Synthesis and Dynamic NMR Studies of Some New Symmetrical Podands of Dithiocarbamates Formed from Bis(N-thiazol)chloroacetamides

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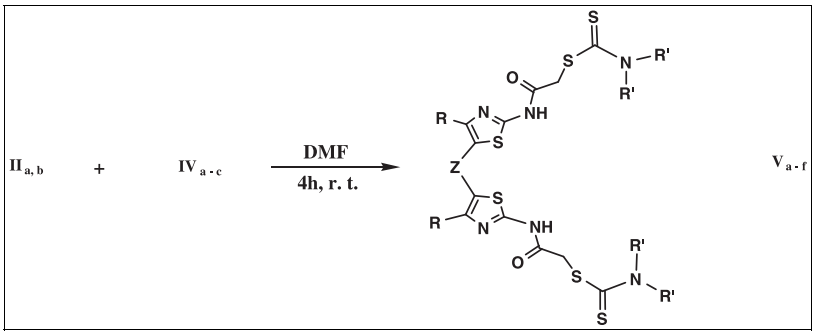

Reactions of dithiocarbamates salts ($\mathbf{IV_{a-c}}$) with bis(N-thiazol) chloroacetamides($\mathbf{II_{a,b}}$) in DMF furnished corresponding podands as $\mathbf{V_{a-f}}$ in high to excellent yields. Two reacting ligands ($\mathbf{II_{a,b}}$) were obtained in the reaction of bis(aminothiazoles) ($\mathbf{I_{a,b}}$) with chloroacetyl chloride. Dynamic NMR spectroscopic data of two series of podands ($\mathbf{V_{a–c}}$ and $\mathbf{V_{d–f}}$) are discussed and figured out their free energy of activation ($\Delta G_c^{\neq}$) at coalescence temperatures. The $\Delta G_c^{\neq}$s of these podands were attributed to conformational isomerization in the range of 14.9–16.2 kcal/mol due to rotation and resonance effect about thioamide C-N bond.

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INTRODUCTION

Carbon–sulfur bond formation is a fundamental approach to introduce sulfur into organic compounds. Organic dithiocarbamates (DTCs) have received much attention due to their interesting chemistry and wide utility. They have been shown to possess a broad view of biological activities such as fungicidal [1–5] and antibacterial [2, 6–9] effects. The antibacterial effect of DTCs was reported results from HS-groups of physiologically important enzymes by transferring the alkyl group of the dithioester to the HS-function of the enzyme [6]. DTCs are known also to be active as anticancer agents [6], [10–13]. Another application of DTCs is their strong ability to bind metal ions and complexation with metals as monodentate and bidentate ligands [14]. Therefore, the synthesis of DTCs has attracted much more attentions recently.

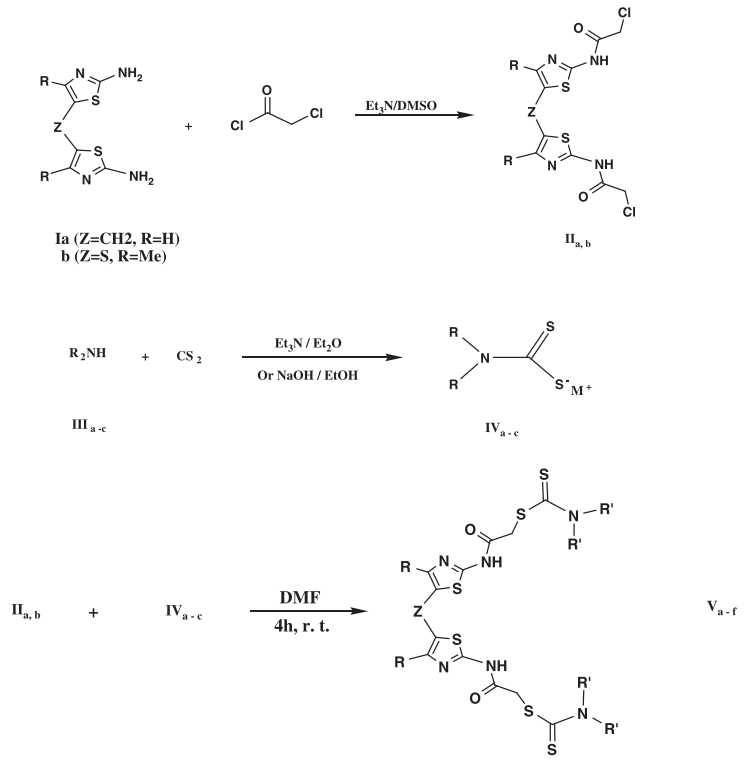
The classical synthesis of DTCs involves the use of thiophosgene [15] and its substituted derivatives [16], which are expensive and toxic reagents. Moreover, their formation using CS_2 employs harsh reaction conditions such as the use of strong bases, high reaction temperatures, and long reaction times [17]. General methods for the synthesis of aryl and vinyl esters of dithiocarbamic acids are based upon the reactions of hypervalent iodine compounds with sodium salt of dithiocarbamic acid [18]. Recently some new and efficacious procedures were published for the synthesis of DTCs [19].

Earlier investigations on structure–activity relationship suggested that the distance between functional groups was the main responsible feature in the pharmacological usefulness [20]. Nevertheless, molecular flexibility also plays an important role in biological activities. Much of this flexibility is dictated by hindered rotation about chemical bonds, as in the case of conjugated C-N linkages [21–25]. Delocalization of the nitrogen lone pair over the N-C-S π system, leads the C-N bond to acquire double-bond character making the rotational barrier substantially higher than simple amines [21–25]. The C-N rotational barrier in DTCs lies on the vicinity of 10–15 kcal/mol 26, [27] and carbamates equals to 15 kcal/mol while in amides the values are ranged from 15 to 22 kcal/mol [21,23,25,28–35]. Amides were extensively studied and much is known about the origin of the C-N rotational barrier and on the influence of the medium. In contrast, only recently thiocarbamates attracted much attention of the chemical community with respect to their molecular structure.

Because of the importance of carbamothioates, we were encouraged to synthesis two series of DTCs ($\mathbf{V_{a-c}}$ and $\mathbf{V_{d-f}}$) using the reacting diamine ligands ($\mathbf{I_{a,b}}$, see Scheme 1) which were already synthesized in our laboratory [36] and converted to their corresponding bis-Schiff's base [37].

In this work we wish also to report the dynamic behavior of these DTCs using dynamic NMR (DNMR) spectroscopy.

Scheme 1



RESULTS AND DISCUSSION

The diamines (**$I_{a,b}$**) were obtained from condensation of thiazoles with formaldehyde or thiourea [36, 38] which upon reaction with chloroacetyl chloride at room temperature led to dichlorodiamides (**$II_{a,b}$**) in 2 h. The dichloro compounds (**II_{a-b}**) easily reacted with dithioate salts at room temperature and produced the podands **V_{a-f}** (Scheme 1 and Table 1).

The coalescence temperatures of five podands **$V_{a,b,d-f}$** were obtained from their corresponding DNMR spectra at about 313–350 k (Table 2). According to Gutwesky-Holms equation ($K_c = \frac{\pi\Delta\nu}{\sqrt{2}}$) we obtained quantities of K_cs. Eyring equation $\left[\Delta G_c^{=} = 4.58\ T_c\left(10.32 + \log\frac{T_c}{K_c}\right]\right.$ was used to calculate the $\Delta G_c^{\neq}$ values (Table 2). On the basis of experimental $\Delta G_c^{\neq}$ values (14–17 kcal/mol) for **$V_{a,b,d-f}$** it is revealed that different six-membered ring do not effect on transition states and intermediates significantly.

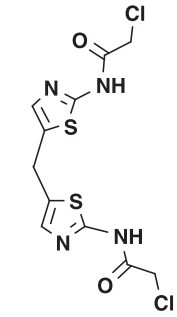
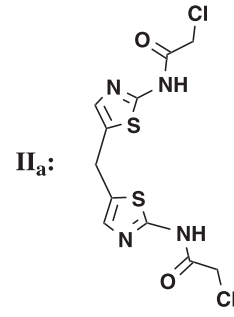
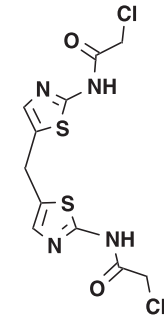
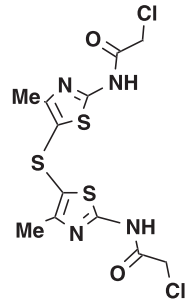
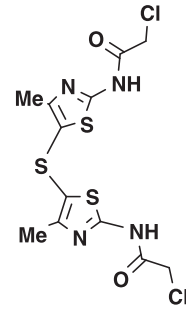
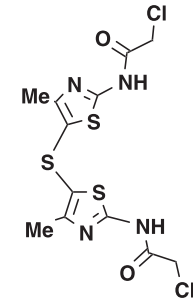
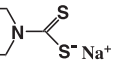
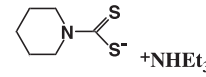
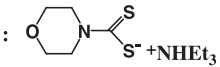
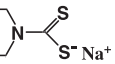
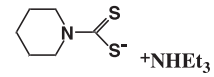
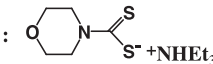
Scheme 1. The energies in Table 2 may end to the conclusion that CH_2 groups are subjected to the nature of adjacent heteroatoms and the amount of resonance effect due to competition between S and N atoms. These data demonstrate that conversion of resonance forms shown in Figure 1 take place hardly at ambient temperature, while increasing the temperature is influential on interconversion of resonance forms.

^{1}H NMR studies of compounds **V_{a-f}** in the chloroform as solvent exhibit two distinct singlet signals for α-protons related to nitrogen at 298 K. The chemical shifts of CH_2 protons (C-1 and C-2, Fig. 1) for podands **$V_{a,b,d-f}$** in $CDCl_3$ at 298 K are listed in Table 2. The temperature-dependent ^{1}H NMR spectra of podand **V_e** is shown in Figure 2. The spectrum exhibits a typical exchange broadening of the C-1 and C-2 methylene resonances in these series of carbamothioates. Below 323 K, two separate signals are observed for C-1 and C-2, while over 328 K, only one signal represents the fast exchange between the two distinct magnetic environments. The maximum separation between protons attached to C-1 and C-2 were observed below 303 K.

Table 2 also lists the experimental rate constants rotation about the C-N bond in compounds **V_{a-e}** in $CDCl_3$ (except V_c that was insoluble in $CDCl_3$) and in the cases of $V_{a,d}$, T_cs were over the boiling points of NMR solvent (b.p. $CDCl_3$ = 334 K). Four dynamic processes (thioamide rotation, nitrogen inversion, ring reversal, and rotation about S-C bond (-S-C═S, see Fig. 1)) are possible in the derivatives of diethylamine ($V_{a,d}$), piperidine (V_{b-e}) and morpholine ($V_{c,f}$). The nitrogen inversion barriers in the derivatives of diethylamine, piperidines and morpholine are too small [39] to be observed by DNMR. Ring reversal barriers in piperidines and morpholines are observed with $\Delta G_c^{\neq}$ of (42–54.4 kJ mol^{-1}). The S-C bond rotation is fast in dithiocarbamtes in which S atom is alkylated [27]. In

Table 1

List of synthetic podands and substartes for synthesis of dithiocarbamates.

Entry	Bis-thia–chlorinated	Thione salt	Dithiocarbamate	Yield (%)	mp (°C)
1	$\mathbf{II_a}$: 	$\mathbf{II_a}$: 	$\mathbf{II_a}$: 	75	186–188
2	$\mathbf{II_b}$: 	$\mathbf{II_b}$: 	$\mathbf{II_b}$: 	80	212–215
3	$\mathbf{IV_a}$: 	$\mathbf{IV_b}$: 	$\mathbf{IV_c}$: 	71	270–271
4	$\mathbf{IV_a}$: 	$\mathbf{IV_b}$: 	$\mathbf{IV_c}$: 	97	186–187
5				89	98–100

(*Continued*)

Table 1
(Continued)

Entry	Bis-thia–chlorinated	Thione salt	Dithiocarbamate	Yield (%)	mp (°C)
6	**V_a:**	**V_b:**	**V_c:**	92	186–187
	V_d:	**V_e:**	**V_f:**		

Table 2

Data acquired from ^{1}H NMR variable temperature.

Podand	$\delta_{H(C-1)}$(ppm) at 298 K	$\delta_{H(C-2)}$(ppm) at 298 K	$\Delta\delta_{H(C-1,2)}$ (ppm) at 298 K	T_c (K)	K_c (s^{-1})	$\Delta G_c^{\neq}$ (kcal mol^{-1})
$\mathbf{V_a}$	3.58	4.04	0.46	[a]> 338	193.367	>16.046
$\mathbf{V_b}$	3.89	4.30	0.41	328	269.70	15.630
$\mathbf{V_c}$	–	–	–	–	–	–
$\mathbf{V_d}$	3.73	4.02	0.29	[a]> 333	187.21	>16.121
$\mathbf{V_e}$	3.86	4.28	0.42	323	275.96	15.368
$\mathbf{V_f}$	4.07	4.31	0.24	313	253.11	14.927

[a]T_c is higher than the boiling point of ^{1}HNMR solvent ($CDCl_3$)

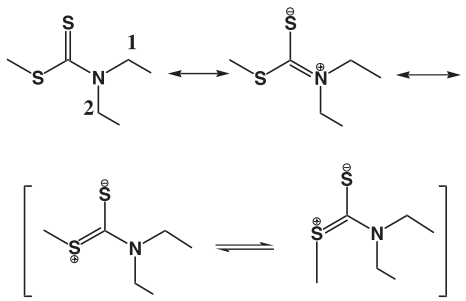


Figure 1. The four most important resonance structures for DTCs.

this study, the thioamide C-N bond rotation was the only process observed. The other two processes are expected to be too small to be directly observed by DNMR. The resonance model (Fig. 1) rationalized the large barrier for rotation about the C-N bond in thioamides as a significant contribution to the stability of the planar amide from a resonance structure in which charge is transferred from the amidic N and the S to the thiocarbonyl C═S via the π system. This predicts that the C-N bond length would shorten. The C-N bond seems to exhibit more double-bond character and bond length would shorten than that in amides and carbamates. This is due to a greater contribution of the dipolar canonical structure (III) in the resonance structures (Fig. 3), because C(2p)-S(3p) overlap in a thioamide bond is less effective than C(2p)-O(2p) overlap in an amide bond. On the other hand, the C═S bond will have only a small polarization since the electronegativities of carbon and sulfur are about the same. Thus, the importance of structure II is markedly reduced. A similar behavior has been observed in thioamides relative to amides [40].

According to Table 2 for compounds with piperidine or morpholine residues instead of ethylamine moiety the ΔG values are lower. In case of piperidine or morpholine derivatives (Fig. 4) the chair conformation (of six-membered rings) decreases the planarity of amidic nitrogen atom. In this case, the portion of pyramidal nitrogen atom increases and therefore, corresponding resonance forms decrease. The presence of oxygen instead of methylene (morpholine vs. piperidine), decrease the portion of planar amide and thus the resonance is further undermines. This is probably due to the steric (1,3-diaxial interactions are reduced in the morpholine ring compared to piperidine) and electronic effects (oxygen atom pulls none bonding electrons of nitrogen). The Figure 4 is suggested for these effects.

EXPERIMENTAL

Chemicals and apparatus. All reactions were carried out on an efficient hood. The starting materials were purchased from

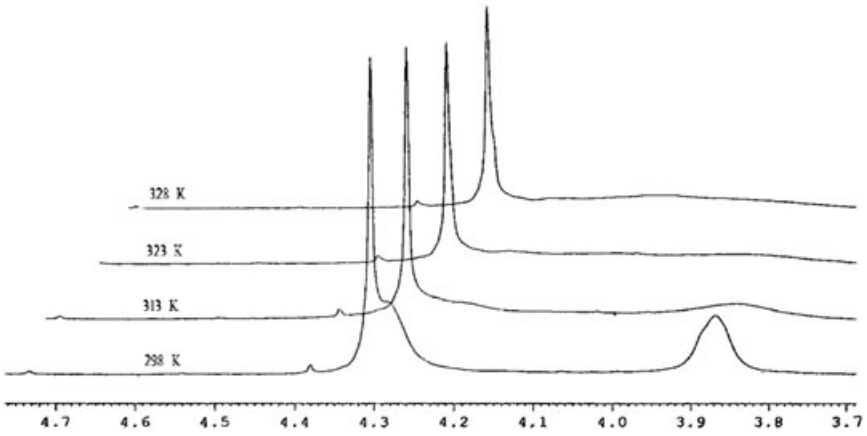


Figure 2. Dynamic ^{1}H NMR for compound $\boldsymbol{V_e}$.

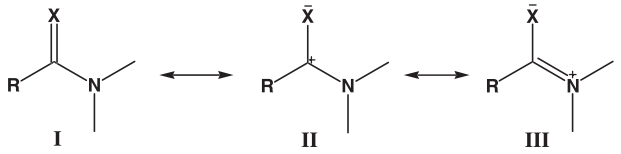


Figure 3. Dipolar canonical structures in amides and thioamides.

Merck and Fluka chemical companies. Melting points were determined with a Branstead Electrothermal model 9200 apparatus and are uncorrected. IR spectra were recorded on a Perkin Elmer RX 1 Fourier transform infrared spectrometer. The ^{1}H and ^{13}C NMR spectra were recorded in DMSO-d_6 and $CDCl_3$ on Bruker Avance 300 MHz spectrometers. Elemental analyses were carried out by a Perkin Elmer 2400 series II CHN/O analyzer.

Typical experimental procedure. *Compounds $II_{a,b}$.* To a solution of the appropriate diamine $\mathbf{I_{a,b}}$ (Scheme 1) (10 mmoles) and triethylamine (22 mmoles) in DMSO (10 mL), were added chloroacetyl chloride (22 mmoles) and stirred for 2 h at room temperature. After completion of the reaction (TLC), water (50 mL) was added to solution, precipitate formed, filtrated, and was washed with water (50 mL) and recrystallized from DMSO and water (1:1) to give pure dichlorodiamide ($\mathbf{II_{a,b}}$).

5,5′-Methylene-bis(2-chloroacetamidothiazole) (II_a). Yield 67%, decomposed above 300 °C; IR (KBr): 3431, 3187, 3052, 2961, 2946, 1683, 773 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6); δ 4.28 (s, 2H), 4.34 (s, 4H), 7.32 (s, 2H), 12.39 (s, 2H, exchangeable with D_2O) ppm; ^{13}C NMR (300 MHz, DMSO-d_6); δ 23.75, 42.71, 132.03, 135.60, 157.25, 165.71 ppm; Anal. calcd. for $C_{11}H_{10}Cl_2N_4O_2S_2$: C, 36.17; H, 2.76, N, 15.34. Found: C, 36.08; H, 2.65; N, 15.74.

Bis(4-methyl-2-chloroacetamidothiazole)sulfide (II_b). Yield 73%, decomposed above 290°C; IR (KBr): 3194, 3061, 2989, 1676, 1267, 808 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6); δ 2.36 (s, 6H), 4.31 (s, 4H), 12.64 (s, 2H, exchangeable with D_2O) ppm; ^{13}C NMR (300 MHz, DMSO-d_6); δ 15.25, 42.14, 115.87, 151.46, 157.78, 165.41 ppm; Anal. calcd. for $C_{12}H_{12}Cl_2N_4O_2S_3$: C, 35.04; H, 2.94, N, 13.62. Found: C, 35.17; H, 2.90; N, 13.73.

Compounds IV_{a-c} (carbamodithioate salts). To a mixture of 1.2 mL (20 mmoles) of CS_2 and 20 mmoles of base (triethylamine or NaOH) in solvent (diethylether or ethanol when NaOH was used). The amine was added very slowly. After 2 h, solvent evaporated to afford a precipitate which was washed with ether to give carbamodithioate salts ($\mathbf{IV_{a-c}}$).

Compounds V_{a-f}. A mixture of **II** (1 mmol) and **IV** (3 mmoles) in DMF (5 mL) was stirred at room temperature for 6 h and then added water (10 mL) to the solution, precipitate formed, filtrated, and washed with water (50 mL). The precipitate was recrystallized from chloroform and petroleum ether (1:3).

5,5′-Methylene-bis[N-(1-oxoethyl diethylamine-2-carbamodithioate)-2-aminothiazole] (V_a). Brownish solid; Yield 75%, mp 186-188°C; IR (KBr): 3179, 3044, 2974, 2932, 1688, 1552, 1300, 1271 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$); δ 1.26-1.34 (m, 12H), 3.76 (q, J = 7.1 Hz, 4H), 4.05 (q, J = 7.1 Hz, 4H), 4.2 (s, 2H), 4.32 (s, 4H), 7.27 (s, 2H), 11.07 (s, b, 2H) ppm; ^{13}C NMR (300 MHz, $CDCl_3$); δ 11.49, 12.50, 24.27, 39.52, 47.35, 50.71, 130.81, 134.89, 157.38, 166.33, 193.43 ppm; Anal. calcd. for $C_{21}H_{30}N_6O_2S_6$: C, 42.69; H, 5.12, N, 14.22. Found: C, 42.55; H, 5.10; N, 14.56.

5,5′-Methylene-bis[N-(1-oxoethyl piperidine-2-carbamodithioate)-2-aminothiazole] (V_b). Light brown solid; Yield 80%, mp 212-215 °C; IR (KBr): 3170, 3044, 2937, 2856, 1684, 1551, 1554, 1314, 1242, 1228 cm^{-1}; ^{1}HNMR (300 MHz, $CDCl_3$); δ 1.64-1.73 (m, 12H), 3.89 (s, b, 4H), 4.20 (s, b, 2H), 4.30 (s, b, 4H), 4.33 (s, 4H), 7.23 (s, 2H), 10.64 (s, 2H) ppm; ^{13}C NMR (300 MHz, $CDCl_3$); δ 24.04, 24.31, 25.45, 26.06, 39.22, 51.99, 54.34, 130.50, 134.82, 157.06, 165.80, 192.68 ppm; Anal. calcd. for $C_{23}H_{30}N_6O_2S_6$: C, 44.92; H, 4.92, N, 13.67. Found: C, 44.81; H, 4.85; N, 13.79.

5,5′-Methylene-bis[N-(1-oxoethyl morpholine-2-carbamodithioate)-2-aminothiazole] (V_c). Light brown solid; Yield 71%, mp 270–271°C; IR (KBr): 3153, 3039, 2964, 2916, 1659, 1559, 1529, 1315, 1270 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6); δ 3.66 (s, b, 8H), 3.78 (s, b, 4H), 4.15 (s, b, 4H), 4.24 (s, 2H), 4.32 (s, 4H), 7.26 (s, 2H), 12.21 (s, 2H) ppm; ^{13}C NMR (300 MHz, DMSO-d_6); δ 23.16, 40.35, 50.35, 51.26, 65.54, 65.48, 130.53, 134.83, 157.02, 165.64, 194.63 ppm; Anal. calcd. for $C_{21}H_{26}N_6O_4S_6$: C, 40.63; H, 4.23, N, 13.85. Found: C, 40.63; H, 4.05; N, 13.77.

Bis[N-(1-oxoethyl diethylamine-2-carbamodithioate)-4-methyl-2-chloroacetamidothi-azole)sulfide (V_d). Dark brown solid; Yield 97%, mp 79–80°C; IR (KBr): 3158, 2974, 2932, 1688, 1532, 1299, 1270 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$); δ 1.28-1.30 (m, 12H), 2.44 (s, 6H), 3.73 (q, J = 6.6 Hz, 4H), 4.02 (q, J = 6.19 Hz, 4H), 4.35 (s, 4H), 10.29 (s, 2H) ppm; ^{13}C NMR (300 MHz, $CDCl_3$); δ 11.49, 12.49, 15.59, 38.44, 47.41, 50.91, 117.75, 151.77, 157.45, 166.76,

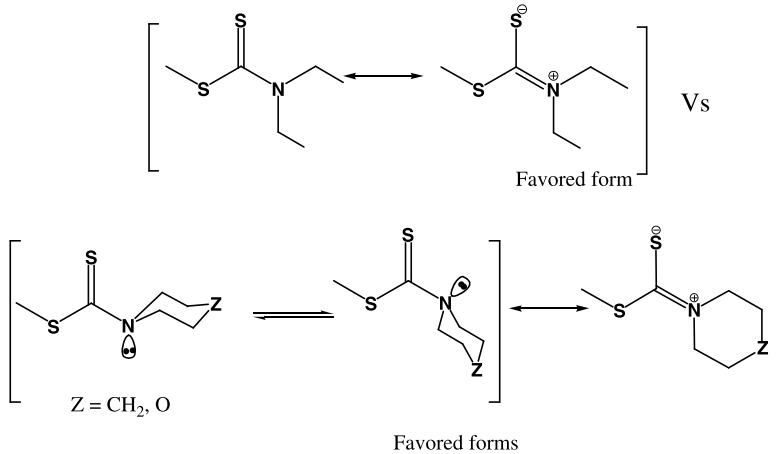


Figure 4. Favored forms for $\mathbf{V_{a-f}}$.

193.31 ppm; Anal. calcd. for $C_{22}H_{32}N_6O_2S_7$: C, 41.48; H, 5.06, N, 13.19. Found: C, 42.52; H, 5.21; N, 13.01.

Bis[N-(1-oxoethyl piperidine-2-carbamodithioate)-4-methyl-2-chloroacetamidothiazo- le)sulfide (V_e). Dark brown solid; Yield 89%, mp 98–100°C; IR (KBr): 3160, 2938, 2855, 1690, 1665, 1533, 1299, 1242 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$); δ 1.72 (s, b, 12H), 2.45 (s, 6H), 3.86 (s, b, 4H), 4.28 (s, b, 4H), 4.38 (s, 4H), 10.26 (s, b, 2H) ppm; ^{13}CNMR (300 MHz, $CDCl_3$); δ 15.53, 23.95, 24.15, 25.37, 39.03, 51.93, 54.28, 117.89, 151.73, 157.45, 166.64, 193.02 ppm; Anal. calcd. for $C_{24}H_{32}N_6O_2S_7$: C, 43.61; H, 4.88; N, 12.71. Found: C, 42.69; H, 4.94; N, 12.65.

Bis[N-(1-oxoethyl morpholine-2-carbamodithioate)-4-methyl-2-chloroacetamidothia- zole)sulfide (V_f). Dark brown solid; Yield 92%, mp 186–187°C; IR (KBr): 3192, 3044, 2964, 1689, 1538, 1301, 1268 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$); δ 2.45 (s, 6H), 3.79 (s, b, 8H), 3.93 (s, b, 4H), 4.31 (s, b, 8H), 10.05 (s, b, 2H) ppm; ^{13}C NMR (300 MHz, $CDCl_3$); δ 15.56, 38.77, 50.83, 52.56, 66.02, 66.34, 118.00, 151.80, 157.36, 166.18, 195.07 ppm; Anal. calcd. for $C_{22}H_{28}N_6O_4S_7$: C, 39.74; H, 4.24; N, 12.26. Found: C, 39.63; H, 4.24; N12.92.

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