180[c]	0[c]	180[c]	0[c]	180[c]	0[c]	+2.3(1)	+15.7(1)

[a] Geometry relative to the central molecules of the complex. [b] Neutron diffraction of single crystal at 15 K, ref. 8. The standard deviations in parentheses refer to the least significant digit. [c] Fixed parameter.

orientations causes a small loss of π-charge (0.01 esu) on the nitrogen atom and a comparable gain (0.03 esu) on the sulfur atom. From this π-charge pattern, it emerges that the polar canonical form where the sulfur atom is negatively charged, the contribution of which increases on dimerization, seems to be favoured from staggered methyl orientations.

An alternative explanation of the stabilization of the staggered rotamer may be found when we take into account the H · · · S hydrogen bond distances. Both the HF/6-31G* and MP2/6-31G* optimized geometries provide S · · · H intermolecular bond distances shorter for the staggered (2.603 Å and 2.405 Å, respectively) than for the eclipsed (2.619 Å and 2.418 Å, respectively) conformations. On these grounds, the stabilization of the staggered isomer, predicted from the energy calculations, seems to be a consequence of the fact that hydrogen bonding is stronger when the molecule adopts staggered rather than eclipsed methyl orientations. The stabilization of the staggered rotamer upon hydrogen bond formation is also consistent with the crystal structure where the two asymmetric molecules forming the cyclic dimer adopt nearly staggered methyl conformations ($\varphi = 178.8°$ and 165.5°). However, a better comparison with the crystal structure necessarily requires consideration of aggregates where all the N–H bonds participate in hydrogen bonding and the S atom is involved in two C=S · · · H–N intermolecular interactions.

Hexamer. The model reproduced in Fig. 2(*c*) was introduced to investigate the effect of lateral hydrogen bonding on the geometry and on the methyl rotation barrier of the ring dimer. The size of the thioacetamide hexamer induced us to impose symmetry constraints and to use a moderately sized basis set for the geometry optimizations. A symmetry plane was imposed and the methyl groups of the four molecules surrounding the central dimer were constrained to assume the staggered orientation. The search for the preferred methyl orientation was then limited to the central dimer for which the staggered and eclipsed rotamers were investigated within the C_{2h} symmetry constraint. Otherwise, the intramolecular and intermolecular geometrical parameters of the thioacetamide hexamers were fully optimized at the HF/3-21G* level. The choice of such a basis set is a reasonable compromise for geometry optimizations since, as described in the previous sections of this work, it reproduces satisfactorily the structural data of the monomer and dimer obtained from larger basis sets. Finally, the stabilities of the eclipsed and staggered orientations of the methyl groups of the central dimer were evaluated by HF/6-31G*//HF/3-21G* energy calculations and compared in Table 3 with the corresponding values obtained for the monomer and dimer. In addition, Table 4 comprises the geometries of thioacetamide, the monomer and dimer along with that of the central molecules of the thioacetamide hexamer.

As expected, the structural changes calculated upon dimerization are further enhanced when the molecule is involved in four hydrogen bonding interactions. Irrespective of methyl conformation, the C=S and C–N bond distances vary in the expected direction (+0.015 Å and −0.01 Å, respectively) in going from the dimer to the hexamer, whereas the H · · · S bond linking to each other the central molecules lengthens by 0.04 Å upon lateral hydrogen bonding interactions.

As for the dimer, the point of interest is the fact that the staggered orientations of the methyl group favour the C=S · · · H–N interaction with respect to eclipsed conformations. This consideration is suggested by the following results. First, the staggered conformer is more preferred (5 kJ mol^{-1}) with respect to the eclipsed rotamer when one goes from the dimer to the hexamer. Secondly, the H ··· S distance separating the molecules of the central dimer is shorter for the staggered (2.591 Å) than for elipsed (2.606 Å) conformers. In addition, it is worth observing that the value of the rotation barrier height increases considerably in going from the dimer to the hexamer. Inspection of all intermolecular geometrical parameters excludes the presence of short-range interactions between neighbouring thioacetamide molecules hindering the methyl torsion. Thus, the further stabilization of the staggered rotamer of thioacetamide hexamer can be reasonably ascribed to lateral C=S ··· H–N hydrogen bonding which, increasing the contribution of the polar canonical form, further stabilizes the staggered orientations of the methyl group.

Comparison with Experiment.—It should be realized that comparisons between *ab initio* and experimental geometries should be made with caution because the experimental parameters include various types of averaging and the *ab initio* geometries are basis and method dependent approximations to an equilibrium structure.[1,18] Notwithstanding these considerations, there are conspicuous discrepancies between the neutron diffraction and the theoretical geometries of thioacetamide, already noted in ref. 8. The solid state results provide longer C=S bonds and shorter C–N bonds than the results obtained for the isolated molecule from all the theoretical levels and irrespective of the methyl conformation. Appreciable differences in the valence bond angles are also matched when theoretical and experimental structures are compared. In particular, the *ab initio* geometries reported in this paper predict that the C–C=S bond angle narrows and the C–C–N bond angle opens when thioacetamide moves from the gaseous to the solid state. Finally, high level *ab initio* calculations including electron correlation up to the MP4/6-311 + G** level suggest that the methyl conformation of the gaseous-phase molecule may be different from that of the solid state molecule. Since the discrepancies between the *ab initio* and crystal molecular geometries emerge from all the quantum mechanical levels, we conclude that whole structural variations described up to now can be taken as a measure of the structural perturbations due to the crystal field.

Such a consideration is fully supported by the fact that the structural changes mentioned previously are confidently matched when we compare the *ab initio* geometry of the thioacetamide monomer with that of the dimer and hexamer. The centrosymmetrical models of the oligomers proposed in this study reproduce the increase of the C=S bond and the decrease of the C–N bond as well as the angular changes of the thiocarbonyl group. In addition, the rotation of the methyl group, predicted by comparing the isolated and crystal molecules, is paralleled in our calculation. As a matter of fact, only one of the two thioacetamide rotamers found in the crystal, the rotamer A, really adopts a staggered orientation. For the rotamer B, there are small differences between the experimental (165°) and theoretical (180°) torsional angles (φ) probably due to the symmetry constraints assumed in our models.

Interestingly, the stabilization of the staggered rotamer, already emerging from the dimeric structure, is further enhanced when the hexameric structure is considered. On the basis of the *ab initio* results presented in this study and although the thioacetamide hexamer is, admittedly, only a crude simulation of the crystal field, we can conclude that the structural changes observed when the molecule goes from gas-phase to solid-state, among which the rotation of the methyl group, are indeed a consequence of the intermolecular hydrogen bonding occurring in the solid state.

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