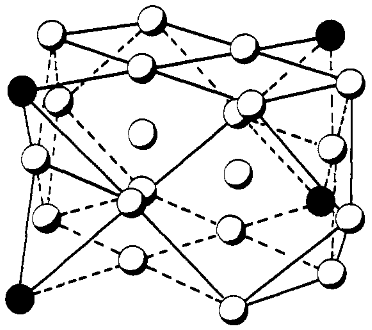

Figure 13. A 24 atom unit cell from which a three-layer fcc slab may be generated. The atoms needed to generate this "cluster" from the 20 atom cluster used in calculations here are shaded.

more localized representation, we can write the wave function for the total slab as,

$$\Psi_{\text{slab}} = \mathcal{A}\{\zeta_1\zeta_2\zeta_3\cdots\zeta_N\chi\}$$

where χ is the necessary spin function, and the ζ_i are products of the Wannier orbitals at the cell i,

$$\zeta_i = \phi_1\phi_2\phi_3\cdots\phi_n$$

Now we may approximate the interaction of a single HD molecule with the slab as the interaction of an HD molecule with one cell imbedded in the array. If we further restrict the states of the surrounding cells to be "frozen", then they serve essentially to provide only a properly screened environment for the cell of interest and establish boundary conditions for the states in that cell. From here, the analysis proceeds precisely as detailed in the previous sections, using this modified basis of occupied (and unoccupied) states in place of the cluster states used there. The validity of these approximations rests completely on the strength of interaction between the perturbed cell and the rest of the lattice.[23] If the cells are chosen to be large enough, this question becomes unimportant, as evidenced by recent chemisorption studies using clusters embedded within larger clusters.[24]

A related but less fundamental topic is the size of isolated clusters that may be adequately used to model bond-breaking processes. Much has been written about the validity of metal clusters as models for chemisorption[25] and conclusions vary. Accurate geometric and spectroscopic properties have been calculated for chemisorption systems in which as few as five metal atoms have been used as bulk models.[26] Energetic accuracy is more difficult to achieve. This difficulty may be associated with two problems: (1) the ground electronic state of the cluster may not strongly bond to the adsorbate, and (2) the excited-state spectrum of a small cluster is generally sufficiently discrete that excitations necessary to promote the cluster to a strongly bonding state may vary widely. Difficulties of this sort have been encountered in some form for clusters as large as 28 atoms.[13] When the problem being considered necessarily involves cluster excited-state character, as does the subject of this study, the difficulties are compounded and the possibility of obtaining anything more than qualitatively useful results becomes a strong function of cluster size.

Acknowledgment. The author gratefully acknowledges useful discussions with A. K. Rappé and M. L. Steigerwald during the course of this work.

Registry No. Hydrogen, 1333-74-0; nickel, 7440-02-0.

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(23) An additional, but minor, concern is that occupation of the Bloch and localized states must be complete; that is, each Wannier orbital must be filled for the transformation not to affect the total energy. For the large unit cells considered here, this is not an important restriction.

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(25) See, for example, R. Messmer in "Chemistry and Physics of Solid Surfaces", Vol. IV, R. Vanselow and R. Howe, Eds., Springer-Verlag, New York, 1982.

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π-Bond Anisotropy in the Molecular Structure of Thioacetamide

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Abstract: The crystal structure of thioacetamide has been refined using single-crystal neutron diffraction data at 15 K. The structure contains two symmetry-independent molecules with different orientations of the methyl groups in space group $P2_1/c$ with $a = 6.972$ (3), $b = 9.873$ (3), $c = 11.009$ (4) Å, $\beta = 99.75$ (1)° at 15 K. One rotamer has close to m symmetry with planar S=C—C—N and C—C—NH$_2$ moieties. In the other rotamer, the methyl group is twisted 15.6° from the m symmetry orientation, and the S=C—C—N, C—C—NH$_2$ moieties are significantly nonplanar. There are no significant differences in the bond lengths and valence angles in the two conformers. The nonplanarity with respect to the sp^2 C atom corresponds to a pyramidalization of 0.6°. This is reproduced in direction and order of magnitude by ab initio molecular orbital calculations at the HF/3-21G and HF/3-21G$^{(*)}$ levels of approximation. Since a similar observation has been made for the asymmetric rotamer of acetamide, this C (sp^2) pyramidalization is believed to be an intrinsic property of the asymmetric rotamers of these molecules. In contrast, the nonplanarity of the C–NH$_2$ groups, also observed in these molecules, is not well reproduced by the theoretical calculations and may be due, in part, to crystal-field forces.

Introduction

The crystal structure of thioacetamide contains two crystallographically independent molecules, which are reported from an X-ray analysis[1] to have different conformations with respect to the orientation of the methyl groups. Crystal structures containing the same molecule in different conformations are uncommon, but not rarities. In the crystal structure of pinacol,[2] for example, the same molecules appear in three different conformations. What

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[†] Research Collaborators at Brookhaven National Laboratory.

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(2) Jeffrey, G. A.; Robbins, A. H. *Acta Crystallogr., Sect. B* **1978**, *34*, 3817–3820.

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Table I. Crystal Data for Thioacetamide

	this work, 15 K	X-ray work,[a] 293 K
	C_2H_5NS, space group $P2_1/c$, $Z = 8$	
a, Å	6.972 (3)	7.170 (5)
b, Å	9.873 (3)	10.005 (5)
c, Å	11.009 (4)	11.062 (5)
β, deg	99.75 (1)	99.5 (2)
D_x, mg/m^3	1.336	1.275
λ_n, Å	1.1611 (3)	
$\lambda_{\mathrm{Cu\ K}\alpha}$, Å		1.542

[a] Reference 1.

makes the crystal structure of thioacetamide especially interesting is that one of the rotamers appears to be symmetrical, while the other is not. In the rhombohedral crystal structure of acetamide, there is also the unsymmetrical rotamer[3] which is calculated by ab initio theory to be 1.29 kJ/mol higher in energy than the symmetrical rotamer. A characteristic of this unsymmetrical rotamer is a small but significant pyramidalization (1.6°) of the C sp^2 bonds. This is reproduced by the ab initio molecular orbital calculations and is believed to be an intrinsic property of carbonyl and olefinic carbon atoms in asymmetric molecular environments.[4] In the crystal structure of monofluoroacetamide,[5] in which the molecule has close to m symmetry, pyramidalization was also observed, but it is almost negligible (0.25°). The crystal structure of thioacetamide, therefore, offers the opportunity to explore further this phenomenon by examining in detail symmetrical and unsymmetrical rotamers of the same molecule in the same crystal structure. The experimental work was carried out using single-crystal neutron diffraction at 15 K in order to accurately define the positions of the hydrogen atoms and to minimize the effects of thermal motion. Distortions from planarity of this order of magnitude can be an intrinsic property of the molecular conformation or can arise from crystal-field effects. To distinguish these two causes, we apply the hypothesis that if the ab initio theory reproduces the distortion for the isolated molecule at rest in direction and order of magnitude, it is an intrinsic molecular property. Conversely, if the theory does not reproduce the distortion, it is a consequence of crystal-field forces.

The theoretical work was carried out using ab initio molecular orbital theory at the Hartree–Fock level of approximation with 3-21G and 3-21G$^{(*)}$ basis sets. This work forms part of a series of combined high-precision, low-temperature, neutron diffraction analysis and ab initio theoretical calculations which, in addition to acetamide[3] and monofluoroacetamide,[5] have included formamide oxime,[6] *N,N'*-diformohydrazide,[7] glyoxime,[8] and 1,2,4-triazole.[9]

Experimental Section

The neutron diffraction data collection at the Brookhaven High Flux Beam Reactor and the structure refinement followed the same methods and procedures as previously described for formamide oxime,[6] except for the information provided below. The monochromated beam was obtained by reflection from the (220) planes of germanium with a neutron wavelength of 1.1611 (3) Å determined by least-squares fit of diffractometer setting angle data for 32 reflections of a standard KBr crystal [A_0 = 6.6000 (1) Å at room temperature]. Crystals of thioacetamide were obtained by slow evaporation of an acetone solution at room temperature. A specimen, 3.10 × 1.30 × 0.50 mm with faces {100} and {011}, was mounted with the a^* axis within 3° of the Φ axis of the diffractometer and was cooled at a rate of 1°/min to a temperature of 15.0 ± 0.5 K which was maintained during data collection. The lattice parameters, given in Table I, were determined from the $\sin^2\theta$ values for 31 reflections with $52.0° < 2\theta \leq 60.0°$. Neutron intensities were measured for one quadrant with scan widths of $\Delta(2\theta) = 2.6°$ for $\sin\theta/\lambda \leq 0.398$ Å^{-1} and varied according to the dispersion formula $\Delta(2\theta) = 0.900 + 3.487 \tan\theta$ for 0.398 Å$^{-1} < \sin\theta/\lambda < 0.688$ Å^{-1}. Neutron absorption corrections were applied using an analytical procedure.[10] The linear absorption coefficient (μ = 227.5 m^{-1}) was calculated assuming the mass absorption coefficient for chemically bonded hydrogen to be 2.6436 M^2 kg^{-1} at λ = 1.611 Å.[11] The resulting transmission factors ranged from 0.697 to 0.893. Of the 2200 reflections in the unaveraged data set, there were 161 with a net negative count. One was significantly different from zero and was attributed to the presence of an aluminum powder line in the background.

The initial positional parameters for the refinement were those of Truter[1] with assumed isotropic temperature factors of U = 0.006 Å^2 for nonhydrogen atoms and U = 0.009 Å^2 for hydrogen atoms. During the initial refinement by differential synthesis, six of the hydrogen atom positions became unreasonable. These were relocated by subsequent structure factor calculations and difference Fourier synthesis. Full-matrix least-squares refinement was carried out with a modified version of the computer program by Busing, Martin, and Levy.[12] The quantity minimized was $\sum w(F_o^2 - F_c^2)$, where $w = 1/\sigma^2(F_o^2)$, with $\sigma(F_o^2) = [\sigma_{\mathrm{counter}}^2 + (0.02F_o^2)^2]^{1/2}$. Anisotropic extinction parameters were used assuming a type I crystal with a Lorentzian mosaicity distribution.[13] After the final cycle of refinement using the 2048 unique unaveraged data, there were no changes in any of the 162 atomic parameters greater than 0.7σ. The largest feature in the final difference map was $1.08\sigma(\rho)$, where the error in the neutron scattering density was estimated from $\sigma(F_o)$. This corresponds to 1.1% of the largest peak in the final scattering density map. Extinction was widespread with 285 reflections having correction factors for F_c^2 of less than 0.90. The most severe correction was for the 080 reflection with $F_o/F_c = 0.56$. The agreement factors are: $R(F) = 0.043$, $R(F^2) = 0.037$, $wR(F) = 0.026$, $wR(F^2) = 0.047$, and S = 1.137. The atomic and extinction parameters are given in Table II. The atomic notation and thermal ellipsoids are shown in Figures 1 and 2. Lists of structure factors are available as supplementary material.

Thermal Motion Analysis and Bond Length Corrections. As in the low-temperature structures of acetamide[3] and monofluoroacetamide,[5] the thermal motion smearing of the proton scattering densities was appreciable, even at 15 K, and especially for the methyl groups. A standard rigid-body thermal motion analysis is not possible. A singularity in the least-squares analysis occurs because of the planarity or near planarity of the nonhydrogen atoms. The segmented body procedure in the program ORSBA[14] was therefore used, as in the previous papers in this series.

The internal motions of the hydrogen atoms are first calculated using ORSBA. The only values which were reasonable and consistent were those for the NH_2 rms "scissor" correction of 0.107 Å for molecule A and 0.111 Å for molecule B. The N–H and C–H rms stretch corrections were then calculated from the relative mean-square amplitude along the N–H and C–H bonds. These corrections were 0.078, 0.072 Å for N–H and 0.075, 0.078 Å for C–H for molecules A and B, respectively. The C–H rms inward bending toward the CH_3 axis was assumed to be 0.124 Å for both molecules.[15] These corrections were then subtracted from the rms displacements of the hydrogen atoms prior to obtaining the best least-squares fit for the segmented model described below.

The segmented model used had three segments: (C)H_3, CCSN, and (N)H_2, with three flexible joints, two between the segments and one from the center of mass to the stationary lattice. The overall fit was good for both molecules, with identical rms $\langle U_{ij}(\mathrm{obsd}) - U_{ij}(\mathrm{calcd})\rangle$ = 0.0003 Å^2 and identical $\sigma(U_{ij})$ = 0.0004 Å^2. The rms torsion for the NH_2 group about the C–N bond was 7.9° for molecule A and 8.5° for molecule B, and that for the CH_3 group about the C–C bond was 10.6° for molecule A and 12.2° for molecule B. The comparable values for acetamide at 23 K were 7 and 15°.[3] The resultant rigid-body motion of the CCSN segment with the internal torsion and hydrogen vibration motions subtracted is given in Table III. As in the other studies in this series, the

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Table II. Final Atomic Parameters for Thioacetamide at 15 K[a]

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
S(1A)	17 332 (19)	−18 787 (14)	24 990 (13)	74 (6)	33 (6)	39 (6)	−5 (4)	11 (5)	−3 (4)
C(1A)	21 487 (8)	−6 107 (6)	35 364 (5)	67 (2)	37 (2)	37 (2)	−1 (2)	9 (2)	2 (2)
C(2A)	23 477 (9)	−8 941 (6)	48 946 (6)	136 (3)	67 (3)	43 (3)	1 (2)	16 (2)	8 (2)
N(1A)	23 171 (6)	6 642 (5)	32 159 (4)	146 (2)	42 (2)	60 (2)	−9 (2)	20 (2)	0 (2)
H(1A)	2 529 (2)	1 413 (1)	3 871 (1)	335 (8)	123 (6)	173 (6)	−34 (5)	38 (6)	−34 (5)
H(2A)	2 240 (2)	933 (1)	2 310 (1)	383 (8)	170 (7)	129 (7)	−20 (6)	40 (6)	27 (5)
H(3A)	2 554 (3)	34 (2)	5 438 (1)	582 (11)	182 (7)	152 (7)	−28 (7)	37 (7)	−52 (5)
H(4A)	3 585 (2)	−1 567 (2)	5 171 (1)	310 (8)	333 (9)	214 (7)	144 (7)	−17 (6)	67 (6)
H(5A)	1 058 (2)	−1 418 (2)	5 087 (2)	289 (8)	379 (9)	231 (8)	−105 (7)	106 (6)	41 (7)
S(1B)	−28 417 (20)	−18 945 (14)	−3 881 (12)	77 (6)	37 (6)	28 (6)	−9 (4)	8 (5)	−5 (4)
C(1B)	−27 042 (8)	−5 967 (6)	6 251 (5)	53 (2)	41 (3)	38 (2)	0 (2)	8 (2)	2 (2)
C(2B)	−33 458 (8)	−7 612 (6)	18 523 (5)	90 (3)	77 (3)	42 (3)	0 (2)	27 (2)	7 (2)
N(1B)	−20 177 (6)	6 018 (4)	3 959 (4)	101 (2)	43 (2)	62 (2)	−10 (2)	26 (1)	−2 (2)
H(1B)	−1 959 (2)	1 366 (1)	1 033 (1)	302 (7)	128 (6)	191 (7)	−31 (5)	70 (5)	−54 (3)
H(2B)	−1 601 (2)	804 (1)	−433 (1)	319 (7)	188 (7)	156 (6)	−41 (5)	113 (5)	9 (5)
H(3B)	−3 520 (3)	216 (2)	2 278 (2)	567 (11)	186 (7)	266 (8)	16 (7)	215 (7)	−54 (6)
H(4B)	−2 251 (3)	−1 341 (2)	2 455 (2)	328 (8)	447 (10)	181 (7)	168 (7)	41 (6)	120 (7)
H(5B)	−4 704 (2)	−1 316 (2)	1 758 (2)	247 (7)	500 (11)	256 (8)	−195 (7)	98 (6)	−57 (7)

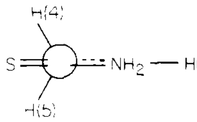
Anisotropic Extinction Parameters, g (rad^2 × 10^8)

g_{11} 0.018 (6) g_{33} 0.75 (4) g_{13} −0.10 (1)
g_{22} 0.78 (8) g_{12} −0.02 (2) g_{23} −0.31 (5)

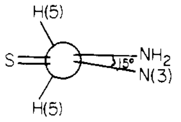
[a] The fractional coordinates are ×10^5 for nonhydrogen atoms, ×10^4 for hydrogen atoms. Anisotropic temperature factors (Å^2 × 10^4) are referred to the crystallographic axis and correspond to the temperature factor expression $T = \exp[-2\pi^2 \sum_i^3 \sum_j^3 h_i h_j a_i^* a_j^* \cdot U_{ij}]$. Estimated standard deviations given in parentheses refer to the least significant digit.

thermally corrected C–H and N–H bonds are longer than expected from theory and microwave data, whereas without the thermal motion corrections, there is close correspondence. This is ascribed to the anharmonicity of the C–H and N–H bond stretching motion. Table IV shows the effect of applying a Kuchitsu and Bartell[16] semiempirical anharmonic correction to reduce this discrepancy between experiment and theory. The bond lengths and bond angles, both uncorrected and corrected for thermal motion, are given in Table V.

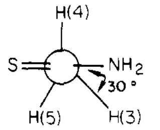
Ab Initio Molecular Orbital Calculations. The theoretical calculations were carried out using a DEC-10 version of GAUSSIAN 80 at the HF/3-21G and HF/3-21G$^{(*)}$ levels of approximation.[18,19] Geometry optimization for thioacetamide was carried out for the four rotamers **1**, **2**, **3**, and **4** with both basis sets. Rotamers **1** and **4** were constrained to be C_s symmetry and the twist angle was fixed in rotamers **2** and **3**; otherwise, the geometry optimization was complete. The optimized bond lengths and valence angles are shown in Table V. The calculated energies and pyramidalizations[20] are shown in Table VI. Analogous calculations were repeated for acetamide and fluoroacetamide using the same program. They are also shown in Table VI.



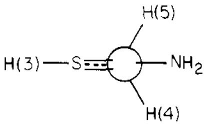
1, χ = 180°



2, χ = −165°



3, χ = −150°



4, χ = 0°

(χ = S–C(1)–C(2)–H(3) angle)

Table III. Rigid-Body Motion of the CCSN Segment[a]

		a, deg	b, deg	c, deg
		Molecule A		
T, Å	0.072	15.5	76.6	82.4
	0.059	75.9	165.3	94.2
	0.056	83.6	84.1	171.3
ω, deg	3.54	39.4	129.2	93.3
	1.87	51.2	39.2	94.7
	1.63	84.5	88.5	5.7
		Molecule B		
T	0.071	68.0	76.3	26.3
	0.065	33.8	120.9	102.2
	0.057	65.7	34.5	112.9
ω	2.85	9.2	99.0	87.7
	2.17	81.1	30.1	118.5
	1.55	87.7	61.5	28.6

[a] Rms values of translational **T**, and oscillational ω, tensors, referred to the crystallographic axes. Internal torsion and hydrogen vibration motion subtracted. Origin at center of mass and the inertial axes X and Y in the CCSN plane, with X nearly parallel to C(1)–S(1) and the Z axis normal to the plane.

Table IV. Effect of Anharmonicity Correction on N–H and C–H Bond Lengths (in Å)

bond	exptl	segmented motion correction	anharmonicity correction[a]	corrected value
		Molecule A		
N(1)–H(1)	1.0256 (14)	0.013	−0.020	1.019
N(1)–H(2)	1.0246 (15)	0.015	−0.019	1.021
C(2)–H(3)	1.0903 (17)	0.024	−0.017	1.097
C(2)–H(4)	1.0903 (16)	0.026	−0.015	1.101
C(2)–H(5)	1.0887 (16)	0.025	−0.017	1.097
		Molecule B		
N(1)–H(1)	1.0263 (14)	0.016	−0.017	1.024
N(1)–H(2)	1.0231 (14)	0.016	−0.017	1.022
C(2)–H(3)	1.0880 (17)	0.030	−0.018	1.100
C(2)–H(4)	1.0855 (16)	0.031	−0.020	1.097
C(2)–H(5)	1.0832 (16)	0.031	−0.016	1.098

[a] The expression used was $-{}^3/_2 a \langle U_{XH}{}^2 \rangle$, where $\langle U_{XH} \rangle$ is the relative mean square amplitude of H and X atoms along the X–H bond; a = 1.98 Å^{-1} for C–H bonds, and a = 2.19 Å^{-1} for N–H bonds (see ref 17).

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(20) Pyramidalization is defined by the mean value of 90° − θ_p', where

$$\theta_p' = \cos^{-1}\left(\frac{V_i \cdot V_j \times V_k}{|V_i||V_j \times V_k|}\right) \text{ in}$$

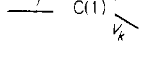

Table V. Experimental and Theoretical Molecular Dimensions[a]

	experimental (at 15 K)				theoretical[b]			
	uncorrected		corrected for thermal motion		rotamer			
	molecule A	molecule B	molecule A	molecule B	**1** $\chi = 180°$	**2** $\chi = 165°$	**3** $\chi = 150°$	**4** $\chi = 0°$
S(1)-C(1)[c]	1.6863 (16)	1.6908 (16)	1.689	1.693	1.716 1.657	1.715 1.655	1.713 1.654	1.710 1.652
C(1)-C(2)[c]	1.5044 (10)	1.5021 (9)	1.508	1.505	1.508 1.519	1.508 1.518	1.509 1.518	1.509 1.518
C(1)-N(1)[c]	1.3178 (8)	1.3167 (8)	1.319	1.319	1.319 1.331	1.319 1.331	1.321 1.333	1.323 1.335
N(1)-H(1)	1.0256 (14)	1.0263 (14)	1.019	1.024	0.999	0.999	0.999	0.999
N(1)-H(2)	1.0246 (15)	1.0231 (14)	1.021	1.022	1.000	1.000	1.000	1.000
C(2)-H(3)	1.0903 (17)	1.0880 (17)	1.097	1.100	1.083	1.084	1.084	1.076
C(2)-H(4)	1.0903 (16)	1.0855 (16)	1.101	1.097	1.082	1.084	1.086	1.086
C(2)-H(5)	1.0887 (16)	1.0832 (16)	1.097	1.098	1.082	1.079	1.078	1.086
S(1)-C(1)-C(2)	120.76 (7)	121.27 (6)	120.8	121.3	121.2 121.5	121.3 121.8	121.7 121.1	122.3 122.7
S(1)-C(1)-N(1)	122.73 (6)	122.44 (6)	122.7	122.4	122.3 123.0	122.3 123.0	122.3 123.1	122.3 123.1
C(2)-C(1)-N(1)	116.51 (5)	116.29 (5)	116.5	116.3	116.5 115.5	116.3 115.2	115.9 114.8	115.3 114.2
C(1)-N(1)-H(1)	120.60 (9)	120.20 (9)	120.3	119.9	122.4	122.3	122.3	122.2
C(1)-N(1)-H(2)	121.04 (9)	120.92 (9)	120.8	120.7	119.4	119.4	119.5	119.6
H(1)-N(1)-H(2)	118.37 (12)	118.81 (12)	118.9	119.3	118.2	118.2	118.2	118.3
C(1)-C(2)-H(3)	111.75 (10)	111.33 (10)	111.5	110.9	112.8	112.5	111.8	110.3
C(1)-C(2)-H(4)	109.05 (10)	108.71 (10)	108.8	108.3	108.8	108.3	108.3	109.7
C(1)-C(2)-H(5)	109.95 (10)	110.91 (10)	109.6	110.5	108.8	109.5	109.9	109.7
H(3)-C(2)-H(4)	109.51 (15)	108.80 (16)	109.8	109.2	109.4	110.0	108.6	109.4
H(3)-C(2)-H(5)	109.25 (15)	109.25 (16)	109.5	109.7	109.4	109.8	109.9	109.4
H(4)-C(2)-H(5)	107.23 (15)	107.75 (16)	107.6	108.2	107.4	106.6	108.2	108.3
S-C(1)-C(2)-H(3)	−177.7 (1)	−165.0 (1)	*d*	*d*	180[e]	−165[e]	−150[e]	0[e]
S-C(1)-C(2)-H(4)	+61.1 (1)	+75.2 (1)			+58.4	+73.3	+90.4	−120.6
S-C(1)-C(2)-H(5)	−56.2 (1)	−43.2 (1)			−58.4	−42.6	−27.7	+120.6
S-C(1)-N-H(1)	+178.2 (1)	+179.9 (1)			180	180	−179.9	180
S-C(1)-N-H(2)	−1.8 (1)	3.1 (1)			0	−0.2	−0.2	0
C(2)-C(1)-N(1)-H(2)	+178.2 (1)	−177.6 (1)			180	+178.5	+178.1	180
N(1)-C(1)-C(2)-H(3)	2.3 (1)	15.7 (1)			0	+16.3	+31.7	180

[a] Distances in angstroms, angles in degrees. Esd's in parentheses refer to the least significant digit. [b] Where two values are given, the top line is from HF/3-21G, the bottom line from HF/3-21G$^{(*)}$. Differences in HF/3-21G and HF/3-21G$^{(*)}$ values are negligible for dimensions involving hydrogen atoms. [c] See ref 17. [d] The thermal motion corrections for pyramidalization and torsion angles are negligible. [e] Fixed parameter.

The calculated energy differences for thioacetamide rotamers are negligible, implying a very small barrier to rotation of the methyl group. For the rotamers **2** and **3**, pyramidalization is predicted at the sp^2 carbon atom C(1) in the direction which is trans to the C-H bond on C(2), which is that closest to being normal to the mean plane of the C(1) sp^2 bonds, i.e., C(2)–H(4). The calculated values for rotamer **2** agree with those observed experimentally both in order of magnitude and in direction. A smaller degree of pyramidalization at the sp^2 N atom is also predicted for **2** and **3**, but the experimental value for **2** is an order of magnitude greater and in the opposite direction.

Discussion

The two symmetry-independent molecules of thioacetamide are different rotamers, as shown in Figure 1, with no significant differences in bond lengths and valence angles (see Table V).[21] The calculated lowest energy rotamer is **4** with $\chi = 0°$, but the rotameric energy differences are negligible at the level of theoretical approximation used. In acetamide, the rotamer observed in the crystal structure is that corresponding to **3** with $\chi \approx 90°$. This was calculated to be 1.29 kJ/mol higher than that with $\chi = 0°$.

The most interesting experimental difference in the two thioacetamide rotamers, A and B, in the crystal structure is shown in Table VII. In rotamer A, C(1) and its three [sp^2] bonded atoms S(1), C(2), and N(1) are *exactly planar*, within the estimated experimental limits of 2.5σ. The same is true for N(1) and the [sp^2] bonded atoms C(1), H(1), and H(2). In rotamer B, there are significant deviations from planarity with respect to both these

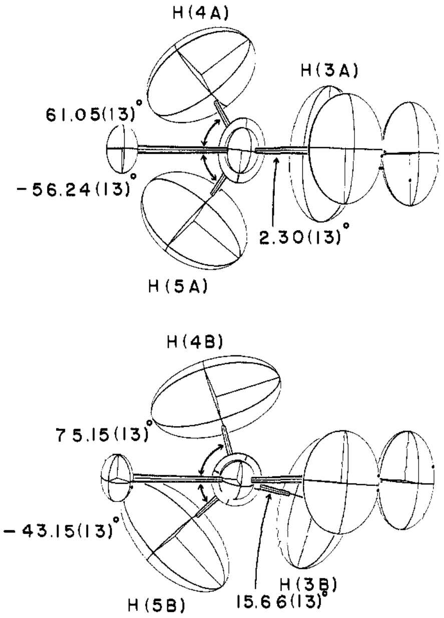

Figure 1. The thermal ellipsoids (at 99% probability) and torsional angles of the two rotamers observed in the crystal structure of thioacetamide at 15 K, viewed down the C-C bond.[21]

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(21) The differences in bond lengths between the room temperature X-ray and the low-temperature neutron analyses are +0.025, −0.010, and +0.007 Å in the C=S, C—C, and C—N bonds, respectively. These differences are of the order of magnitude frequently observed between internuclear and interelectronic atomic distances, but the precision of the X-ray analyses is insufficient to make them significant. The corresponding torsional angles for the room temperature X-ray study were 0, 60, −69° and 28, 71, −37°, which, in view of the large oscillatory motion of the methyl group, even at 15 K, were remarkably accurate.

Table VI. Calculated Energies and Pyramidalization in Rotamers of Thioacetamide, Acetamide, and Fluoroacetamide[a]

	τ (deg)	E_{cal} (hartrees)	rel E_{cal} (kJ/mol)	θ[C(1)] (deg)	θ[N] (deg)
		Thioacetamide			
4	0	−527.929 46	0	0	0
		−528.030 72	0		
3	150[b]	−527.929 46	0	+1.52	−0.21
		−528.030 51	0.55	+1.76	−0.34
2	165	−527.929 41	0.13	+1.12	−0.18
		−528.030 30	1.10	+1.44	−0.11
1	180	−527.929 38	0.21	0	0
		−528.030 19	1.39		
expt A	177.7			+0.03	−0.02
B	165			+0.60	−2.72
		Acetamide			
	0	−206.815 79[c]	0	0	0
	150[b]	−206.815 30	1.29	+1.57[c]	−0.38[c]
	165	−206.814 87	2.42	+1.24	−0.28
	180	−206.814 67	2.94	0	0
exp	148.8			+1.50	−6.60
		Fluoroacetamide			
	0	−305.132 01	0	0	0
	180	−305.120 11	31.24	0	0
exp	1.0			−0.25	−1.00

[a] τ is angle S=C(1)–C(2)–H(3) in thioacetamide and acetamide, O=C(1)–C(2)–F in fluoroacetamide. θ is pyramidalization. Where two values are given, the top line is from HF/3-21G, the bottom line from HF/3-21G$^{(*)}$. [b] This rotamer has a C–H normal to the C–C=S or C–C=O plane. [c] These energy and pyramidalization values differ from those previously reported[3,5] (+1.70 and −0.90° for pyramidalization), owing to differences in the convergence criteria and integral cutoff tolerances used for the gradient optimization. For consistency, all current results were calculated with a local DEC-10 version of GAUSSIAN 80, while the previous result was computed with the Carnegie-Mellon University VAX version.

four-atom groups. In neither rotamers do all six atoms lie in one plane. In A, the dihedral angle between the least-squares planes of S=C—C—N and C—NH_2 is 1.85°; in B it is 1.25°.

The pyramidalization[20] corresponding to these deviations from nonplanarity is shown in Table VI. The pyramidalization at C(1B) is trans to the C(2B)–H(4B) bond, which is that most nearly normal to the sp^2 C(1B) plane. It is reproduced by the HF/3-21G and 3-21G$^{(*)}$ theoretical calculations to within 0.5° in the same direction. For this reason it is believed to be an intrinsic property of the molecule in this rotameric conformation. It is the same direction and order of magnitude as observed in acetamide and in the amino acids, and has been predicted theoretically for similar asymmetric conformers of the carboxylates and amides.[4]

In contrast, the larger pyramidalization at the nitrogen atom in molecule B is not reproduced either in magnitude or direction by the theoretical calculations. An even larger N-pyramidalization was observed in the acetamide structure, which was also much larger than calculated theoretically (see Table VI).

Since the NH_2 groups in both acetamide and thioacetamide are involved in hydrogen bonding, it is reasonable to assume that the lack of correspondence between experiment and theory is due to the directional property of intermolecular hydrogen bonding in the crystal. If so, the crystal structure does not provide a simple explanation. The hydrogen bond sulfur acceptor atoms are out of the NH_2 plane for both thioacetamide molecules: by −0.11 and +0.48 Å for N(A)H(1)···S(1B) and N(A)H(2)···S(1B), and by −0.01 and +0.93 Å for N(B)H(1)···S(1A), and N(B)H(2)···S(1A). Although the hydrogen bonds are less linear when the amine group of molecule B is the donor, this cannot satisfactorily account for the 0.6° deviation from planarity of the C–NH_2 group in molecule A and the 2° deviation in molecule B. Other interactions involving van der Waals or dipole forces must be involved.

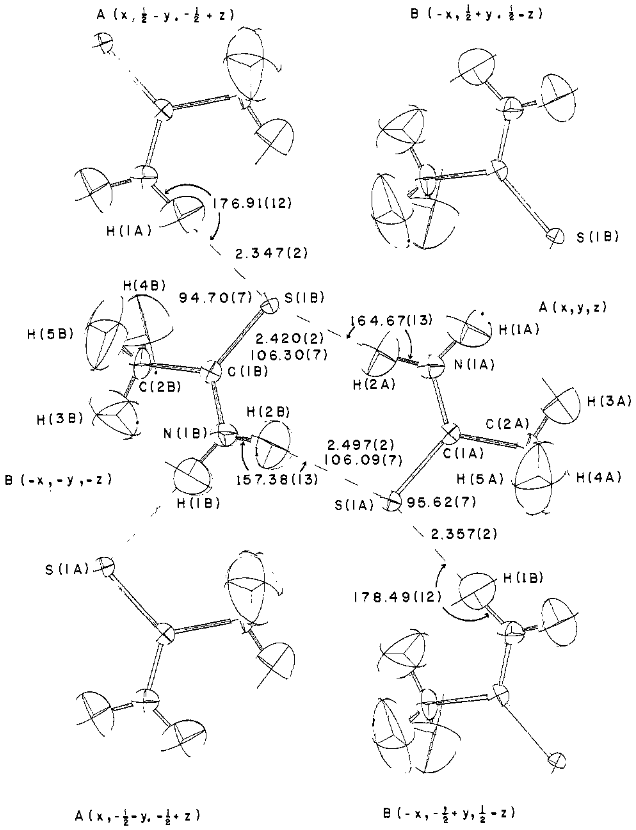

Figure 2. The hydrogen-bonded layers in the crystal structure of thioacetamide at 15 K. The dimensions are uncorrected for thermal motion.

The agreement between the theoretical and experimental bond lengths and valence angles, corrected for thermal motion, shows the same degree of correspondence as was found in the other investigations in this series.[3,5-9] Hydrogen bonding is expected to lengthen the C=S bonds and shorten the C—N bonds relative to the isolated molecule. Since N—H···S=C hydrogen bonds are weaker than N—H···O=C bonds, this effect should be smaller than that calculated for the formamide dimer,[5] i.e., +0.018 Å for C=O, −0.023 Å for C—N.

The experimental C=S bond lengths lie between the two theoretical values. This is consistent with the results for CS and H_2CS in which the 3-21G and 3-21G* basis calculations overestimate and underestimate, respectively, the C–S bond lengths by 0.02–0.03 Å.[19] The agreement for both the C–N and C–C bonds is definitely better with the basis set that does not have d functions on the S atoms. It is known that, in Hartree–Fock

Table VII. Planarity of Thioacetamide Conformers

	deviations (Å × 10^4) from least-squares planes					
	molecule A			molecule B		
atom	plane 1A	plane 2A	plane 3A	plane 1B	plant 2B	plane 3B
S(1)	1 (14)		−124 (14)	−12 (13)		−64 (13)
C(1)	−2 (6)	0 (6)	3 (6)	39 (5)	37 (3)	11 (5)
C(2)	1 (6)		134 (6)	−13 (6)		91 (6)
N(1)	1 (4)	1 (4)	−2 (4)	−15 (4)	−131 (4)	−137 (4)
H(1)		0 (15)	−208 (15)		47 (14)	−72 (14)
H(2)		0 (17)	196 (17)		47 (15)	170 (15)

calculations at these levels of basis set approximation, there can be cancellation of errors, such that the agreement with observation is not necessarily improved for every type of bond with each improvement of the basis set.[22-24] The discrepancy in the N–H bond lengths is partially accounted for by the lengthening effect of hydrogen bonding, which is calculated to be +0.018 Å in the formamide dimer.[5]

As was observed in the other comparisons of this type, the agreement between the theoretical and experimental valence angles is very good, only exceeding 0.5° for bonds involving hydrogen atoms.

The hydrogen bonding is as described in the X-ray analysis. It consists of hydrogen bond dimers linked laterally to form buckled layers, as in the crystal structure of formamide.[25] The dimensions are shown in Figure 2. There is no hydrogen bonding between layers which have a mean separation of 3.49 Å. It is interesting to note that the lateral hydrogen bonds are slightly shorter and more linear than those involved in the dimer association.

This study provides an example of how high-precision crystal-structure analysis and ab initio theoretical calculations can be used in combination to distinguish between those small distortions which are the intrinsic properties of asymmetrical molecules and those of similar magnitude that arise from crystal-field effects.

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Registry No. Thioacetamide, 62-55-5.

Supplementary Material Available: Tables of observed and calculated structure factors for thioacetamide (11 pages). Ordering information is given on any current masthead page.

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Theoretical Comparison between Nucleophilic and Electrophilic Transition Metal Carbenes Using Generalized Molecular Orbital and Configuration Interaction Methods

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Abstract: Ab initio calculations are reported on several transition metal carbenes and their dissociated fragments. In a better than minimal basis set, the orbitals involving the metal–carbene double bond (σ, π, π*, and σ*) are optimized by the generalized molecular orbital (GMO) method and used in a full configuration interaction (CI) calculation for the four electrons in the M=C bond. In this manner we maintain the physical significance inherent only in small CI calculations while obtaining the major portion of near-degenerate correlation energy for these four electrons. Our results suggest electrophilic and nucleophilic metal carbenes arise from two different bonding schemes. Electrophilic, 18-electron, metal carbenes can be considered as bonding between singlet metal and singlet carbene fragments, whereas nucleophilic, often electron-deficient, metal carbenes can be considered as bonding between triplet metal and triplet carbene fragments. This conclusion is illustrated using fragment and atomic deformation densities, molecular orbital maps, molecular orbital diagrams, and theoretical thermodynamics. Interchanging singlet and triplet carbene fragments with the metal fragments indicates the metal fragment is slightly more important than the carbene fragment in determining the stability and the electronic properties of metal carbenes. The M=C dissociation energy for electrophilic $(CO)_5Mo{=}CH(OH)$ is calculated to be 60 kcal/mol. The calculated M=C dissociation energy for nucleophilic $CpCl_2Nb{=}CH_2$ is 74 kcal/mol. The latter compound appears to have a stronger π bond. The calculated rotational barrier of the methylene in $CpCl_2Nb{=}CH_2$ is 14.6 kcal/mol, in good agreement with NMR experiments on similar compounds.

Introduction

Transition metal carbene complexes are important to our understanding of many catalytic reactions, including olefin metathesis and Fischer–Tropsch synthesis.[1] Most complexes fall into one of two distinct groups. The Fischer-type complexes,[2] the first of which was $(CO)_5W{=}C(Ph)(OMe)$, are 18-electron species, have the metal in a low (0 or 1+) oxidation state, and are stabilized by heteroatom or phenyl substituents on the carbene carbon. Recently, Schrock prepared a number of tantalum complexes,[3] including $(Me_3CCH_2)_3Ta{=}CH(CMe_3)$ and $(\eta_5\text{-}C_5H_5)_2MeTa{=}CH_2$. These complexes are usually electron deficient (10 to 16 e^-), have the metal in a high oxidation state (3+), and have only hydrogen or simple alkyl substituents on the carbene. Although the M=C bond distance for both types of complexes are similar and in agreement with a typical metal–carbon double bond, there are some important chemical differences. For example, the Fischer-type complexes are electrophilic at the carbon double bonded to the metal, while the tantalum complexes are nucleophilic

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