The Vibrational Spectra of Ethylene Trithiocarbonate and Ethylene Thiourea

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The infrared spectra of two cyclic thioketones, ethylene trithio-
carbonate and ethylene thiourea, were recorded in the region 4000—
220 cm⁻¹ as solids. Raman spectra of both compounds in the solid
state were obtained with He—Ne laser excitation. Ethylene trithio-
carbonate is soluble in organic solvents and infrared and Raman
spectra of this compound were recorded in solution and semiquantita-
tive polarization data presented.

The vibrational spectra of both molecules suggest non-planarity
of the 5-membered rings and the molecular symmetry is not higher
than C_s or C_2. A tentative assignment of the vibrational fundamentals
for both molecules are presented. The complex formation between
these molecules and iodine have been studied qualitatively.

The spectral data of very few five-membered heterocyclic rings have been
reported. These molecules are of special interest regarding their stereo-
chemistry and it is of importance to determine if they are planar in the various
states of aggregation. In a planar configuration they have C_{2v} symmetry,
which should be evident from the vibrational spectra since the vibrations of
species A_2 should be Raman active, but infrared inactive.

The infrared spectra of ethylene trithiocarbonate (ETC) and ethylene
thiourea (ETU) have been reported by Mecke and co-workers.[1] However,
they obtained only a very incomplete Raman spectrum of ETU and no spec-
trum of ETC. This was undoubtedly caused by the strong yellow colour of the
latter which completely prevents the use of the 4358 Å Hg-line for Raman
excitation. The infrared and Raman spectra in the high frequency region of
the related ethylene carbonate have been reported and a partial interpreta-
tion of the spectra presented.[2] The vibrational spectra of the five-membered
heterocyclic ring tetramethylene sulphone is interpreted on the basis of non-
planarity.[3] Data to be presented for tetramethylene sulphoxide [4] suggest a
puckered ring also for this compound.

Various papers have dealt with the vibrational spectra of thiourea and
its complexes with metal halides [5,6] and hydrogen chloride.[7] Solvent effect

studies of the thiocarbonyl group have been reported [8] and the group frequency of the C=S group found to be strongly sensitive to neighbouring N-atoms.[9-10] X-Ray crystallographic studies of ETU [11] and ethylene carbonate [12] reveal that these molecules deviate from planarity in the solid state.

Since a Raman spectrometer with laser excitation was available for some time, we decided to record the infrared and Raman spectra of ETC and ETU. A tentative assignment of the fundamental frequencies for both molecules is reported, but because of the large number of atoms and low symmetry of these compounds it should be considered as tentative.

EXPERIMENTAL

The two compounds studied were commercial samples from the K & K laboratories (ETC) and the Eastman company (ETU). They were both purified by fractional recrystallization from alcohol. The solvents were of spectroscopic quality (Merck, uvasole) and they were not purified further.

The infrared spectra were recorded with Beckman model IR-9 (4000−400 cm^{-1}) and Perkin-Elmer model 621 (4000−220 cm^{-1}) spectrometers, calibrated with NH_3, CH_4, and atomspheric H_2O and CO_2. The solid samples were recorded as KBr-tablets and as mulls in nujol and fluorolube. ETC is soluble in organic solvents and was dissolved in CCl_4, CS_2, and $CHCl_3$. ETU on the other hand is only slightly soluble in practical solvents and only the most intense infrared bands could be detected in solution.

Table 1. Infrared spectral data for ethylene trithiocarbonate in solution (in cm^{-1}).

| Solvent | | Solvent | |
CHCl$_3$	CS$_2$	CHCl$_3$	CS$_2$
3920 w,[a] bd		1152 s	1156 s
3815 w		1106 w, sd	1112 w, sd
3661 w		ca. 1063 vvs	1075 vvs
3440 vw			1054 w, sd
2986 s			1040 w
2930 s		1008 m	1010 m
2860 w		984 s	988 s
2836 m		956 s, sd	958 s, sd
2714 vw		946 s	951 s
2361 w		930 w	935 w
2295 vw	2302 w	880 vs	886 vs
2260 m	2261 vw	831 vs	836 vs
2132 m			750 m
2086 vw		668 vs, sp	677 vs, sp
1950 w			657 w
1761 m	1761 m	583 vw	579 vw, bd
1711 w	1707 w	501 s	502 s
1606 vw		475 s	476 s
1576 w		453 s	453 s
1422 s	1422 s	381 s	382 s
1383 vw	1384 vw	246 m?	
1308 vw	1311 vw		
1280 vs, sp	1286 vs, sp		
1251 s, sp	1254 s, sp		

[a] The following abbreviations have been used: w, weak; m, medium; s, strong; v, very; sp, sharp and bd, broad.

We tried to record the infrared spectra of ETC in the vapour phase by means of a 10 m folded cell and by a 9 cm cell which was heated to *ca*. 100°C. However, not even the strongest absorption bands could be detected in any of the spectra.

Mixed solutions of ETC−I_2 and ETC−ICl in CS_2 were prepared and scanned immediately. The complexes exhibited a number of new infrared bands compared to ETC itself. Negligible spectral changes occurred when the ETC−I_2 solution was rescanned after 1 h. In the ETC−ICl solution, however, the spectrum changed with time, probably because of irreversible oxidation or substitution reactions.

The Raman spectra were recorded with a Cary 81 Raman spectrometer equipped with a Spectra Physics model 125, 50 MW He−Ne laser, using the 6328 Å radiation. The solutions were filled in capillary tubes of silica, approximately 0.7 mm in diameter and 5 cm long, containing approximately 20 μl. The capillary was "sealed" with glycerol, which was also used between the sample tube and the spectrometer lens to achieve good optical contact. Solid pellets of pure ETC and ETU were prepared in a micro die, wetted with glycerol and placed in contact with the spectrometer lens.

Table 2. Raman spectral data for ethylene trithiocarbonate (in cm⁻¹).

Solutions in					Solid		
CHCl₃ [a]			CCl₄ [a]				
2980	vs [b]	D	2981	vs	2972	vs	
2933	vs	P	2935	vs	2920	vs	
2860	w	P	2866	m, bd	2854	m	
2834	m	P			2828	m	
					1441	vw	
1434	s	P			1433	s	
					1427	s	
1422	s	D			1422	s	
					1411	vvw?	
1280	w	P			1273	w	
1250	m	D	1252	m	1242	m	
1151	m	P?	1153	m	1147	m	
1108	m	D?	1112	m	1104	w	
					1066	s	
1065	vs	P	1079	vs	1054	vw	
					1045	vs	
ca. 1035	vw, sd				1029	w	
1008	w	P			1006	w	
982	m	P	983	m	984	m	
947	m	P	947	m	948	m	
883	m	D			887	m	
832	w				840	w	
ca. 673	vs		676	vs	672	vs	
					634	vw?	
505	vs	P	505	vs	504	vs	
474	m	D			483	m	
453	w	D	453	w	460	w	
383	vs, sp	P	384	vs	383	vs,	sp
247	s, sp	D	247	s	251	vs,	sp
230	vvw				237	w	
127	w, sd		126	w	147	m	
					89	w	

[a] The solutions were saturated.
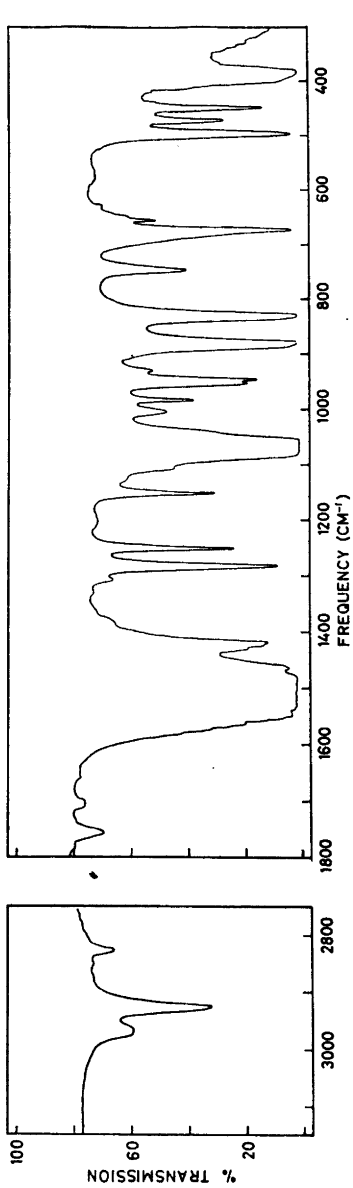[b] For abbreviations, see Table 1.

Fig. 1. The infrared spectrum of ethylene trithiocarbonate (0.008 M) dissolved in CS₂: cell thickness 0.02 mm.
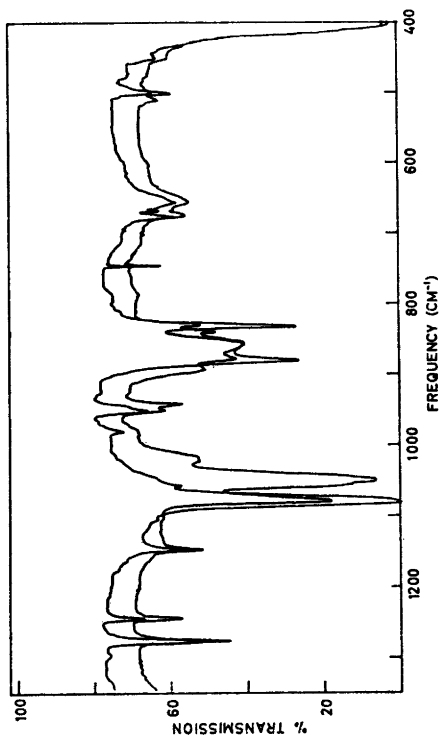
Fig. 2. The infrared spectra of: 0.01 M ethylene trithiocarbonate in CS₂ and 0.01 M ethylene trithiocarbonate + 0.08 M iodine in CS₂; cell thickness 0.02 mm.

An attempt was made to record the Raman spectrum of a mixed ETC—I_2 solution in CHCl$_3$. One of the shifted ETC bands was detected, although this technique is very difficult with the Raman effect.[13]

Semiquantitative polarization measurements were carried out, using a half wave plate between the laser and the sample tube. A polarizer which can be rotated 90° was

Table 3. Vibrational spectral data of solid ethylene thiourea and tentative fundamental assignments.

Infrared			Raman			Assignments	
3907	w						
3722	vw						
3660	vw					NH	stretch
3425	w					NH	stretch
3030	s						
2965	s		2965	w		CH	stretch
			2947	m		CH	stretch
			2895	w		CH	stretch
			2864	m		CH	stretch
2668	w						
2505	w						
2395	w						
2291	m						
2158	w						
1714	w						
1525	w,	sd					
1518	vs		1518	w		NH	bend
1499	vs		1498	w,	sd	NH	bend
1493	m,	sd					
1485	m		1480	s		CH$_2$	scissor
			1466	m			
1457	s		1456	w		CH$_2$	scissor
1370	s		1375	w		CH$_2$	wag
1308	s		1307	m		CH$_2$	wag
1276	s		1275	w		ring	stretch
1208	s		1210	s		C=S	stretch
1198	w,	sd	1195	m,	sd	CH$_2$	twist
			1101	m		CH$_2$	twist
1046	w		1049	m		ring	stretch
			1020	vw?			
1002	s		996	w		ring	stretch
974	vw		975	m		CH$_2$	rock
			952	vw?			
920	s,	sp	921	vs		ring	stretch
			853	w		CH$_2$	rock
			740	w		NH	bend
680	s		673	m		NH	bend
588	vs,	bd	586	vw		ring	bend
506	vs		507	vs		ring	breath
			390	w,	bd	ring	bend
336	s,	sp	333	w		C=S	bend
246	w		244	w,	bd	ring	bend
			200	m,	bd	C=S	bend
			124	m,	bd	ring	bend
			86	s			

a For abbreviations see Table 1.

placed between the sample tube and the spectrometer entrance slit. No polarization data could be obtained for ETU which was recorded as a solid pellet only.

A qualitative Raman spectrum of ETC dissolved in CCl_4 was recorded, using the green Hg line at 5461 Å in a conventional Cary 81 spectrometer with Toronto arc. This spectrum was very poor compared to the one obtained with laser excitation and wide spectral regions were covered by other Hg lines.

The infrared spectra of ETC in CS_2 solution is shown in Fig. 1 and the spectra of the ETC—I_2 solutions are shown in Fig. 2. The Raman spectra of ETC are shown in Fig. 3 and the observed infrared and Raman frequencies are listed in Tables 1 and 2. For ETU the infrared and Raman frequencies are listed in Table 3.

RESULTS AND DISCUSSION

Ethylene trithiocarbonate

No structural determination has been reported for ETC and the symmetry of this molecule is therefore uncertain. The related ethylene carbonate is reported to be non-planar in the crystal [12] but it has been tentatively considered planar in solution.[2] A planar molecule of ETC should have C_{2v} symmetry, non-planar models C_2, C_s or C_1 symmetry. The activities of the 24 normal vibrations for the appropriate point groups are listed in Table 4. The most

Table 4. Classification of the normal modes in ethylene trithiocarbonate for various possible point groups.

C_{2v}			C_s			C_2			C_1		
Species	IR	Ra	Species	IR	Ra	Species	IR	Ra	Species	IR	Ra
$8 A_1$	a	P									
$4 A_2$	ia	D	$13A'$	a	P	12A	a	P			
$7 B_1$	a	D							$24A$	a	P
$5 B_2$	a	D	$11A''$	a	D	12B	a	D			

The following abbreviations have been used: a, active; ia, inactive; P, Polarized and D, depolarized.

prominent spectral feature in assigning the right point group would be the fact that vibrations belonging to species A_2 are infrared inactive, but Raman active and such non-coincidences should be fairly easy to pick out. To distinguish between the point groups C_2, C_s, or C_1 is hardly possible in this case since it is a well known fact that depolarized Raman lines are very difficult to determine. Band-contours of infrared vapour spectra can in many cases give very useful information about the symmetry, but the vapour pressure of ETC was much too low.

It appears from Tables 1 and 2 that no clear-cut cases are observed in which Raman bands have no infrared counterparts. This observation cannot be considered absolutely conclusive since inactive infrared vibrations might show up in solution because of breaking-down of the selection rules. However,

it seems justified to conclude that ETC is non-planar in the solid as well as in solution. The number of Raman bands which appear polarized, suggest that the point group should be C_2 (two-fold axis) or C_s (symmetry plane).

Vibrational assignments. Exactly four bands are observed in the infrared and the Raman spectra around 3000 cm^{-1} and they are assigned to the four C—H stretching modes. If ETC had C_{2v} symmetry, one of these modes should be of species A_2. However, all the four Raman bands have infrared counterparts, and the very weak infrared band at 2857 cm^{-1} cannot be an A_2 fundamental since the corresponding Raman band is definitely polarized.

The remaining fundamental modes are all expected below 1500 cm^{-1}. It seems significant that approximately 20 certain Raman bands which all have infrared counterparts are observed in this region and it seems reasonable to assign these bands to the remaining 20 fundamentals. The bands in the region 1450—1100 cm^{-1} of which three are polarized and three seem depolarized have been assigned to the six CH$_2$ deformation modes: scissoring, wagging and twisting. With C_2 or C_s symmetry, one vibration of each type should be symmetrical, the other asymmetrical in agreement with the polarization data. The 1065 cm^{-1} band is very intense in infrared and Raman, it is affected by solvent polarity and state of aggregation and is undoubtedly connected with the C=S stretching mode. The two methyl rocking modes are somewhat

Table 5. Tentative vibrational fundamentals in ethylene trithiocarbonate.

Infrared		Raman		Approx. motion	
2986	s [a]	2980	vs	CH	stretch
2930	s	2933	vs	CH	stretch
2860	w	2860	s	CH	stretch
2836	m	2834	w	CH	stretch
		1434	s	CH$_2$	scissor
1422	s	1422	s	CH$_2$	scissor
1280	vs	1280	w	CH$_2$	wag
1251	s	1250	m	CH$_2$	wag
1152	s	1151	m	CH$_2$	twist
1106	w	1108	m	CH$_2$	twist
ca. 1063	vvs	1065	vs	C=S	stretch
1040	vw	ca. 1035	vw	CH$_2$	rock
1008	m	1008	w	CH$_2$	rock
984	s	982	m	ring	stretch
946	s	947	m	ring	stretch
882	vs	883	m	ring	stretch
831	vs	832	m	ring	stretch
ca. 668	vs	ca. 673	vs	ring	stretch
501	s	505	vs	ring	breath
475	s	474	m	ring	bend
453	s	453	w	ring	bend
381	s	383	vs	C=S	bend
246	m?	247	s	C=S	bend
		127	w	ring	bend

[a] For abbreviations see Table 1.

arbitrarily assigned to the bands at 1035 and 1008 cm⁻¹, which both are weak to medium intense in infrared and Raman.

The remaining 11 fundamentals are all connected with the ring stretching, bending and torsional modes for which the group frequency concepts are of no use. Moreover, there are very few other aliphatic 5-membered rings with heteroatoms which have been thoroughly studied spectroscopically. In the 5-membered, planar heteroaromatic rings as, $e.g.$, thiophene,[14] pyrrole [15] or the oxadiazoles [16] no fundamental frequency is reported below 600 cm⁻¹. In ETC, six bands believed to be fundamentals are observed below 600 cm⁻¹, indicating that this molecule is "soft" and flexible with much lower ring bending and stretching force constants. No real distinction can be made between most of the skeletal stretching and deformation modes, except for a planar ring in which the A'' modes are pure bending vibrations. The bands in the region 1000—700 cm⁻¹ are assumed to involve mainly stretching vibrations, with the strong, polarized Raman band at 505 cm⁻¹ assigned to the ring "breathing" mode. The "in plane" and "out of plane" C=S bending modes are assigned to the bands at 383 and 247 cm⁻¹, respectively. The "envelope" bending mode around the S—S line should be the lowest fundamental, observed at 127 cm⁻¹.

The remaining infrared bands can be interpreted as binary combinations or overtones. Practically all the infrared bands below 1500 cm⁻¹ are assigned to fundamentals, exceptions are those at 956 and 750 cm⁻¹ which can be explained as $453+505=958$ and $247+505=752$, respectively.

Complex formation. ETC contains a thiocarbonyl and two sulphide groups which are all potentially strong donor sites for complex formation to iodine. Dissolved in CCl_4 ETC has electronic absorption bands at 456, 314, and 294 mμ. The visible absorption band of iodine dissolved in CCl_4 at 517 mμ is blue shifted to 469 mμ on complex formation with ETC, suggesting an intermediately strong interaction.[17] Solutions with a constant iodine concentration and varying ETC concentrations pass through an isosbestic point at 497 mμ, suggesting a 1:1 complex. Because of the strong ETC absorption in the ultraviolet region we were not able to observe any charge transfer band, characteristic of the ETC—I_2 complex. The data: Kc (25°)=45 l mole⁻¹ and $-\Delta H°=8.5$ kcal mole⁻¹ are reported for the ETC—I_2 complex.[18]

The ETC—I_2 complex was studied in CS_2 and CCl_4 solution in the infrared region. Solutions in CS_2 containing the same amount of ETC and varying iodine concentrations are shown in Fig. 2. It appears that in agreement with our earlier observations on iodine complexes,[19] the spectral changes can be classified as displaced bands and enhanced bands. Most significant is the "red shift" observed for the C=S stretching band at 1071 cm⁻¹, revealing that the complex formation occurs from the thiocarbonyl sulphur. The shifted and enhanced bands are listed in Table 6. It appears that certain bands are "blue shifted" on complex formation. The C=S bending and some of the skeletal bending modes are expected to be "blue shifted", but these effects are not very easy to predict. A further complex formation of 1:2 or even 1:3 stoichiometry cannot be excluded under these conditions of high iodine concentrations.

Perturbations of the I—I stretching mode on complex formation to ETC have been reported.[13] An attempt was made to study perturbations in the Raman spectrum of ETC on complexing with iodine. In a 1 M solution of
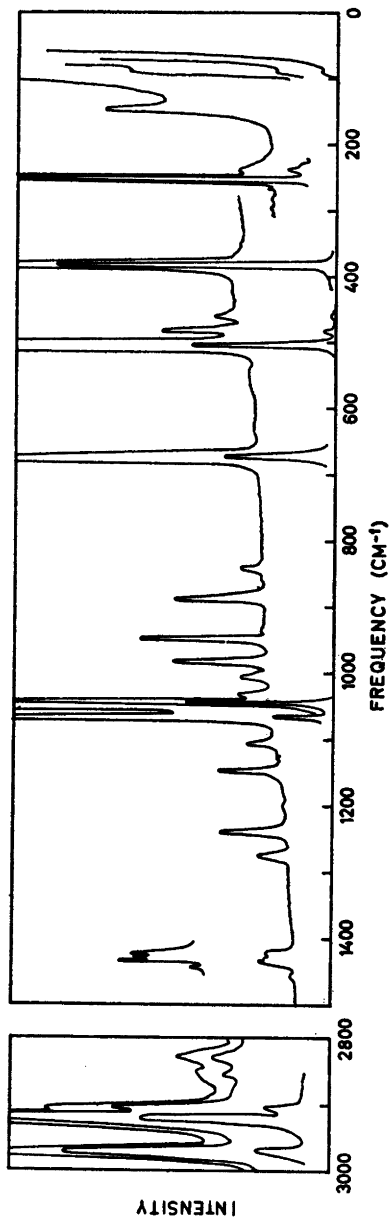
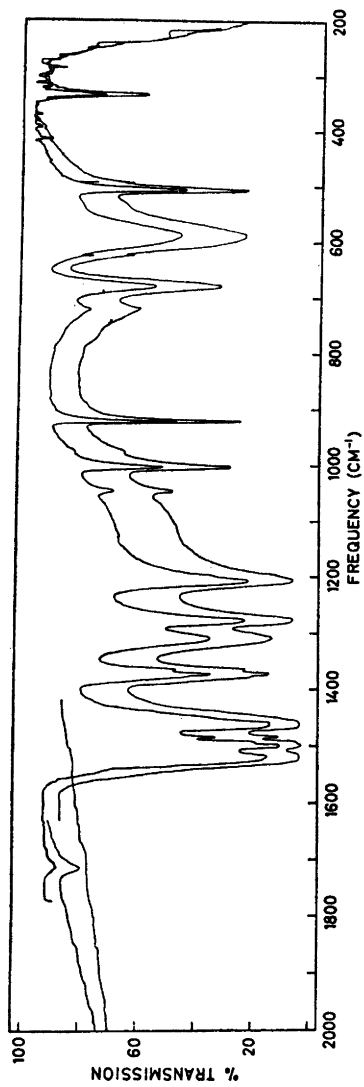Fig. 3. The Raman spectrum of solid ethylene trithiocarbonate.

Fig. 4. The infrared spectrum of ethylene thiourea in nujol mull.

Table 6. Infrared spectral shifts for the ethylene trithiocarbonate complex with iodine in carbon disulphide.

Displaced bands			Enhanced bands
ETC	ETC$-$I$_2$	$\varDelta\nu$	
1071 vs	1043 vs	28	
			1051 vw
			936 vw
873 w	890 w	-17	
825 m	834 m	-9	
731 w	751 w	-20	
673 m	676 m	$+3$	
			650 m
497 s	507 m	-10	

For abbreviations, see Table 1.

ETC in CHCl$_3$, iodine was added to a 0.1 M concentration, which was the maximum that would permit a Raman spectrum to be recorded with the 6328 Å excitation. A small peak was observed at 1040 cm^{-1}, the shift corresponding to the infrared results. However, the low intensity of the peak would suggest that the C=S stretching mode in the complex is weaker than for the ETC itself. To our knowledge this is the first time spectral shifts of the donor on complexing with iodine has ever been reported in Raman, and attempts [13] with other donors like dimethyl sulphoxide, diethyl sulphide and pyridine N-oxide were negative.

Ethylene thiourea

ETU is only slightly soluble in organic solvents and this molecule could therefore only be studied in the solid state. The point group for ETU is probably C_s, since the ring appears planar, but the S atom is lying outside this plane.[11] Our vibrational spectra suggest that the point group cannot be C_{2v}, but since no polarization data were available, any distinction between C_s, C_2, or C_1 in the crystal is not possible.

The tentative vibrational assignments are listed in Table 3 and only a few comments will be made. Since ETU contains 12 atoms, there are 30 fundamentals. In addition to those encountered in ETC there are two N$-$H stretching modes around 3400 cm^{-1}, two N$-$H in plane (around 1500 cm^{-1}) and two N$-$H out of plane deformation modes (around 700 cm^{-1}). The assigned frequencies agree reasonably well with those found for ETC and again there are surprisingly many low frequencies, indicating a "soft" flexible framework. The C=S stretching mode has been assigned to the bands at 1208 cm^{-1} in agreement with Mecke *et al.*[1] It is well known that for C=S groups geminal to an N-atom strong coupling with the N$-$H deformation modes occur.[9] The very strong band at 506$-$508 cm^{-1} is assigned to the ring breathing mode,

very close to the corresponding band in ETC. The strong, very low Raman band at 86 cm⁻¹ cannot be a fundamental and is assigned as a lattice mode.

It is well known that thiourea itself forms strong charge transfer complexes with iodine.[20] A qualitative study of the ETU$-I_2$ complex dissolved in CH_2Cl_2 was carried out in the ultraviolet and visible regions. The curves were very similar to those reported for thiourea.[20] No infrared study of the ETU$-I_2$ complex could be carried out because of the low solubility. Such studies would have been of interest for ETU and might have given more information about the vibrational coupling of the C=S stretching mode.

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