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Infrared Spectra and Conformation of *N*-Acetylthiourea

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Infrared spectra of *N*-acetylthiourea (ATU) and its *N,N,N'*-trideuterated compound have been examined in the range 4000—50 cm^{-1}. A complete vibrational assignment with a normal coordinate treatment based on a Urey-Bradley type intramolecular potential function supplemented with valence force function for the out of plane and torsional modes is proposed and the feature of the thioureido vibrations explained. A molecular orbital study by the CNDO/2 method of ATU and its oxygen analog is undertaken and the results are analyzed for a comparative study of the molecular electronic structure and conformation.

Thiourea is a compound of considerable importance for the study of spectroscopic, structural and ligational properties. Many sulfur-nitrogen compounds containing $-NHCSNH_2-$ skeleton have been shown to possess carcinostatic and antiviral activities.[1)] In this regard the vibrational spectra of thiourea and its various *N*-alkyl derivatives have received detailed attention.[2—10)] In this context, it was of interest to study the spectral and structural features of *N*-acetylthiourea (ATU). ATU is isoelectronic with monothiobiuret and is the sulfur analog of *N*-acetylurea (AU), for both of which detailed vibrational spectroscopic studies have been reported very recently.[11,12)] We have now examined the infrared spectra of ATU and its *N,N,N'*-trideuterated species and propose an assignment of all the fundamentals. A complete normal coordinate analysis has been carried out for ATU-d_0 and ATU-d_3 employing an intramolecular potential field of the Urey-Bradley type supplemented with valence force functions for the out of plane modes.

Another interesting problem concerning ATU is the identification of the minimum energy conformation. Four planar conformations may be conceived for ATU (Fig. 1). For this purpose, the all valence self consistent field molecular orbital method by the CNDO/2 procedure is employed. The computed bond orders and electron populations are employed to discuss the electronic structure. The calculations have been performed on both ATU and AU to note the electronic effects of the amide/thioamide grouping.

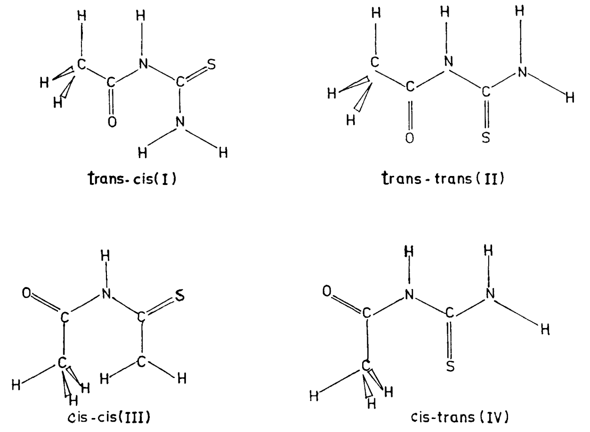

Fig. 1. Planar conformations of ATU.

Experimental

N-Acetylthiourea (Aldrich Chemical) was recrystallized from ethanol. The *N,N,N'*-trideuterated compound was obtained by exchange reaction with heavy water. The infrared spectra (both polycrystalline and solution) were recorded using Perkin-Elmer Model 580 spectrophotometer (4000—200 cm^{-1}) employing KBr pellet and Nujol mull techniques. Far infrared spectra (250—50 cm^{-1}) were recorded on Polytec FIR30 Fourier transform spectrometer as polyethylene pellets. The observed frequencies were calibrated with the usual standards.

Theoretical Treatment

The calculations were done on a DEC 1090 computer system using programs written in FORTRAN IV.

Normal Coordinate Analysis. The observed frequencies of ATU and its *N,N,N'*-trideuterated derivative were used in the calculations cast in terms of the GF matrix formulation.[13)] The molecular structure adopted is shown in Fig. 2. This was based on the results of the CNDO/2 calculations and the preliminary X-ray structure determination.[14)]

In the C_s point group model, the 33 fundamentals of ATU are classified amongst the symmetry species as 22A′ (In-plane), and 11A″ (out of plane) modes. The structural parameters were transferred from AU[12)] and the C–S distance was taken to be 1.72 Å as in thioacetamide.[15)] The internal valence coordinates and the local symmetry coordinates adopted were similar to those employed for AU.[12)] A simple Urey-Bradley force field supplemented with valence force function for the out of plane deformation and torsional coordinates was employed. The initial values of the intramolecular force constants were transferred from thioacetamide[16—18)] (TA), *N*-methylthioacetamide[16)] (NMTA), and *N*-methylacetamide[16,19)] (NMA), for

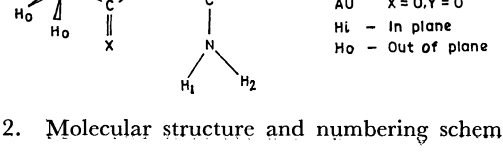

Fig. 2. Molecular structure and numbering scheme.

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which previously developed reliable potential constants are available. Only a small number of force constants required modification within a narrow range in the iteration process to obtain a desired agreement between the observed and calculated frequencies for ATU-d_0 and ATU-d_3. The programs employed were similar to the normal coordinate package of Schachtschneider.[20]

Molecular Orbital Studies. The calculations were made using the self consistent field CNDO/2 method. A full basis set of orbitals were explicitly considered including the 3d orbitals of sulfur. The geometrical parameters used were the same as those employed for the normal coordinate treatments. The total molecular energy was calculated, for the four more likely planar conformations of AU and ATU assuming the bond lengths and interbond angles to remain the same during the internal rotations. The standard program of Pople and Beveridge was employed.[21]

Results and Discussion

Table 2 gives the values of the final force constants. The values of the force constants appear reasonable and are similar to those of the initial ones indicating the good transferability property of the Urey-Bradley force constants as observed in other amide[16] and thioamide[16,18] derivatives. The force constant values compare well with the appropriate ones of AU.[12]

Spectral Interpretations. The observed spectra are shown in Fig. 3. In Table 1, the observed frequencies are compared with the calculated frequencies for ATU-d_0 and -d_3, wherein calculated potential energy distributions (PED), omitting for simplicity those less than 15%, are shown. A brief discussion of the features of thioureido vibrations of ATU will now be given.

The characteristic bands of interest are due to C=S and C–N stretching vibrations and NH inplane bending corresponding to thioamide I, III, and II bands respectively. The results of the coordinate analysis indicate a delocalized C=S mode contributing chiefly to the 820 cm^{-1} band akin to the 808 cm^{-1} band of thiosemicarbazide[22,23] and in contrast to a localized C=S stretching mode of *N*-methylthiourea at 778 cm^{-1}. Thus the C=S stretching frequency of ATU is higher than that in thiourea[2] and sym. *N*,*N*′-dimethylthiourea[8,9] assigned near 730 cm^{-1}. In monothiobiuret,[11] which is isoelectronic with ATU, the C=S stretching is assigned at 825 cm^{-1}. The C=S stretching frequency is lowered to 735 cm^{-1} in the *N*-deuterated derivative, the shift is comparable to that in *N*-methylthiourea -d_0 and -d_3.

The high and low C–N stretching frequencies (amide III bands) corresponding to the asymmetric and symmetric modes are assignable at 1525 and 1420 cm^{-1} which compare reasonably with those of *N*-methylthiourea[5] (NMTU) at 1565 and 1500 cm^{-1} and of sym·*N*,*N*′-dimethylthiourea[8,9] (DMTU) at 1560 and 1355 cm^{-1}. The differences are attributable to the different nature of the coupling of the vibrations involved.

The thioamide II band of the –CSNH$_2$ group due to NH$_2$ bending is observed at 1590 cm^{-1} which is lower than the 1642 cm^{-1} band of *N*-methylthiourea (NMTU). The thioamide II of –CSNH-grouping contributes to two bands at 1525 and 1315 cm^{-1}. The analogous NH bending frequencies are found in the region 1350 to 1400 cm^{-1} in NMTU,[5] DMTU[8,9] and thiosemicarbazide.[22,23] The thioamide VI band due to in-plane C=S bending occurs at 475 cm^{-1} as in thioacetamide.[16,18] In contrast, *N*-methylthiourea exhibits a more delocalized C=S bending mode. The assignments of other frequencies are compatible with the general features of *N*-methylthiourea[5] sym. *N*,*N*′-dimethylthiourea[8,9] and monothiobiuret[11] and are not discussed here further for brevity.

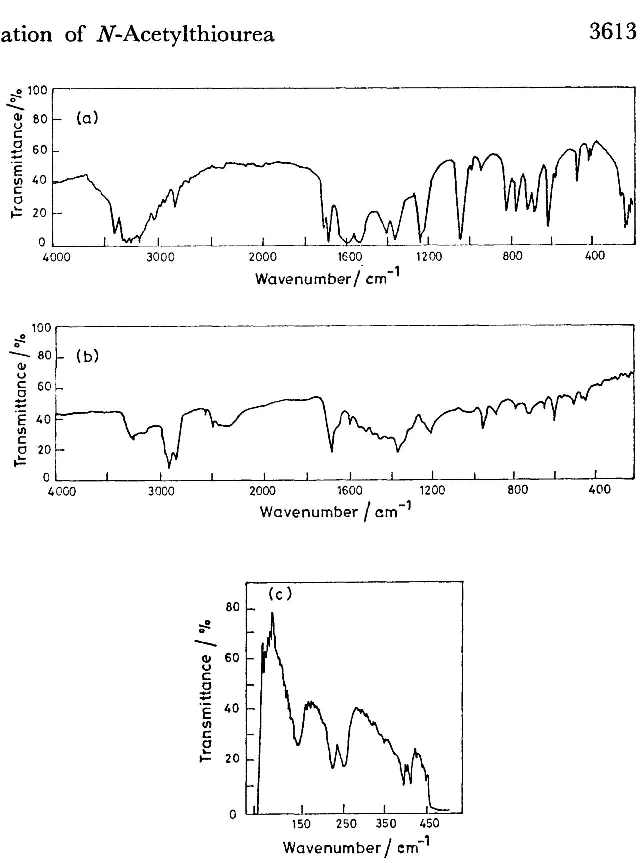

Fig. 3. Spectra of ATU.
a): ATU-d_0, b): ATU-d_3, c): far IR of ATU.

The intense band at 1680 cm^{-1} of ATU corresponds to the carbonyl stretching mode. The related band in the spectrum of AU occurs at 1670 cm^{-1}.

Molecular Conformation. The calculated total energies (Table 3) reveal that the most stable conformation accessible for ATU is the trans-cis (Fig. 1) concordant with the preliminary X-ray structure data in the solid state.[14] The next stable conformation is trans-trans which lies only some 5.02 kcal mol^{-1} above the lowest energy conformation. The calculations indicate the same trend for AU. The results rule out the accessibility of cis-cis structure and interestingly reveal that only a small activation energy is required for the conversion of cis-trans to the trans-trans form. This energy difference however should not be regarded as significant within the framework of this method. Moreover, the preference for one or the other form can also be affected by such factors as solvent and solid state interactions which are obviously not taken into consideration in the calculations. The implication is that the trans-cis structure is stabilized over

Table 1. Observed and calculated fundamental frequencies in cm^{-1} and assignments[a)] for ATU-d_0 and -d_3

Species	ATU-d_3		ATU-d_0		Assignment[b)] (PED, %)
	Obsd	Calcd	Obsd	Calcd	
A′	2500	2514	3400	3392	$\nu_a\mathrm{NX_2}$ (100)
	2420	2414	3300	3304	$\nu_s\mathrm{NX}$ (100)
	2360	2376	3280	3290	$\nu_s\mathrm{NX_2}$ (99)
	3040	3039	3040	3039	$\nu_a\mathrm{CH_3}$ (100)
	2940	2953	2943	2953	$\nu_s\mathrm{CH_3}$ (100)
	1670	1679	1680	1687	νCO (69), νCN (15)
	1130	1144	1590	1591	$\delta\mathrm{NX_2}$ (76), νCN (20)
	1460	1465	1525	1522	νCN′ (36), δNX (31)
	1440	1434	1430	1438	$\delta_a\mathrm{CH_3}$ (58), δCN (17)
	1485	1483	1420	1430	νCN (40), $\delta_a\mathrm{CH_3}$ (22)
	1370	1380	1360	1360	$\delta_s\mathrm{CH_3}$ (83)
	1040	1034	1315	1313	δNX (35), νCC (16), νCN (15)
	810	809	1260	1273	$\nu\mathrm{NX_2}$ (33), νCS (17), δNCN (16)
	980	989	1040	1023	$\nu\mathrm{CH_3}$ (31), νCC (28), $\nu\mathrm{NX_2}$ (19)
	960	973	985	994	$\nu\mathrm{CH_3}$ (64)
	1244	1244	945	955	νCN′ (32), $\gamma\mathrm{NX_2}$ (26), νC′S (18)
	735	736	820	818	νCS (40), $\nu\mathrm{NX_2}$ (40)
	580	589	610	598	δCO (48), νCS (19)
	450	444	475	484	δCS (43), δCO (19), δNCN (15)
	385	384	400	396	δNCN (36), δCCN (29), δCS (19)
	305	298	290	301	δCCN (39), δCS (19)
	143	138	133	133	δCNC (65)
A″	3040	3036	3040	3036	$\nu\mathrm{CH_3}$ (100)
	1430	1435	1430	1435	$\delta\mathrm{CH_3}$ (93)
	1005	1006	1005	1006	$r\mathrm{CH_3}$ (86)
	540	546	715	779	$\tau\mathrm{NX_2}$ (99)
	560	563	715	715	$\omega\mathrm{NX_2}$ (73)
	500	483	680	681	νCN′ (43), $\omega\mathrm{NX_2}$ (26)
	580	588	580	570	πCO (87)
	250	252	250	259	πCS (68), πNH (21)
	136	139	136	140	$\tau\mathrm{CH_3}$ (95)
	100	100	100	105	νCN′ (43), τCN (34)
	78	78	78	79	πN′X (55), τCN′ (24)

a) The fundamentals of ATU-d_3 have been arranged so as to give as far as possible approximately matching potential energy distributions (PED) stated for ATU-d_0. b) ν: Stretching, δ: bending, γ: rocking, π: out of plane bending, ω: waggingg, τ: torsion, a: asymmetric, and s: symmetric. X:H in ATU-d_0. X:D in ATU-d_3.

the other structures in the solid state. Factors such as steric effects, dipole-dipole interaction, hydrogen bonding and crystal packing determine the conformation of ATU. The large dipole-dipole interaction between the C=O and C=S dipoles is minimized in the trans-cis rotamer, so also the steric hindrance. Examination of the molecular model of ATU showed that this structure is very favourable for strong S···HN intermolecular and O···HN intramolecular hydrogen bonds. The more polarizable nature of the thiocarbonyl sulfur leads to stronger S···HN intermolecular hydrogen bonding between ATU molecules. Isoelectronic monothiobiuret[11)] and other related molecules[12,24–26)] are shown to possess a similar type of trans-cis structure.

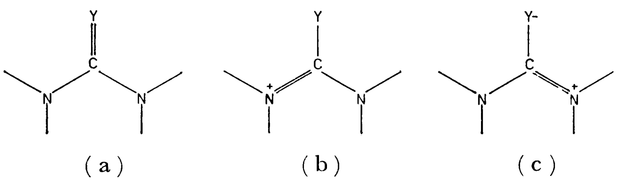

Fig. 4. Resonance structures.

Electronic Structure. Molecular orbital calculations of charge distributions have given an insight into the electronic structures of molecules and the effects of substituents.[27)] In Table 4, the σ and π electron densities and the net electron populations have been shown for AU and ATU. While the electron densities quoted for a single molecule may not be a good guide, comparisons between related molecules by the same procedure of calculation may be more reliable. On comparing ATU with AU, we find significantly less electron populations for the atoms of the thioureido group excepting for the amide Y (O/S) atom, for which the reverse is true. This indicates increased delocalization in the thioureido group as is to be expected, suggesting an increased contribution from resonance structures (b) and (c) to the description of bonding of ATU over that in AU shown in Fig. 4. This result is shown clearly in the values of the π bond orders. Table 4 demonstrates that in ATU, there is a significant decrease in the C–S(Y) bond order with consequent increase in the C–N (and C–N′) bond orders compared to those of AU. The C=O bond is also strengthened slightly in ATU relative to AU. From the low C–C π bond orders, it is evident that it hardly contributes to the conjugation of AU or ATU, while C′–N′ acquires slight π bond character. The acetyl carbonyl stretching frequency is observed at a higher wave number in ATU (1680 cm^{-1}) compared to AU in accord with the π bond order values. NH_2 and NH stretching frequencies of ATU should occur at lower wave numbers than those of AU because of increasing positive charge on nitrogen in ATU compared to AU (Table 4). But (Table 1), these frequencies are observed at higher frequencies than those in AU.[12] This demonstrates clearly, possible intermolecular (S···HN) and intramolecular (O···HN) hydrogen bonding between ATU molecules. More information can be obtained on this on the basis of detailed crystal structure analysis.[14]

Table 2. Force constants[a] of ATU

Urey-Bradley constants					
$K(NH_2)$	5.90	H(HNH)	0.40	F(HNH)	0.00
K(NH)	5.45	H(HNC)	0.27	F(HNC)	0.45
K(CH)	4.70	H(NCS)	0.28	F(NCS)	1.10
K(CO)	8.95	H(NCN)	0.50	F(NCN)	0.65
K(CN)	5.90	H(N′CS)	0.24	F(N′CS)	0.85
K(C′N)	5.50	H(CNC)	0.30	F(CNC)	0.30
K(CN′)	3.60	H(HNC′)	0.29	F(HNC′)	0.65
K(CS)	3.15	H(HNC)	0.16	F(HNC)	0.35
K(CC)	3.30	H(NCC)	0.15	F(NCC)	0.40
		H(CCO)	0.30	F(CCO)	0.50
$k(CH_3)$	−0.05	H(NCO)	0.42	F(NCO)	1.50
		H(CCH)	0.25	F(CCH)	0.45
		H(HCH)	0.42	F(HCH)	0.04
Valence constants					
$f(\pi CS)$	0.070	$f(\tau NH_2)$	0.136	$f(\tau C'N)$	0.117
$f(\pi CO)$	0.434	$f(\omega NH_2)$	0.088	$f(\tau CH_3)$	0.0055
$f(\pi NH)$	0.040	$f(\tau CN)$	0.060		

a) Units: K, H, F are in mdyn Å^{-1} and k, f in mdyn Å rad^{-2}.

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Table 3. Calculated total molecular energies

Conformation	ATU		AU	
	Total energy[a]	Difference[b]	Total energy	Difference
trans-cis	−78.4913	0.0	−85.9587	0.0
trans-trans	−78.4833	5.02	−85.9481	6.65
cis-trans	−78.3941	61.01	−85.9423	10.29
cis-cis	−77.9244	355.84	−85.4437	323.27

a) Hartree. b) In kcals mol^{-1}.

Table 4. Electron populations and bond orders[a] for ATU and AU

Atom	Electron population ATU			Electron population AU			π Bond order		
	σ	π	Total	σ	π	Total	Bond	ATU	AU
H_1	0.8860	—	0.8860	0.8148	—	0.8148	C–N	0.540	0.443
H_2	0.8473	—	0.8473	0.8703	—	0.8703	C=Y	0.578	0.781
N	3.4232	1.7624	5.1856	3.4664	1.8392	5.3056	C–N	0.495	0.372
C	3.0195	0.7042	3.7237	2.7615	0.7763	3.5378	C′–N	0.388	0.429
Y	4.7388	1.6881	6.4269	4.9154	1.4989	6.4143	C=X	0.856	0.823
N′	3.4692	1.6660	5.1352	3.4916	1.7287	5.2203	C–C	0.232	0.235
H′	0.8917	—	0.8917	0.8609	—	0.8609			
C′	2.8549	0.8040	3.6589	2.8879	0.7553	3.6432			
X	4.9139	1.3623	6.2762	4.9223	1.4434	6.3657			
C″	3.0741	1.0109	4.0850	3.0770	1.0098	4.0868			
H_i	0.9830	—	0.9830	0.9795	—	0.9795			
H_o	0.9502	—	0.9502	0.9502	—	0.9502			

a) Numbering schemes and abbreviations as in Fig. 2.

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