

Infrared Spectra and Configurations of Alkylthiourea Derivatives. Normal Vibrations of N,N'-Dimethyl- and Tetramethylthiourea¹

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Abstract: Normal coordinate analyses of N,N'-dimethylthiourea and tetramethylthiourea have been carried out employing the Urey-Bradley force field. The observed and computed frequencies agree well with each other. The majority of the observed bands in the infrared spectra of alkylthiourea derivatives arise from mixed vibrations just as in secondary amides. Dialkylthioureas show evidence of rotamers with N-H bonds *cis* and *trans* with respect to the thiocarbonyl sulfur. The configuration of these derivatives have been examined both by infrared and nmr spectroscopy. The perturbations of the various mixed vibration bands in charge-transfer as well as metal complexes of alkylthioureas have been discussed.

Frequencies ranging from 1550 to 850 cm^{-1} have been attributed to the C=S stretching vibration in the literature.³ Recently, Rao and Venkataraghavan⁴ have pointed out that the assignments of very high or low frequencies for the C=S stretching vibration are always found in thioamide or thiourea type derivatives due to strong vibrational mixing. Normal coordinate analysis of N-methylthioformamide and N-methylthioacetamide by Suzuki⁵ show clear evidence for vibrational mixing in these compounds. The infrared bands of the secondary thioamides with considerable contribution from the C=S stretching vibration are found in the region 870–700 cm^{-1} , considerably lower than in simple thiocarbonyl compounds where the C=S vibration is localized.⁴ In thiourea, two bands in the region 1080–730 cm^{-1} are found to have appreciable contribution from the C=S stretching vibration.⁶

In the present investigation, we have examined the infrared absorption spectra of alkylthioureas, particularly since these derivatives act as ligands where the donor site could either be nitrogen or sulfur.⁷ For this purpose, the normal coordinate treatment for the in-plane vibrations of N,N'-dimethylthiourea and tetramethylthiourea have been carried out employing the Urey-Bradley force field in the calculations. Based on these calculations, the nature of the observed bands are explained in terms of the potential energy distributions. Another aspect of interest in the present study was the configuration of dialkylthiourea derivatives. The configurational aspects have been studied by infrared as well as nuclear magnetic resonance spectroscopy. The perturbations in the position and intensity of the mixed vibration bands of alkylthioureas in their charge-transfer as well as metal complexes have been examined.

Results and Discussion

Normal Coordinate Treatment and Infrared Spectrum of N,N'-Dimethylthiourea. The normal coordinate treatment⁸ for the in-plane vibrations of N,N'-dimethylthiourea was carried out as an eight-body problem by assuming a *trans*-planar structure for the molecule with C_{2v} point group.⁹ Of the 18 normal vibrations, 5 are out-of-plane ($2A_2 + 3B_1$) vibrations and 13 are in-plane ($7A_1 + 6B_2$) vibrations. The internal coordinates of the molecule are shown in Figure 1 and the symmetry coordinates are shown in Table I. The

Table I. In-Plane Symmetry Coordinates of N,N'-Dimethylthiourea

S_i	$S = UR$	Vibrational mode ^a	Abbrev
A ₁ Type			
S_1	$(\Delta r_1 + \Delta r_1')/\sqrt{2}$	N—H sym str	$\nu_s(\text{NH})$
S_2	$(\Delta r_2 + \Delta r_2')/\sqrt{2}$	C—N sym str	$\nu_s(\text{CN})$
S_3	$(\Delta r_3 + \Delta r_3')/\sqrt{2}$	C'—N sym str	$\nu_s(\text{C}'\text{N})$
S_4	ΔR	C=S str	$\nu(\text{CS})$
S_5	$(\Delta\alpha_{12} + \Delta\alpha_{12}' - \Delta\alpha_{31} - \Delta\alpha_{31}')/2$	N—H sym bending	$\delta_s(\text{NH})$
S_6	$(2\Delta\alpha_{23} + 2\Delta\alpha_{23}' - \Delta\alpha_{12} - \Delta\alpha_{31} - \Delta\alpha_{12}' - \Delta\alpha_{31}')/2\sqrt{3}$	C—N—C' sym def	$\delta_s(\text{CNC}')$
S_7	$(2\Delta\delta - \Delta\delta_1 - \Delta\delta_1')/\sqrt{6}$	N—C—N def	$\delta(\text{NCN})$
B ₂ Type			
S_8	$(\Delta r_1 - \Delta r_1')/\sqrt{2}$	N—H asym str	$\nu_a(\text{NH})$
S_9	$(\Delta r_2 - \Delta r_2')/\sqrt{2}$	C—N asym str	$\nu_a(\text{CN})$
S_{10}	$(\Delta r_3 - \Delta r_3')/\sqrt{2}$	C'—N asym str	$\nu_a(\text{C}'\text{N})$
S_{11}	$(\Delta\alpha_{12} - \Delta\alpha_{12}' - \Delta\alpha_{31} + \Delta\alpha_{31}')/2$	N—H asym bending	$\delta_a(\text{NH})$
S_{12}	$(2\Delta\alpha_{23} - 2\Delta\alpha_{23}' - \Delta\alpha_{12} - \Delta\alpha_{31} + \Delta\alpha_{12}' + \Delta\alpha_{31}')/2\sqrt{3}$	C—N—C' asym def	$\delta_a(\text{CNC}')$
S_{13}	$(\delta_1 - \delta_1')/\sqrt{2}$	N—C—S def	$\delta(\text{NCS})$

^a str, stretching; def, deformation.

(1) R. K. Gosavi, Ph.D. Thesis (in part), Indian Institute of Technology, Kanpur, India.

(2) To whom all the correspondence should be addressed.

(3) C. N. R. Rao, "Chemical Applications of Infrared Spectroscopy," Academic Press Inc., New York, N. Y., 1963.

(4) C. N. R. Rao and R. Venkataraghavan, *Spectrochim. Acta*, **18**, 541 (1962).

(5) I. Suzuki, *Bull. Chem. Soc. Japan*, **35**, 1456 (1962).

(6) A. Yamaguchi, R. B. Penland, S. Mizushima, T. J. Lane, C. Curran, and J. V. Quagliano, *J. Am. Chem. Soc.*, **80**, 527 (1958).

(7) T. J. Lane, A. Yamaguchi, J. V. Quagliano, J. A. Ryan, and S. Mizushima, *ibid.*, **81**, 3824 (1959).

structural parameters and force constants¹⁰ used in the calculations are given in Table II. The structural parameters were based on the crystallographic data

(8) E. B. Wilson, J. C. Decius, and P. C. Cross, "Molecular Vibrations," McGraw-Hill Book Co., Inc., New York, N. Y., 1955.

(9) It will be shown later in this paper, while discussing the configuration of alkylthiourea derivatives, that this assumption is correct.

(10) The potential function employed in the calculation is of Urey-Bradley type; see T. Shimanouchi, *J. Chem. Phys.*, **25**, 35 (1955).

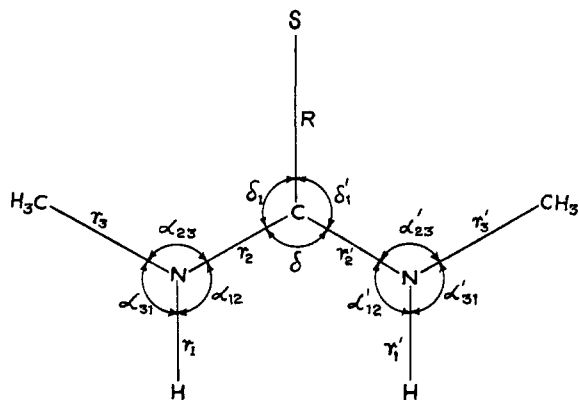


Figure 1. Internal coordinates of N,N'-dimethylthiourea.

of thiourea⁶ and tetramethylthiourea,¹¹ and the force constants were chosen from the studies on N-methylthioacetamide,⁵ thiourea,⁶ and thioformamide.¹² In the calculations the high frequency due to the N-H stretching vibration was separated from the lower frequencies.

Table II. Structural Parameters of N,N'-Dimethylthiourea

Bond distances (Å)		
$r_1 = 1.00, r_2 = 1.37, r_3 = 1.47, \text{ and } R = 1.68^a$		
Bond angles (deg)		
$\alpha_{12} = \alpha_{23} = \alpha_{31} = \alpha_{12}' = \alpha_{23}' = \alpha_{31}' = \delta = \delta_1 = \delta_1' = 120$		
Force constants (mdynes/Å) ^b		
$K_{\text{NH}} = 5.52^c$	$H_{\text{HNC}} = 0.30$	$F_{\text{C} \dots \text{H}} = 0.46$
$K_{\text{CN}} = 6.15$	$H_{\text{C}'\text{NC}} = 0.35^e$	$F_{\text{C} \dots \text{C}'} = 0.30$
$K_{\text{C}'\text{N}} = 3.15$	$H_{\text{C}'\text{NH}} = 0.25$	$F_{\text{C}' \dots \text{H}} = 0.36$
$K_{\text{CS}} = 3.95$	$H_{\text{NCS}} = 0.15$	$F_{\text{N} \dots \text{N}} = 0.60^d$
	$H_{\text{NCCN}} = 0.57^d$	$F_{\text{N} \dots \text{S}} = 1.02$

^a Reference 11. ^b Reference 5. ^c Reference 12. ^d Reference 6. ^e C' denotes the carbon of the CH₃ group while C denotes the carbon of the C=S group.

The computed and observed frequencies, the per cent deviations, and the potential energy distributions (calculated from the normalized *L* matrix) among the symmetry coordinates for each normal mode are shown in Table III. There is good agreement between the observed and calculated frequencies, indicating that the Urey-Bradley force constants are truly transferable. Calculations made with $K_{\text{CN}} = 5.00, K_{\text{CS}} = 4.30, H_{\text{HNC}} = 0.25, H_{\text{NCS}} = 0.25, r_2 = 1.35 \text{ Å}, \text{ and } R = 1.70 \text{ Å}$ did not affect the correlation appreciably. The detailed assignments of the major bands in the infrared spectrum of N,N'-dimethylthiourea are shown in Table IV.

It can be seen from Table IV that the majority of the bands arise from mixed vibrations. The bands at ~ 1560 and $\sim 1420 \text{ cm}^{-1}$ have both high contributions from $\nu(\text{CN})$ and $\delta(\text{NH})$. The contribution from $\delta(\text{NH})$ is also high in the case of the 1505-cm^{-1} band. The contribution from $\nu(\text{CS})$ is found to be greatest in the band around 750 cm^{-1} . The mixed vibration bands of N,N'-dimethylthiourea are in the regions of the so-called $>\text{N}-\text{C}=\text{S}$ bands proposed by Rao and Venkataraghavan.^{4,13} Since the force constants $K_{\text{C}'\text{N}}$

(11) Z. V. Zvonkova, L. I. Astakhova, and V. P. Glushkova, *Kristallografiya*, **5**, 547 (1960).

(12) I. Suzuki, *Bull. Chem. Soc. Japan*, **35**, 1286 (1962).

(13) C. N. R. Rao, R. Venkataraghavan, and T. R. Kasturi, *Can. J. Chem.*, **42**, 36 (1964).

Table III. The Observed and Calculated Frequencies, Potential Energy Distribution, $(F_{ij}L_{iN}^2/\lambda_N) \times 100$, and Per Cent Deviations^a of N,N'-Dimethylthiourea

Frequency, ν			Potential energy distribution						
Obsd ^b	Calcd	Δ	S ₂	S ₃	S ₄	S ₅	S ₆	S ₇	
A ₁ Type									
1506	1514	0.5	4	2	10	77	3	10	
1420	1398	1.6	68	2	20	22	9	11	
1038	1029	0.9	8	65	3	2	6	17	
754	757	0.4	9	6	74	1	4	0	
446	438	1.8	14	28	3	1	19	30	
...	227	...	2	0	0	0	60	38	
B ₂ Type									
1568	1594	1.7	S ₉	S ₁₀	S ₁₁	S ₁₂	S ₁₃		
1420	1395	1.8	79	4	34	0	7		
882 ^c	907	2.8	2	87	0	9	2		
650 ^c	634	2.5	1	11	0	52	34		
...	229	...	1	0	0	39	58		

^a Per cent deviation = $\Delta = (\nu_{\text{calcd}} - \nu_{\text{obsd}}) \times 100/\nu_{\text{obsd}}$. ^b Spectra recorded as a thin film. ^c Spectra recorded in chloroform solution.

Table IV. Final Assignments of Infrared Vibrational Bands of N,N'-Dimethylthiourea

Band position		Assignment
Thin film	CHCl ₃ soln	
	3440	$\nu(\text{NH})$ free, <i>trans</i>
3282	3355	$\nu(\text{NH})$ bonded, <i>trans</i>
3145	3150	Fermi resonance
2840	2840	(NCH ₃)
1568	1555	70% $\nu_{\text{a}}(\text{CN})$ + 30% $\delta_{\text{a}}(\text{NH})$
1506	1504	79% $\delta_{\text{a}}(\text{NH})$ + 10% $\nu(\text{CS})$ + 10% $\delta(\text{NCCN})$
1446	1471	$\delta_{\text{a}}(\text{CH}_3)$
1420	1420	76% $\delta_{\text{a}}(\text{NH})$ + 24% $\nu_{\text{a}}(\text{CN})$ or 62% $\nu_{\text{a}}(\text{CN})$ + 20% $\delta_{\text{a}}(\text{NH})$ + 18% $\nu(\text{CS})$
1358	1354	$\delta_{\text{a}}(\text{CH}_3)$
1287	1290	2×667 or $\nu(\text{CS})$ + $\delta(\text{NCS})^a$
1082	1088	(CH ₃) rock or $2 \times \delta(\text{NCS})^a$
1038	1048	79% $\nu_{\text{a}}(\text{C}'\text{N})$ + 21% $\delta(\text{NCCN})$
850	882	91% $\nu_{\text{a}}(\text{C}'\text{N})$ + 9% $\delta_{\text{a}}(\text{CNC}')$
754	752	83% $\nu(\text{CS})$ + 10% $\nu_{\text{a}}(\text{CN})$ + 7% $\nu_{\text{a}}(\text{C}'\text{N})$
726	722	(NH) out-of-plane bending
667	650	53% $\delta_{\text{a}}(\text{CNC}')$ + 35% $\delta(\text{NCS})$ + 11% $\nu_{\text{a}}(\text{C}'\text{N})$
551	551	$\delta(\text{NCS})^a$
446	448	33% $\delta(\text{NCCN})$ + 31% $\nu_{\text{a}}(\text{C}'\text{N})$ + 21% $\delta_{\text{a}}(\text{CNC}')$ + 16% $\nu_{\text{a}}(\text{CN})$
416	412	(CS) out-of-plane deformation or CNC' deformation ^a

^a Tentative assignment.

and K_{CS} are quite similar, the major contributions from $\nu(\text{C}'\text{N})$ and $\nu(\text{CS})$ are found in the bands which are quite close to each other (850 and 750 cm^{-1}). The skeletal deformation vibration involving the $\delta(\text{NCS})$ and $\delta(\text{CNC}')$ modes is found at $\sim 650 \text{ cm}^{-1}$. In this vibration, the NCS angle increases while the CNC' angle decreases and *vice versa*. This may be considered as a kind of asymmetrical deformation vibration. The corresponding symmetrical vibration probably occurs at considerably lower frequency. The bands at 550 and 415 cm^{-1} have been tentatively assigned to $\delta(\text{NCS})$ and $\delta(\text{CS})$ out-of-plane vibrations. The out-of-plane deformation of the N-H bond is assigned to the band around 725 cm^{-1} .

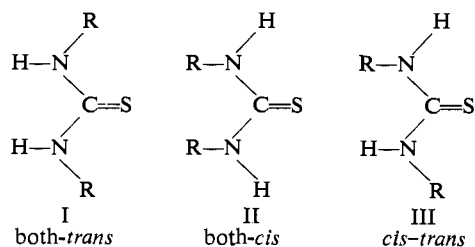
Table V. Observed Infrared Absorption Band Positions (cm⁻¹) of Dialkylthiourea Derivatives^a (R₁HNC(S)NHR₂)

Assignment	R ₁ , R ₂ = C ₂ H ₅	R ₁ = CH ₃ , R ₂ = <i>i</i> -C ₃ H ₇	R ₁ , R ₂ = <i>i</i> -C ₃ H ₇	R ₁ = CH ₃ , R ₂ = <i>t</i> -C ₄ H ₉	R ₁ , R ₂ = <i>t</i> -C ₄ H ₉
ν(NH) free, <i>trans</i>	3428	3442	3415	3462	3445
ν(NH) free, <i>cis</i>	...	3416	3395	3415	3412
ν(NH) bonded	3350	3337	3352
Fermi resonance (NCH ₃)	3155	3150	3150	3145	3150
...	...	2840	...	2840	...
70% ν _a (CN) + 30% δ _a (NH)	1553	1551	1549	1551	1550
79% δ _s (NH) + 10% ν(CS) + 10% ν(NCN)	1499	1502	1495	1503	1505
δ _a (CH ₃)	1457	1468	1467	1472 ^c	1483 ^c
...	1455	1455
76% δ _a (NH) + 24% ν _a (CN) or 62% ν _s (CN) + 20% δ _s (NH) + 18% ν _s (CS)	1384	1388	1389	1399	1398
δ _s (CH ₃)	1340	1369 ^c	1369 ^c	1362 ^c	1370 ^c
...	...	1342	1348	1340	1335
2 × ~650 or ν(CS) + δ(NCS) ^b (CH ₃) rock or 2 × δ(NCS) ^b	1288	1281	1300	1278	1280
...	...	1091	1086	1063	1118
79% ν _s (C'N) + 21% δ(NCN)	1063	1040	1055	1033	1048
91% ν _a (C'N) + 9% δ _a (CNC')	889	892	878	887	932
83% ν(CS) + 10% ν _s (CN) + 7% ν _s (C'N)	773	787	779	767	757
(NH) out-of-plane bending	735	737	732	725	712
53% δ _a (CNC') + 35% δ(NCS) + 11% ν _a (C'N)	665	650	645	650	648
δ(NCS) ^b	563	565	578	579	548
33% δ(NCN) + 31% ν _s (C'N) + 21% δ _s (CNC') + 16% ν _s (CN)	458	463	471	463	459
...	445	...

^a Spectra were recorded in chloroform solution (0.025 M) with 0.1-cm path length cell. ^b Tentative assignment. ^c Typical doublet due to isopropyl and *t*-butyl groups.

Infrared Spectra of Dialkylthioureas. The important bands in the infrared absorption spectra of various dialkylthioureas are shown in Table V where the assignments have been made on the basis of the results of the normal coordinate treatment of N,N'-dimethylthiourea.

The N-H Stretching Region and Rotational Isomers of Dialkylthioureas. The C-N bonds of the thiourea molecule possess appreciable double-bond character, and the molecule takes the nearly planar configuration. In disubstituted thiourea derivatives different configurations are possible where the thioamide hydrogen and the thiocarbonyl sulfur take *cis* and *trans* positions with respect to each other.



In secondary amides, the presence of two closely spaced N-H stretching bands have been found due to such rotamers by Russell and Thompson.¹⁴ The higher N-H stretching frequency was assigned by them to the *trans* isomer and the lower frequency to the *cis* isomer. These assignments have found further support from dielectric and infrared studies of Suzuki and others.^{15,16} The N-H stretching band of two di-

alkylthioureas are shown in Figure 2. N,N'-Dimethylthiourea as well as N,N'-diethylthiourea show only one sharp N-H stretching band corresponding to the *trans* rotamer. In the extreme case of N,N'-di-*t*-butylthiourea, the *cis* and *trans* N-H peaks are of nearly equal intensity. The percentage *trans* isomer was estimated to be approximately 55% from the band intensity data. These studies, however, do not show whether the *cis* N-H band arises from the *cis-trans* (III) or the both-*cis* (II) isomer. It is interesting that bulky groups favor the *cis* form just as in secondary amides.^{14,17}

In order to confirm that the observation of the doublet N-H band was due to rotational isomers, the spectra were recorded in different solvents. The relative intensities of the two peaks varied with the solvent, indicating the existence of an equilibrium. By recording the spectra at different temperatures in the first N-H overtone region, it was found that the *cis/trans* ratio increases with temperature and that the barrier height to rotation was of the order of 500 ± 200 cal mole⁻¹.

The N-H stretching region of dialkylthioureas showed bonded N-H bands due to self-association (Figure 2 and Table V). Examination of the concentration dependence of the N-H stretching vibration bands of N,N'-diethylthiourea and N,N'-di-*t*-butylthiourea indicated that there was negligible association in the latter case. Apparently, the magnitude of association of the *trans* N-H bonds is greater. This kind of steric inhibition of hydrogen bonding has been noticed

(14) R. A. Russell and H. W. Thompson, *Spectrochim. Acta*, **8**, 138 (1956).

(15) I. Suzuki, *J. Chem. Soc. Japan, Pure Chem. Sect.*, **80**, 353, 697 (1959).

(16) I. Suzuki, M. Tsuboi, T. Shimanouchi, and S. Mizushima, *Spectrochim. Acta*, **16**, 470 (1960).

(17) L. A. LaPlanche and M. T. Rogers, *J. Am. Chem. Soc.*, **86**, 337 (1964).

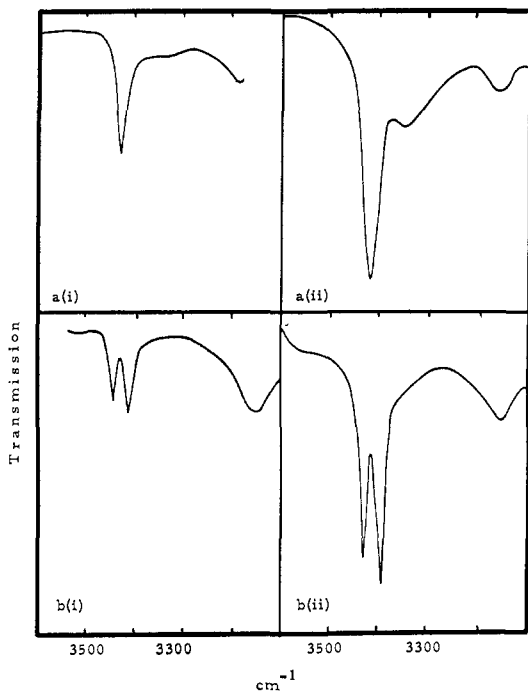


Figure 2. Concentration dependence of the infrared absorption of the N-H stretching bands of (a) N,N'-diethylthiourea and (b) N,N'-di-*t*-butylthiourea: (i) $1 \times 10^{-2} M$, (ii) $5 \times 10^{-2} M$ (0.1-cm cell, CHCl_3 solvent).

earlier in the case of secondary amides.¹⁸ Addition of donors such as benzophenone to the dilute solutions of N,N'-diethylthiourea and N,N'-di-*t*-butylthiourea was also found to affect the *trans* N-H band to a greater extent. In addition to the free and bonded N-H stretching bands, all the dialkylthioureas show a band around 3150 cm^{-1} which probably arises from Fermi resonance just as in secondary amides.¹⁹

Normal Coordinate Treatment and Infrared Spectrum of Tetramethylthiourea. The normal coordinate analysis of the in-plane vibrations of tetramethylthiourea was carried out as an eight-body problem. Although two of the C' atoms are known to be slightly out-of-plane,¹¹ for the sake of simplicity a planar C_{2v} structure was assumed for the calculations. The bond distances and force constants were similar to those in the case of N,N'-dimethylthiourea. In spite of the approximation made regarding the structure, the agreement between the observed and the calculated positions of bands of tetramethylthiourea was quite satisfactory. The deviations were in the range 5-9% only for the low-frequency skeletal vibration bands below 600 cm^{-1} , and within 3% for the higher frequency bands. The band assignments based on the potential energy distribution calculations are shown in Table VI. It can be seen that most of the bands of tetramethylthiourea also arise from mixed vibrations.

Nmr Studies of the Configuration of Alkylthioureas. The signal due to the CH_3 protons of N,N'-dimethylthiourea (τ 7.49 ppm) was found to be a doublet ($J \sim 5$ cps). The splitting disappears in acid solution and is considered to be due to the spin-spin coupling between the CH_3 protons and the NH proton just as in secondary amides.^{17,20} There was no spin-spin

(18) R. L. Jones, *Spectrochim. Acta*, **20**, 1879 (1964).

(19) T. Miyazawa, *J. Mol. Spectry.*, **4**, 168 (1960).

Table VI. Final Assignments of the Infrared Vibrational Bands of Tetramethylthiourea

Band position, ^a cm^{-1}	Assignment
1505	89% $\nu_a(\text{CN})$ + 11% $\delta(\text{NCS})$
1468 } 1441 } 1408 }	$\delta_a(\text{CH}_3)$
1372 } 1358 } 1278 } 1219 } 1137 } 1119 } 1097 } 1060 }	37% $\nu_s(\text{CN})$ + 25% $\nu(\text{CS})$ + 23% δ - ($\text{NCN})$ + 15% $\delta_s(\text{NCH}_3)$
1013 } 990 } 889 }	$\delta_a(\text{CH}_3)$
640 } 494 } 462 }	2×640 (tentative)
422 } 410 } 402 }	54% $\nu_{an}(\text{C}'\text{N})$ + 32% $\nu_s(\text{CN})$ + 14% $r_s(\text{NCH}_3)$
	55% $\nu_a(\text{C}'\text{N})$ + 27% $\nu_{an}'(\text{C}'\text{N})$ + 18% $\delta_a(\text{NCH}_3)$
	50% $\nu_s(\text{C}'\text{N})$ + 50% $\nu(\text{CS})$
	66% $\nu_{an}'(\text{C}'\text{N})$ + 21% $r_a(\text{NCH}_3)$ + 14% $\delta(\text{NCS})$
	53% $\nu_s(\text{C}'\text{N})$ + 47% $\nu_{an}(\text{C}'\text{N})$
	63% $r_a(\text{NCH}_3)$ + 38% $\nu_a(\text{C}'\text{N})$
	37% $\nu(\text{CS})$ + 23% $\nu_{an}(\text{C}'\text{N})$ + 23% δ_a - (NCH_3) + 18% $\delta(\text{NCN})$
	66% $\delta_a(\text{NCH}_3)$ + 34% $r_a(\text{NCH}_3)$
	73% $r_s(\text{NCH}_3)$ + 27% $\nu_s(\text{CN})$

^a Spectrum in carbon tetrachloride solution.

coupling between the NH proton and the protons of the *t*-butyl group of N,N'-di-*t*-butylthiourea. In N,N'-diethylthiourea, the CH_2 signal shows increased multiplicity due to coupling with the NH proton. In the nmr spectrum of N,N'-di-*t*-butylthiourea, the signal due to the *t*-butyl group was seen as a triplet with peaks at τ 9.16, 9.01, and 8.80. This is considered to be due to three different rotamers since the separation between the peaks was greater by a factor of $10/6$ in a 100-Mc instrument compared to a 60-Mc instrument. It is to be noted that infrared spectra only show the presence of the *cis* and *trans* N-H bonds in N,N'-di-*t*-butylthiourea but do not give any indication as to the number of rotamers present. Tetramethylthiourea shows only a single sharp signal unlike dimethylthioacetamide which shows a rotamer doublet due to the CH_3 protons.²¹ The singlet absorption of tetramethylthiourea is likely to be due to the steric repulsion of the CH_3 groups which forces the $\text{C}'_2\text{NCSNC}'_2$ skeleton to deviate from planarity. In such a nonplanar structure, the steric strain is relieved by the rotation of the dimethylamino group to give a nonzero dihedral angle between the two planes.²¹

Infrared Spectra of Charge-Transfer Complexes of Alkylthioureas with Iodine. The positions and intensities of all the mixed vibration bands involving $\nu(\text{CN})$ or $\nu(\text{CS})$ are markedly affected in the charge-transfer complexes. The frequency of the bands around 770 cm^{-1} in dialkylthioureas (Table V) with appreciable contribution from $\nu(\text{CS})$ decreases as one would expect if sulfur were the donor atom. The $\delta(\text{NCS})$ frequency also seems to decrease on charge transfer. In the case of tetramethylthiourea, the band at 990 cm^{-1} (Table VI) is shifted to lower frequency and

(20) G. Fraenkel and C. Niemann, *Proc. Natl. Acad. Sci. U. S.*, **44**, 688 (1958).

(21) R. J. Niedzielski, R. S. Drago, and R. L. Middaugh, *J. Am. Chem. Soc.*, **86**, 1694 (1964).

markedly intensified on charge transfer to iodine. There appears no doubt that sulfur is the donor site in the charge-transfer complexes of alkylthioureas with iodine.

Infrared Spectra of Metal Complexes of Alkylthioureas. Examination of the infrared spectra of the Cu(I), Pd(II), Cd(II), and Zn(II) complexes of N,N'-dimethylthiourea seem to show evidence for two different types of coordination, the Cu(I) and Pd(II) belonging to the first group and the other two belonging to the second group. The first group of complexes show a smaller increase (10–15 cm^{-1}) of the 1506- cm^{-1} band compared to the second group (25–37 cm^{-1}). The 1287- cm^{-1} band shows a marked increase in frequency and intensity in the second group of complexes. The out-of-plane $\delta(\text{NH})$ frequency decreases in the first group and increases in the second group. The $\delta(\text{NCS})$ frequency decreases while the 1568- cm^{-1} band frequency increases in all the complexes. The band at $\sim 760 \text{ cm}^{-1}$ [$\nu(\text{CS}) + \nu(\text{CN}) + \nu(\text{C}'\text{N})$] is shifted to higher frequencies in the first group and to lower frequencies in the second group. These results clearly show that the metal complexes of N,N'-dimethylthiourea fall into two groups just as in the case of the N-methylthiourea complexes.⁷ The results, however, are not as conclusive as in metal-urea complexes.²² This is because the C=O stretching frequency in urea is considerably higher than the C–N stretching frequency, while the $\nu(\text{CS})$ frequency is quite close to the latter.

The infrared spectra of the Pd(II), Cd(II), and Hg(II) complexes of tetramethylthiourea show an increase in the frequency of the 1500- cm^{-1} band and a decrease in the 1120-, 660-, and 490- cm^{-1} bands. The band at $\sim 1000 \text{ cm}^{-1}$ with appreciable contribution from $\nu(\text{CS})$ is not affected greatly.²³

(22) R. B. Penland, S. Mizushima, C. Curran, and J. V. Quagliano, *J. Am. Chem. Soc.*, **79**, 1575 (1957).

(23) After this work was completed a paper appeared [M. Schafer and C. Curran, *Inorg. Chem.*, **5**, 265 (1966)] where the 1120- cm^{-1} band

From the preceding discussion it becomes clear that great care has to be exercised in the interpretation of the infrared spectra of metal complexes where the bands due to the ligands arise from mixed vibrations, and it often becomes difficult to establish the donor site or the nature of metal–ligand interaction on the basis of the shifts of infrared bands alone.

Experimental Section

All the dialkylthiourea derivatives were prepared by standard procedures reported in the literature.²⁴ Infrared absorption spectra were recorded (in solutions, mulls, pellets, or thin films) employing a Carl-Zeiss UR 10 spectrophotometer fitted with LiF, NaCl, and KBr prisms. The spectrophotometer was calibrated with indene.⁸ Infrared spectra in the first N–H overtone region were recorded with a Cary 14-R spectrophotometer fitted with a variable-temperature cell compartment. Nmr spectra were recorded with Varian A-60 as well as HR-100 spectrometers. An IBM 1620 computer was employed in the calculations of normal vibrations.

Infrared spectra of the charge-transfer complexes of alkylthioureas with iodine were recorded in CCl_4 or CHCl_3 solutions in presence of a slight excess of iodine.

The metal complexes of alkylthioureas were prepared by mixing aqueous or alcoholic solutions of the corresponding salts with the solutions of the ligands. The Cu(I) complex of N,N'-dimethylthiourea was prepared according to the method described in the literature.²⁵ The complexes were purified and analyzed²⁶ before use. The infrared spectra of the metal complexes were recorded in Nujol mulls or KBr pellets.

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has been assigned to $\nu(\text{CS})$ and the decrease in the frequency of this band in metal complexes has been ascribed to metal–sulfur bonding. The results of the present study based on the normal coordinate analysis of the ligand clearly shows that it is difficult to draw such unequivocal conclusions when bands arise from mixed vibrations.

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The Absorption, Emission, and Excitation Spectra of Diarylmethylenes

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Abstract: The absorption, emission, and excitation spectra of a series of substituted diphenylmethylenes have been observed in a variety of rigid organic matrices at 77°K. These triplet ground-state molecules were obtained by the low-temperature photolysis of the appropriate diazo compound. The emission is assigned to fluorescence from the lowest excited triplet level to the ground state. No phosphorescent emission was observed in the wavelength range studied. ESR spectroscopy was used to monitor the formation and disappearance of the triplet diphenylmethylenes. The absorption spectra were characteristic of odd-alternant radicals, showing a strong band near 300 $\text{m}\mu$ and a much weaker band in the visible range. These transitions are consistent with a $\pi\text{--}\pi^*$ assignment.

The chemistry of methylenes, $\ddot{\text{C}}\text{R}'_2$, has been interpreted in terms of two electronic configurations: (a) a singlet configuration (I) in which the unshared

electrons are paired in an sp^2 orbital, leaving an empty p orbital; or (b) a triplet configuration (II) in which the two unshared electrons are unpaired, each in a p