Molecular Conformation of *N,N′*-Diarylthioureas: an Assessment by ^{1}H NMR and Infrared Spectroscopy

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Several *N,N′*-dipyridyl- and *N*-phenyl-*N′*-pyridyl-thioureas were examined in different solvents at various temperatures by ^{1}H NMR in order to study their conformational properties. The influence of concentration and the methyl substituent in the pyridine ring on the chemical shifts of the NH and pyridine groups was investigated. The observed chemical shifts are analysed in terms of the conformational properties of the molecules. Free energy barriers to the internal rotation about the C—N bonds have been determined. Infrared spectra have been measured to supplement the NMR studies. Intramolecular hydrogen bonding played a major role in the preferred conformation of pyridylthioureas. The data further revealed an interesting dynamic exchange phenomenon occurring in symmetric *N,N′*-dipyridylthioureas between two intramolecularly hydrogen bonded conformers.

INTRODUCTION

A stimulating problem of substituted thioureas concerns the identification of minimum energy conformations. Many investigations, especially in the field of dynamic NMR spectroscopy, have been carried out and the rotational barriers around the C—N bond have been reported. Many results have been obtained on *N,N′*-dialkylthioureas but relatively few activation parameters have been determined for *N,N′*-diaryl- and *N,N′*-arylalkyl-thioureas.[1–12]

N,N′-Disubstituted thioureas normally exist in solution as an equilibrium mixture of three planar rotamers *E–Z*, *Z–E* and *Z–Z* (Fig. 1). The *E–E* rotamer is thought to be unstable owing to steric hindrance. The roles and relative importance of electronic and steric factors in substituted thioureas are not always clear. This paper presents the results of ^{1}H NMR studies, supplemented with IR spectral data, of several *N,N′*-dipyridyl- and *N*-phenyl-*N′*-pyridyl-thioureas in order to understand further the role of electronic and steric factors in determining the minimum energy conformations. *N,N′*-Diarylthioureas with certain substituents in the aromatic ring have been characterized as prospectives in antiviral chemotherapy,[13,14] and a knowledge of the conformational situation in these molecules is useful in the structure–activity correlations.

Other workers have previously published ^{1}H NMR studies of some *N,N′*-diarylthioureas.[9–12] For example, Kessler and Liebfritz[9] determined the effect of *ortho* substituents on the barrier to internal rotation in some *N,N′*-diphenylthiourea systems. ^{1}H and ^{13}C NMR studies of *N,N*-di-*o*-tolylthiourea have also been published.[11,12] The effect of hydrogen bonding on the conformational stability of some *N,N′*-diaryl- and *N,N′*-arylalkyl-thioureas was investigated by Walter and Ruess.[10] Except for *N,N′*-diphenylthiourea, which has been included for the sake of comparison, none of the other compounds considered here have been previously studied.

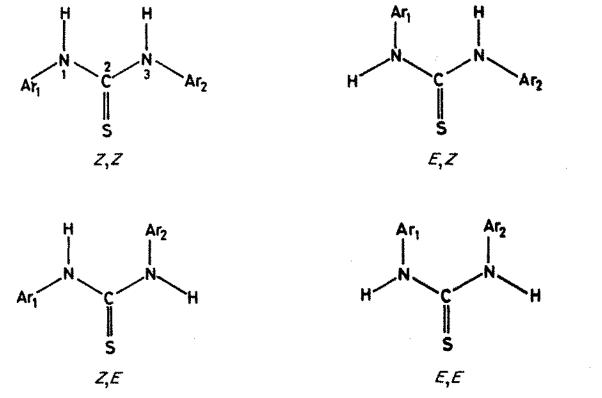

Figure 1. Planar conformations of *N,N′*-disubstituted thiourea.

EXPERIMENTAL

Materials

N,N′-Diphenylthiourea was a commercial product (E. Merck), which was recrystallized from ethanol.

N,N′-Dipyridylthioureas were prepared according to the following general procedure. A mixture of pyridylamine (1 M), powdered sulphur (0.25 M) and carbon disulphide (1 M) in absolute ethanol was refluxed for over 24 h. After cooling, the reaction mixture was acidified. The residual sulphur that separated was filtered off and the filtrate neutralized with

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sodium hydrogen carbonate. The resulting product was recrystallized from an ethanol–chloroform mixture. For the synthesis of *N,N'*-(2,3'-dipyridyl)thiourea, an equimolar proportion of 2- and 3-pyridylamines was employed. The separation of the compound from *N,N'*-(2,2'-dipyridyl)thiourea and *N,N'*-(3,3'-dipyridyl)thiourea was effected by preparative TLC.

N-Phenyl-*N'*-pyridylthioureas were synthesized by refluxing a mixture of phenyl isothiocyanate (1 M) and pyridylamine (1 M) in absolute ethanol for approximately 3 h. The compounds which separated on cooling were recrystallized from an ethanol–chloroform mixture.

The compounds included in this study (Ar_1-$NHCSNHAr_2$) and their melting points (°C) are listed below; they were found to be spectroscopically pure:

1 $Ar_1 = Ar_2$ = phenyl (149–151)
2 $Ar_1 = Ar_2$ = 2-pyridyl (153)
3 Ar_1 = 3-pyridyl, Ar_2 = 2-pyridyl (184)
4 $Ar_1 = Ar_2$ = 3-pyridyl (173)
5 $Ar_1 = Ar_2$ = 2-(3-picolinyl) (147)
6 $Ar_1 = Ar_2$ = 2-(4-picolinyl) (188)
7 $Ar_1 = Ar_2$ = 2-(6-picolinyl) (198)
8 Ar_1 = phenyl, Ar_2 = 2-pyridyl (169)
9 Ar_1 = phenyl, Ar_2 = 2-(3-picolinyl) (124)
10 Ar_1 = phenyl, Ar_2 = 2-(4-picolinyl) (157)
11 Ar_1 = phenyl, Ar_2 = 2-(6-picolinyl) (181)

Spectral measurements

^{1}H NMR spectra were recorded at 270 MHz on a Bruker WH 270 FT spectrometer attached to a computer with a 20K memory. The experimental parameters were spectral width 4000 Hz, pulse width 5×10^{-6} s, acquisition time 3.0 s and number of pulses 20–30. Spectra were recorded for $CDCl_3$ and/or DMSO-d_6 solutions, depending on the solubility of the compound. The chemical shifts were measured in ppm with respect to TMS as an internal reference. The temperature was controlled with a variable-temperature accessory capable of maintaining the temperature with an accuracy of ±1°.

Rate constants, k_c, corresponding to the process of interconversion of the conformers at the coalescence temperature, T_c, were calculated in the usual way from the maximum separation of the signals ($\Delta\nu$). The free energy of activation at the coalescence temperature ($\Delta G_{T_c}^{\neq}$) was calculated using the coalescence temperature method[15,16] according to the Eyring equation:[17]

$$\Delta G_{T_c}^{\neq}(\text{kcal mol}^{-1}) = 4.57 T_c(10.32 + \log T_c/\Delta\nu)$$

The IR absorption spectra were obtained on a Perkin-Elmer 597 spectrophotometer. The spectra of the solid samples were recorded as Nujol mulls. The solution spectra were measured in chloroform using KBr cells of path length 0.5 mm. The spectrophotometer was calibrated with the usual standards. The semiempirical molecular orbital calculation at the CNDO/2 level and the NMR simulation using LAOCOON I and LACOON II were performed on a DEC-1090 computer system.

RESULTS AND DISCUSSION

Spectral assignments and conformations

The chemical shifts for the NH protons of diarylthioureas **1–11** at ambient temperature are listed in Table 1. For the sake of comparison, *N,N'*-diphenylthiourea (**1**) was included. The influence of temperature on the chemical shifts of the NH protons was determined for symmetric *N,N'*-diarylthioureas **1**, **2**, **5**, **6** and **7**, and the results are given in Table 2. At subambient temperatures the spectrum of **1** shows two signals of equal intensity near 7.7 and 9.5 ppm, in contrast to all the other compounds, which display two signals, one at approximately 9.0 and the other near 14.0 ppm (Table 2). The presence of this extremely low-field signal suggests the existence of strong hydrogen bonding.[18,19] The position of the lowest field signal was found to be independent of concentration and fairly independent of temperature, indicating that the hydrogen bonding is intramolecular in origin.

Models show that the *EZ* (or *ZE*) isomer (Fig. 1) of pyridylthioureas possess an ideal geometry for the formation of strong intramolecular hydrogen bonds in solution. The experimental results can thus be interpreted by assuming that the NH amide proton bonds to the basic pyridine nitrogen in the *EZ* (or *ZE*) isomer as depicted in Fig. 2. The extreme downfield signal can then be assigned to the *E*-NH group, and the other signal at $\delta \approx 9.0$ to the *Z*-NH group of the *Z*, *E* (*E*, *Z*), isomer. The 1s electron densities were calculated by the semiempirical molecular orbital method at the CNDO/2 level using the standard form

Table 1. Chemical shifts (δ, ppm) of the NH protons of diarylthioureas in $CDCl_3$ at 293 K

Compound	$(NH)_Z$	$(NH)_E$	Compound	$(NH)_Z$	$(NH)_E$
1	7.86	—	7	8.87	14.63
2	8.96	14.29	8	9.38	13.73
3	9.13	13.90	9	8.12	13.96
4	10.12[a]		10	10.83	13.96
5	8.43	13.84	11	9.11	14.09
6	8.59	14.32			

[a] In DMSO-d_6, representing an average value for the two NH groups.

Table 2. Influence of temperature on the chemical shifts (δ, ppm) of the NH protons for diarylthioureas in $CDCl_3$

	Temperature (K)						
Compound	213	233	243	253	263	273	283
1	7.67	7.64	8.24	8.16			
	9.46	9.03					
2	9.97	9.78	9.64	9.49	9.33	9.23	9.09
	14.61	14.56	14.52	14.48	14.44	14.40	14.35
5			8.47	8.47	8.46	8.45	8.44
			14.05	14.00	13.96	13.91	13.86
6				8.70	8.69	8.67	
				14.42	14.39	14.37	
7			9.36		9.03	8.89	
			14.72		14.65	14.64	

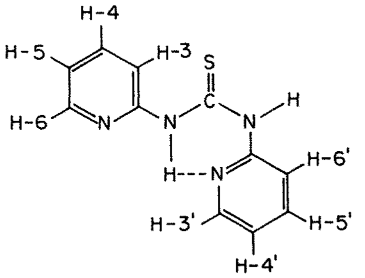


Figure 2. Intramolecular hydrogen bonded conformation of **2**. The dotted line represents the hydrogen bond.

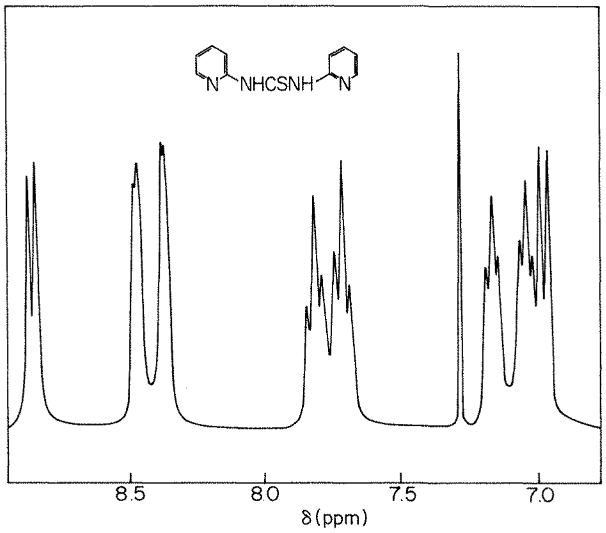


Figure 3. NMR spectrum of the pyridyl protons of *N,N'*-(2,2'-dipyridyl)thiourea in $CDCl_3$ at 253 K.

and parameterization suggested by Pople and co-workers.[20,21] The computed 1s electron densities for the protons of the NH group in the *E* and *Z* configurations of the identical *Z, E* and *E, Z* rotamers were 0.799 and 0.858, respectively, which support the above assignment.

Apparently the *EZ* (or *ZE*) conformation for *N,N'*-dipyridylthioureas is stabilized by the intramolecular hydrogen bonding. Further support in favour of this structure comes from the values of the chemical shifts of the aromatic protons, shown in Table 3. It accounts, for example, for the large downfield shift of H-3 of the pyridyl group in the *Z* configuration, owing to the anisotropic deshielding effect of the thiocarbonyl group. The chemical shift of the corresponding proton of the pyridyl ring in the *E* configuration is comparable to that of the corresponding proton in simple 2-substituted pyridines. The data in the current literature support this conclusion. In *N*-(2-pyridyl)thioacetamide,[22] which is found to be stabilized in the *Z* conformation, H-3 of the *Z*-pyridyl group resonates at 8.39 ppm compared with a value of 6.45 ppm for the corresponding proton of 2-aminopyridine.[23,24] Anisotropic effects on protons *meta* and *para* to the amide function are small in comparison with those at the *ortho* position.[24]

At subambient temperatures, the spectra of *N,N'*-dipyridylthioureas display distinct signals of equal intensity for the pyridyl groups in the *E* and *Z* configurations. The spectrum of **2** is shown in Fig. 3. The protons of the pyridyl group in the *E* configuration are assigned with the aid of the spectra of the corresponding *N*-phenyl-*N'*-pyridylthioureas **8–11**. Figure 4 shows the spectrum of a representative compound, **8**, over a large temperature range. The spectrum shows two resonances near 14.0 and 9.0 ppm in the NH region in the temperature range covered. The variable-temperature spectra of **8–11** exhibited little change, leading to the conclusion that these compounds possess a rigid (*ZE*) conformation, presumably stabilized by the intramolecular hydrogen bonding. The signals due to the pyridyl ring protons are assigned to the pyridine ring in the *E* configuration. The spectrum of **3** is assigned similarly, the 2-pyridyl group adopting the *E* configuration in the *ZE* conformation of the molecule. The assignment of the aromatic proton chemical shifts has been verified by analysing the spectra of **3** by LAOCOON I and LAOCOON II calculations.[25] The approximate coupling constants for the 4-spin pyridine systems were taken from Brugel.[26] The coupling constants obtained are shown in Table 4. Assignments for the low-temperature spectrum of **2** were made from the above observations. As a consequence of intramolecular hydrogen bonding, the pyridyl ring in the *E* configuration is in a fixed coplanar position with the thioureide group, leading to an increased conjugative interaction between the amide nitrogen lone pair with the hydrogen-bonded pyridyl ring. This is consistent with the observed upfield shifts

Table 3. ^1H chemical shifts (δ, ppm) of the pyridyl and methyl groups of diarylthioureas

		$(Pyridyl)_Z$					$(Pyridyl)_E$					
Compound	Temperature (K)	H-2	H-3	H-4	H-5	H-6	H-3'	H-4'	H-5'	H-6'	$(CH_3)_Z$	$(CH_3)_E$
2	213		8.84	7.86	7.21	8.51	7.06	7.73	7.07	8.37		
3	293	8.73	—	8.35	7.37	8.50	6.91	7.73	7.06	8.27		
5	213		—	7.59	7.30	8.48	—	7.71	7.05	8.11	2.45	2.36
6	213		8.58	—	7.00	8.32	6.67	—	6.86	8.22	2.44	2.37
7	213		8.53	7.71	7.04	—	6.77	7.59	6.89	—	2.60	2.56
8	293						6.96	7.70	7.03	8.23		
9	293						—	7.55	6.96	8.11	—	2.34
10	293						7.08	—	6.97	8.19	—	2.31
11	293						6.71	7.56	6.85	—	—	2.50

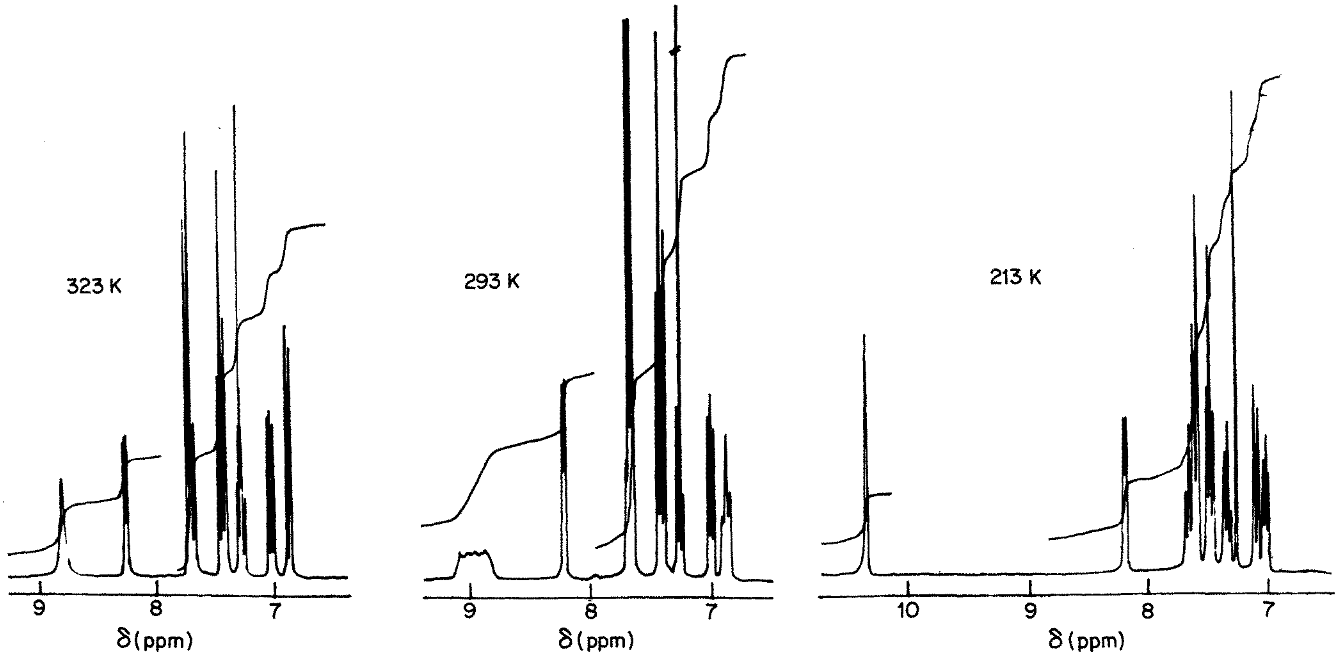


Figure 4. Representative NMR spectra of *N*-phenyl-*N'*-pyridyl-thioureas. Spectrum of **8** in $CDCl_3$.

for the pyridyl protons in the *E* configuration relative to those in the *Z* configuration.

The assignment of the signals of the methyl protons of picolinylthioureas was made in an analogous manner to the assignment of the aromatic protons in *N*-phenyl-*N'*-picolinyl systems. The high-field signal is assigned to the methyl substituent of the pyridyl group in the *E* configuration, and the low-field signal to that of the methyl group of the pyridine ring in the *Z* configuration.

The chemical shifts in two different solvents, and at various temperatures, for the pyridyl protons which best lend themselves to conformational analysis are reported in Table 5 for the representative compound **2**. The ring protons show only a very small temperature dependence in the range investigated. This behaviour has been previously found for compounds possessing similar intramolecular hydrogen bonding.[19]

Table 4. Proton spin–spin coupling constants for compounds 2–4

	Coupling constants (Hz)								
Compound	*J*(24)	*J*(25)	*J*(26)	*J*(34)	*J*(35)	*J*(36)	*J*(45)	*J*(46)	*J*(56)
2	—	—	—	8.61	0.32	0.25	7.22	1.94	5.12
4	2.53	0.0	0.0	—	—	—	8.25	1.32	4.95
3									
2-P ring	—	—	—	8.67	0.38	0.27	7.32	1.93	5.09
3-P ring	2.06	0.0	0.0	—	—	—	8.25	1.39	4.95

Table 5. Influence of temperature on the chemical shifts (δ, ppm) of the aromatic protons of 2

Solvent	Temperature (K)	H-3	H-4	H-5	H-6	H-3'	H-4'	H-5'	H-6'
$CDCl_3$	213	8.84	7.86	7.21	8.51	7.06	7.73	7.07	8.37
	233	8.85	7.84	7.20	8.49	7.04	7.72	7.06	8.37
	253	8.87	7.82	7.18	8.47	6.99	7.71	7.05	8.37
	273	8.87	7.75	7.10	8.40	6.94	7.70	—	—
	293	—	7.70	7.08	8.40				
	313	—	7.70	7.07	8.40				
DMSO-d_6	293	—	7.89	7.21	8.40				
	323	8.06	7.85	7.18	8.39				
	353	8.04	7.83	7.15	8.37				
	383	8.03	7.82	7.14	8.36				
	393	8.03	7.80	7.13	8.35				

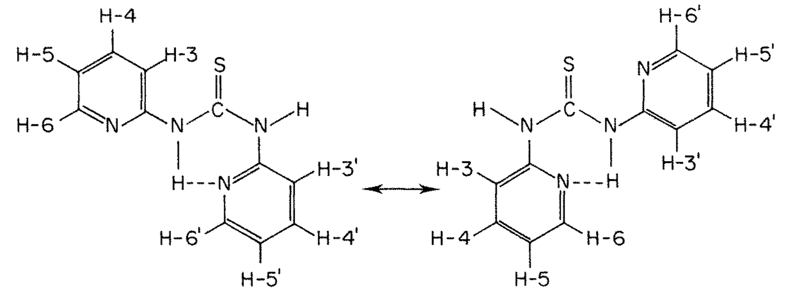


Figure 5. Dynamic exchange process in symmetrical *N,N′*-dipyridylthioureas.

Free energy barriers

For symmetric *N,N′*-dipyridylthioureas, distinct peaks for the pyridyl protons in the *E* and *Z* configuration are observed at low temperatures. On warming the solutions, gradual broadening and coalescence of the signals were observed, and the reversibility of the spectral changes verified. These findings indicate the occurrence of a dynamic process which can be identified as a fast exchange between $EZ \rightleftharpoons ZE$ conformations of dipyridylthioureas at ambient temperature, as depicted in Fig. 5. As noted from the existence of the extreme downfield signal at *ca* 14.0 ppm in the temperature range investigated, the $EZ \rightleftharpoons ZE$ isomerization is between two hydrogen-bonded conformers. The broadening of the pyridyl H-3 line is probably due to this intramolecular exchange process. A probable mechanism for this dynamic exchange is a concerted rotation about the two C–N bonds in a disrotatory fashion. The free energy of activation ($\Delta G^{\neq}$) for this process was determined from a variable-temperature ^{1}H NMR study, employing the coalescence temperature method. The $\Delta G^{\neq}$ values at the coalescence temperature (T_c) determined by this method, together with all the pertinent data, are presented in Table 6.

The energy barrier about the C—N bond in thioureas seemingly arises from two complementary effects. Firstly, the competitive conjugative interaction between the two C—N bonds and the C=S group and, secondly, the steric inhibition that prevents the coplanarity of the thiocarbonyl group with the thioureide nitrogens and their substituents. In *N,N′*-diarylthioureas, the aryl group can also compete with the nitrogen lone pair (cross-conjugation), thereby reducing the barrier about the C—N bond compared with that for *N,N′*-dialkylthioureas (Fig. 6). The rotational barrier about the C—N bond of **1**[9] is lower than that for *N,N′*-dimethylthiourea[5] (13.8 kcal mol^{-1}; Table 6). This decrease gives an estimate of the increased conjugation across the N—C (aryl) bond. The rotational barrier about the C—N bond in **2** is also higher than that in **1**. For **2**, this rotational barrier is energetically affected by the intramolecular hydrogen bond, since the rate of interconversion of $ZE \rightleftharpoons EZ$ involves cleavage of hydrogen bonds and, hence, an increase in the free energy of activation. The increase in the barrier to internal rotation brought about by methyl substitution on the pyridine ring (Table 6) is most readily explained in terms of the well established inhibition of the resonance interaction, resulting from sterically induced twisting of the pyridine ring from coplanarity with the thioureide plane. Marked steric inhibition can be predicted for the 3-methyl substituent, and the least steric repulsion is in the 6-position of the pyridine ring. The trend of increasing energy barriers with increasing steric repulsion could thus be well explained (Table 6).

The internal rotation about the N—C(Py) bond in **2** and related compounds has a low energy barrier which stabilizes isomer (b) relative to isomer (a), depicted in Fig. 7. The interaction between the lone pairs on the pyridine nitrogen and on sulphur destabilizes structure (a). Further, weak hydrogen bond formation between the pyridine nitrogen with the NH group in the *E* configuration is possible, which would stabilize isomer (b). This weak hydrogen bonding will produce a small downfield shift of the NH signal. As a consequence, we expect the NH signal in the *E* configuration of *N,N′*-dipyridylthioureas to appear at low field relative to that of the analogous *N*-phenyl-*N′*-pyridyl systems. The data in Table 1 are consistent with this inference except in **5**, where the steric effect of the 3-methyl group does not favour structure (b). As expected, this barrier is absent in 3-pyridyl systems, as seen from the value of the chemical shifts of the NH groups.

Table 6. Free energy of activation for the intramolecular exhange process ($EZ \rightleftharpoons ZE$) of diarylthioureas

Compound	T_c (K)	$\Delta\nu$ (Hz)	$\Delta\nu$ (source)	$\Delta G_{T_c}^{\neq}$ kJ mol^{-1}	kcal mol^{-1}
1	243	483	N-H	44.94	10.74
2	273	38.0	H-5	56.74	13.56
5	295	32.4	H-6	61.63	14.73
6	283	27.0	H-6	59.45	14.21
7	273	32.4	H-4	56.86	13.59

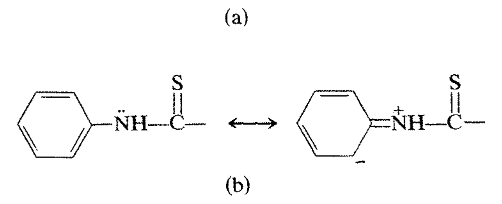
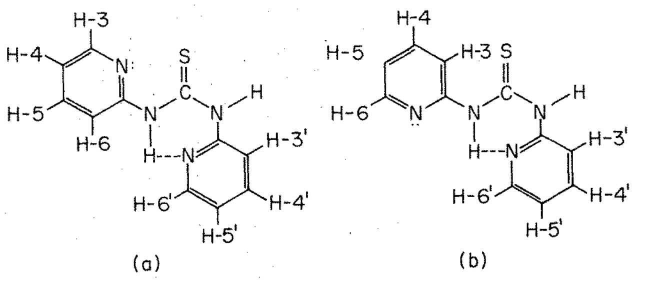


Figure 6. Canonical structures of *N,N*-diarylthioureas.



(a) (b)

Figure 7. Non-bonded interaction between pyridine nitrogen and thiocarbonyl sulphur.

The spectrum of **2** in DMSO-d_6 shows single resonances for both aromatic and NH protons. It is obvious that DMSO, being capable of forming strong hydrogen bonds with NH protons, disrupts the intramolecular hydrogen bond, thus giving only one set of signals.

Infrared spectra

The frequencies of the infrared bands in the region 2800–3700 cm^{-1} are listed in Table 7 for the solid samples and for the solutions. In the solid, except for **1**, **5** and **9**, there are only two fairly intense broad absorptions at *ca* 3220 and 3180–3100 cm^{-1} in the NH stretching region. In solution, the compounds exhibit an additional sharp band at a higher frequency, *ca* 3400 cm^{-1}. The higher (*ca* 3400 cm^{-1}) and the middle (*ca* 3220 cm^{-1}) frequency bands can easily be assigned to the monomeric and intermolecularly hydrogen-bonded NH stretching modes, respectively, from the fact that with decreasing concentration the former band increases at the expense of the latter. The lower frequency band (*ca* 3200 cm^{-1}) is attributable to the intramolecularly hydrogen bonded NH group, since dilution studies show little effect on this band. The lower and middle frequency bands overlap in some cases. According to literature data,[27–30] the NH stretching frequency of the CSNH group is 20–40 cm^{-1} higher for the E isomer than the Z isomer. The higher frequency band of **1** is assigned to the NH in the E configuration and the lower one to the NH in the Z configuration. The reverse situation occurs with compounds **2–11**, with the exception of **4**, owing to intramolecular hydrogen bonding. Intramolecular hydrogen bonding of the type proposed is not possible for **1** and **4**, and in the solid phase they show NH stretching bands below 3200 cm^{-1}, possibly owing to an intermolecular hydrogen bond; both the NH groups seem to be involved. The spectra of **5** and **9** display an absorption peak near 3400 cm^{-1} in the solid state, as in solution, indicating that the steric effect of the 3-methyl substituent prevents intramolecular hydrogen bonding. These results are therefore in accordance with the conformational properties deduced from the NMR spectra.

Table 7. NH stretching frequencies (cm^{-1}) of diarylthioureas

Compound	Solid	Solution
1	3180 s, 3120 sh	3360 s, 3400 s, 3160 w
2	3215 w, 3170 w	3400 s, 3200 w, 3160 m
3	3215 s, 3180 s	3410 s, 3220 m
4	3200 sh, 3160 mw, 3100 w	Insoluble
5	3430 s, 3080 w	3430 s, 3080 mb
6	3250 ms, 3220 sh	3408 s, 3200 mb
7	3200 ab, 3120 w	3420 s, 3220 mb, 3180 mb
8	3230 s, 3180 sh	3420 s, 3220 w, 3180 mb
9	3400 mw, 3080 w	3430 s, 3100 mb
10	3210 mb	3420 s, 3200 mvb
11	3195 s, 3110 mb	3410 s, 3220 sh, 3190 mb

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