© 1984 by: Schweizerische Chemische Gesellschaft, Basel,
Société suisse de chimie, Bâle – Società svizzera di chimica, Basilea
ISSN 0018-019X
Nachdruck verboten –Tous droits réservés – Printed by Birkhäuser AG, Basel, Switzerland
Erscheint 9mal jährlich – Paraît 9 fois par an

195. Studies on the Stereochemistry of 2-(Nitromethylidene)-Heterocycles¹)²)

by **Srinivasachari Rajappa** and **Kuppuswamy Nagarajan**
Hindustan *Ciba Geigy* Ltd., Research Centre, Goregaon, Bombay 400063, India,

Kailasam Venkatesan and **Nirupa Kamath**
Department of Organic Chemistry, Indian Institute of Science, Bangalore 560012, India,

Vapanjeri Madabhusi Padmanabhan
Neutron Physics Division, Bhabha Atomic Research Centre, Bombay 400080, India,

and **Wolfgang von Philipsborn***, **Ban Chin Chen**³) and **Raffaello Müller**
Organisch-chemisches Institut, Universität Zürich, Winterthurerstrasse 190, CH–8057 Zürich

(16.VII.84)

Summary

The ^{1}H-NMR spectra of 2-(nitromethylidene)pyrrolidine (**7**), 1-methyl-2-(nitromethylidene)imidazolidine (**10**) and 3-(nitromethylidene)tetrahydrothiazine (**11**) in $CDCl_3$ and $(CD_3)_2SO$ indicate that these compounds have the intramolecularly H-bonded structures (*Z*)-**7**, (*E*)-**10** and (*Z*)-**11** while the *N*-methyl derivative **8** of **7** is (*E*)-configurated in both solvents. 1-Benzylamino-1-(methylthio)-2-nitroethylene (**13**), an acylic model, has the H-bonded configuration (*E*)-**13** in $CDCl_3$ and in $(CD_3)_2SO$. 2-(Nitromethylidene)thiazolidine (**3**) has the (*E*)-configuration in $CDCl_3$ but exists in $(CD_3)_2SO$ as a mixture of (*Z*)- and (*E*)-isomers with the former predominating. Both species are detected to varying proportions in a mixture of the two solvents. ^{15}N-NMR spectroscopy of **3** ruled out unambiguously the nitronic acid structure **6** and the nitromethyleneimine structure **5**. The *N*-methyl derivative **4** of **3** is (*Z*)-configurated in $(CD_3)_2SO$. Comparison of the olefinic proton shifts of (*Z*)-**3** and (*Z*)-**4** with those of analogues and also of 1,1-bis(methylthio)-2-nitroethylene (**12**) shows decreased conjugation of the lone pair of electrons of the ring N-atom in (*Z*)-**3** and (*Z*)-**4**. This is also supported by ^{13}C-NMR studies. Plausible explanations for the phenomenon are offered by postulating that the ring N-atoms are pyramidal in (*Z*)-**3** and (*Z*)-**4** and planar in other cases or, alternatively, that the conjugated nitroenamine system gets twisted due to steric interaction between the NO_2-group and the ring S-atom. Single-crystal X-ray studies of **3** and **8** show that the former exists in the (*Z*)-configuration and the latter in (*E*)-configuration; the ring N-atom in the former has slightly more pyramidal character than in the latter.

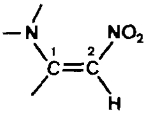
---

¹) Contribution No. 557 from the Research Centre.

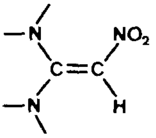
²) Nitroenamines, Part X. For Part IX see [1].

³) Present address: Department of Chemistry, University of Florida, Gainesville, FL 32611 (USA).

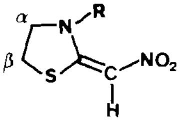
1. Introduction. – In our earlier reports on the ^{1}H-NMR spectra of 1-aminocycloalkenes [2], 1-amino-2-nitro- (**1**), and 1,1-diamino-2-nitroethylenes (**2**) [3], we have established a correlation between the chemical shifts of the *H*–C(2) and C(2) nuclei with the reactivities of the enamines. Parallel studies on the ^{13}C [4] and ^{15}N [5] chemical shifts of 1-aminocycloalkenes largely corroborated our findings. In an extension of our investigations to the ^{1}H- and ^{13}C-NMR spectra of 2-(nitromethylidene)-heterocycles **3**, **4**, **7**–**11**, and two acyclic nitroethylenes **13** and **14**, we have found solvent-dependent (*E*)→(*Z*) transformation rather uniquely in **3**[4]) and present in this paper results of our enquiry into the causes of the phenomenon. We have also used ^{15}N-NMR spectroscopy to study the nitroenamine-iminonitronic acid tautomerism.



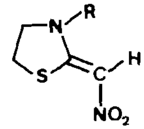
1



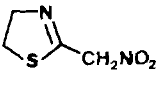
2



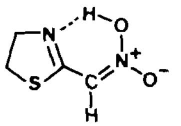
(*E*)-**3** R=H
(*E*)-**4** R=CH₃



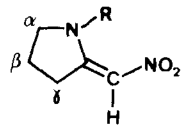
(*Z*)-**3** R=H
(*Z*)-**4** R=CH₃



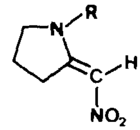
5



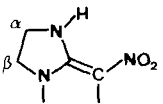
6



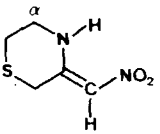
(*Z*)-**7** R=H
(*Z*)-**8** R=CH₃



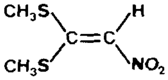
(*E*)-**7** R=H
(*E*)-**8** R=CH₃



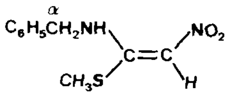
9 R=H
(*E*)-**10** R=CH₃



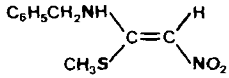
(*Z*)-**11**



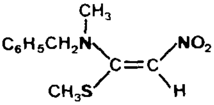
12



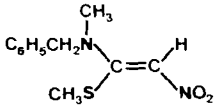
(*E*)-**13**



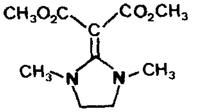
(*Z*)-**13**



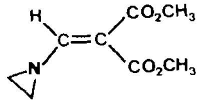
(*E*)-**14**



(*Z*)-**14**



15



16

2. ^{1}H- and ^{13}C-NMR Studies. – The ^{1}H-NMR spectra of the compounds mentioned were run in CDCl₃ and (CD₃)₂SO or in mixtures of the two; the chemical shifts are reported in *Table 1*. Only **3** exhibited a significant change in the chemical shift of the vinyl proton upon changing the solvent from CDCl₃ to (CD₃)₂SO. Other regions of the spectrum also registered some changes.

---

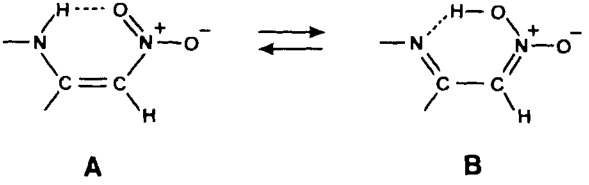
[4]) For use of ^{13}C-NMR in determining the configuration of aliphatic enamines see [6].

Table 1. *^1H Chemical Shifts* (δ, [ppm])

Compound[a]	Solvent	H–C(α)	H–C(β)	H–C(γ)	=CH	Others	Comments
3 [1] [30]	$CDCl_3$	4.03	3.39	–	6.75 (*E*)		100% (*E*)
	$CDCl_3 + (CH_3)_2SO$ (3:1)	4.02 (*E*)	3.40 (*E*)	–	6.69 (*E*)	9.80 (NH)	(*Z*)/(*E*) = 1:1
		3.83 (*Z*)	3.21 (*Z*)		7.16 (*Z*)	8.89	
	$CDCl_3 + (CD_3)_2SO$ (1:1)	4.00	3.39	–	6.70	9.84 (NH)	(*Z*)/(*E*) = 3:2
		3.82	3.21	–	7.13	8.96	
	$CDCl_3 + (CD_3)_2SO$ (1:3)	3.97	3.39	–	6.74	9.87 (NH)	(*Z*)/(*E*) = 2:1
		3.80	3.21	–	7.11	9.02	
	$(CD_3)_2SO$	3.86	3.28	–	6.75	9.70 (NH)	(*Z*)/(*E*) = 4:1
					7.07	8.92	
	CD_3COCD_3	4.12	3.49	–	6.72		(*Z*)/(*E*) = 1:3
		3.91	3.29	–	7.18		
	Dioxane	–	–	–	6.70		100% (*E*)
4 [31]	$(CD_3)_2SO$	3.92	3.20	–	7.15	3.0 (NMe)	100% (*Z*)
7 [32]	$CDCl_3$	3.77	2.13	2.77	6.65	9.33 (NH)	100% (*Z*)
	$(CD_3)_2SO$	3.62	1.95	2.70	6.58	9.67 (NH)	100% (*Z*)
8 [33]	$CDCl_3$	3.60	2.08	3.42	6.62	2.92 (NMe)	100% (*E*)
	$(CD_3)_2SO$	3.58	1.93	3.30	6.60	2.88 (NMe)	100% (*E*)
9 [34]	$CDCl_3 + (CD_3)_2SO$ (9:1)	3.75	3.75	–	6.61	8.21 (NH)	[b]
	$(CD_3)_2SO$	3.70	3.70	–	6.47	8.42 (NH)	
10 [35]	$CDCl_3$	3.75	3.75	–	6.55	8.53 (NH) 2.87 (NMe)	100% (*E*)
	$(CD_3)_2SO$	3.57	3.57	–	6.53	8.67 (NH) 2.78 (NMe)	100% (*E*)
11[c]	$CDCl_3$	3.78	3.05	–	6.67	10.2 (NH) 3.30 (SCH_2)	100% (*Z*)
	$(CD_3)_2SO$	3.63	2.95	–	6.70	10.12 (NH) 3.37 (SCH_2)	100% (*Z*)
12 [34]	$CDCl_3$	–	–	–	7.12	2.55 (SMe)	
13 [8]	$CDCl_3$	4.63 (*d*, $J = 6$ Hz)	–	–	6.60	2.44 (SMe)	100% (*E*)
	$CDCl_3 + (CD_3)_2SO$ (1:1)	4.68 (*d*)	–	–	6.62	2.49 (SMe)	100% (*E*)
	$(CD_3)_2SO$	4.71 (*d*)	–	–	6.72	2.50 (SMe)	100% (*E*)
14	$CDCl_3$	4.75	–	–	6.77	2.47 (SMe) 3.07 (NMe)	
	$(CD_3)_2SO$	4.82	–	–	6.83	2.45 (SMe) 3.00 (NMe)	

[a] References refer to the syntheses of the compounds. [b] Not soluble in $CDCl_3$ alone. [c] Prepared from the corresponding iminoether [36] and nitromethane, m.p. 98–100°.

Scheme



Before an explanation can be sought for these changes on the basis of (*E*)→(*Z*) isomerism, we considered the possibility of **3** existing as **5** or **6** in $(CD_3)_2SO$. The absence of a two-proton singlet for a CH_2-group readily ruled out **5**. Compound **6** was also rejected for several reasons. Compounds **3** and **6** are related to each other by a nitroenamine-iminonitronic acid tautomerism *(Scheme)*. The nitroenamine with a free NH-group would have structures with intramolecular H-bonding in solvents like $CDCl_3$ with a low dielectric constant. This has been shown to be the case with 1-(*tert*-butylamino)-2-nitro-1-propene from chemical-shift considerations [7] and 1-anilino-1-(methylthio)-2-nitroethylene from NOE experiments [8]. The IR spectra of **3** and **7** in $CHCl_3$ in fact showed a highly chelated NH or OH absorption, which both **A** and **B** would possess. The latter could be ruled out with certainty in the case of **11** and **13** because the α-protons exhibited an unmistakable coupling with N*H* both in $CDCl_3$ and in $(CD_3)_2SO$ which was suppressed by addition of D_2O. Since the chemical shifts of the vinylic proton in compounds **3**, **7** and **9** in $CDCl_3$ were comparable to that of in **11**, by extrapolation, nitronic-acid structures could be ruled out for these. However, in the ^1H-NMR spectra of these compounds, we could not detect any coupling of the α-protons with the N*H*-proton. We tentatively ascribe this to an unfavourable dihedral angle for coupling in these cases. In this context, such a coupling is not apparent in 2-pyrrolidine [9], and in cyclopentene the coupling of the vinylic with the alicyclic proton is 0.5 Hz [10]. In $CDCl_3$-solution, one can thus assign the intramolecularly H-bonded nitroenamine structure with the (*Z*)-configuration to **7** and **11**, and the (*E*)-configuration to **3**, **10** and **13**. The nitronic-acid structure **6** for **3** was further firmly ruled out by detailed ^{15}N-NMR and X-ray studies *(vide infra)*.

Comparison of the ^1H-NMR spectra of **7** and **8** in $CDCl_3$ shows a pronounced deshielding of the γ-protons in the latter ($\Delta\delta = 0.65$ ppm). Since **7** was deduced to have the H-bonded (*Z*)-configuration, **8** must exist in the (*E*)-configuration in $CDCl_3$. This has been confirmed by X-ray studies *(vide infra)*. The situation is similar in $(CD_3)_2SO$. The chemical shifts of the vinylic proton in (*Z*)-**7** (6.65 ppm in $CDCl_3$) and (*E*)-**8** (6.62 ppm) are, however, not significantly different. This has a parallel in the case of ethyl β-(methylamino)crotonate wherein the chemical shifts of the olefinic proton have been observed to differ only by 0.1 ppm for the (*E*)- and (*Z*)-isomers in $CDCl_3$. In $(CD_3)_2SO$, they have identical chemical shifts [11]. It is clear that in such molecules an (*E*)/(*Z*)-change does not necessarily have to generate differences in the δ-values of their vinylic protons.

For compound **9**, the question of (*E*)→(*Z*) isomerisation does not arise. In $CDCl_3$, **10** exists almost certainly in the (*E*)-configuration owing to the energy gained by steric release of the $N{-}CH_3\cdots NO_2$ interaction ((*Z*)-isomer) and intramolecular H-bonding. The same geometry perhaps persists in $(CD_3)_2SO$ since there is no deshielding of the CH_3-group. For the same reasons, **11** has the (*Z*)-configuration in both solvents.

The ^1H-NMR spectrum of **13** in $CDCl_3$ showed only one species with the vinyl proton as a singlet at 6.60, the benzylic CH_2-protons as a doublet at 4.63 and the S–C*H*$_3$-group as a singlet at 2.44 ppm. The ^{13}C-NMR spectrum in the same solvent gave rise to only one set of signals, confirming the presence of a single species. This, together with the facts mentioned earlier, indicated the (*E*)-configuration for **13**. The same species persists in $(CD_3)_2SO$ alone or mixed with $CDCl_3$. There was no evidence for the presence of (*Z*)-**13**. Compound **14**, the *N*-methyl derivative of **13**, exists as only *one* species in the two solvents, probably (*Z*)-**14**.

We can now consider the interesting solvent-dependent behaviour of **3**. We have argued earlier that in $CDCl_3$, **3** exists as a single species, the (*E*)-isomer with intramolecular H-bonding. In mixtures of $CDCl_3$ and $(CD_3)_2SO$, two species were simultaneously observed, with two distinct sets of signals arising for the three types of C-bound protons and the N*H*-proton, the most explicit signals being due to the vinyl protons at about 7.16–7.11 and 6.69–6.74 ppm. The intensity of the former (and associated high-field multiplets) increased at the expense of the latter with increasing proportions of $(CD_3)_2SO$. In freshly prepared solution of **3** in some samples of 100% $(CD_3)_2SO$, we had a single signal for the vinylic proton at 7.02 ppm (*cf.* 6.75 for (*E*)-**3** in $CDCl_3$) as a slightly broadened singlet. This was recognized as being due probably to a rapidly equilibrating mixture of (*Z*)-**3** and (*E*)-**3** with the former predominating, since upon keeping the solution for some time, the spectrum displayed two separate broadened singlets for the olefinic proton, one at 7.07 ((*Z*)-**3**) and the other at 6.75 ppm ((*E*)-**3**) in the approximate ratio of 3–4:1. In solutions of **3** in some other samples of $(CD_3)_2SO$, the olefinic signals displayed an intermediate equilibrium composition. All these spectra showed two broadened triplet signals in the CH_2-region, whereas explicit and partially overlapping signals for the two species were seen in mixtures of $CDCl_3$ and $(CD_3)_2SO$[5]. Other possibilities such as **5** and **6** have been ruled out already for the new species showing the olefinic signal at 7.07 ppm. The higher polarity of $(CD_3)_2SO$ must aid the disruption of the intramolecular H-bonding in (*E*)-**3** in favour of intermolecular bonding. The isomers (*Z*)-**3** and (*E*)-**3** were present in the ratio of 1:3 in $(CD_3)_2CO$ with a dielectric constant between those of $CDCl_3$ and $(CD_3)_2SO$; predictably in dioxane, with a low dielectric constant, only the (*E*)-isomer was visible. Compound **4** was not available to us, but the ^1H-NMR spectrum in $(CD_3)_2SO$[6]) showed the olefinic proton to have about the same chemical shift (7.15 ppm) as **3**. It is quite likely that **3** exists in the (*Z*)-configuration in this solvent.

While solvent-dependent (*E*)/(*Z*)-isomerisation of enamines is known [7], **3** presents an interesting case for two reasons: first, (*Z*)-**3** (and (*Z*)-**4**) show a more deshielded olefinic proton (less enaminic) in the ^1H-NMR spectrum compared to (*E*)-**8** which has the same geometry (> N- *trans* to NO_2); second, **3** alone exhibits (*E*)/(*Z*)-isomerism while similar compounds like **7**, **10** and **11** and the acyclic analogues **13** and **14** do not. With respect to the first point, one must consider the contribution, if any, of the S-atom in **3** and **4**. Interestingly, the chemical shifts of the vinyl proton in 1-nitropropene (7.0 ppm) [12] and the bis(methylthio) compound **12** (7.12 ppm) are about the

---

[5]) This phenomenon was also noted in the ^{13}C-NMR spectrum. We feel that differences in moisture content may influence the equilibrium and the rate of exchange.

[6]) We thank Dr. *J. E. Powell*, *Shell* Development Co., California, for the spectrum.

same, indicating that the S-atom has little donor effect in this case, a manifestation of reversed polarity [13]. Furthermore, the *ortho-* and *para-*protons of thioanisole do not show any upfield shift relative to benzene [14]. Thus, actually compared to the situation in compounds **7**–**11** and **13** and **14** the lone pair of electrons on the N-atom in (*Z*)-**3** and (*Z*)-**4** has decreased interaction with the double bond. One explanation for this could be that owing to steric interference between the S-atom and the NO_2-group, the double bond in (*Z*)-**3** and (*Z*)-**4** gets 'twisted'; such twisting has been postulated for **15** [15]. Although the steric requirement of an S-atom is less than that of a CH_2-group [16], after an inspection of CPK space filling models it is clear that there is considerable strain in the 2-methylenethiazolidine ring, but also that the steric interaction between the NO_2-group and the S-atom is more severe than between the NO_2-group and the two CH_2-H-atoms. This is so since the O-atom of the NO_2-group can assume a staggered conformation relative to the two γ-CH_2-H-atoms, which is not possible in the sulfur case. On this basis, (*Z*)-**4** may have a more twisted double bond than (*E*)-**8**. An alternative or additional explanation would be that the N-atom in (*Z*)-**3** and (*Z*)-**4** exists in a pyramidal state, with the lone pair unable to conjugate effectively with the π-electrons of the double bond. Such a proposal has been made for the N-atom of the aziridine ring in **16** [17]. *Dreiding* models indicate that the strain introduced in a thiazolidine ring having an sp^2-hybridized C(2)-atom, by the small valence angle of an S-atom, is relieved better by having a pyramidal rather than a planar N-atom. In the penicillin molecule, it is known that the N-atom is pyramidal unlike in the 'naked' β-lactam [18]. Some simple enamines have also been shown to have a pyramidal N-atom in the solid state [19].

Table 2. *^{13}C Chemical Shifts* (δ, [ppm])

Compound	Solvent	C(α)	C(β)	C(γ)	=C(H)	$\overset{\vert}{-C=}$	Others
3	$CDCl_3 + (CD_3)_2SO$	48.4 (*Z*) 50.9 (*E*)	29.2	–	108.2 (*Z*) 104.4 (*E*)	169.8 (*Z*) 165.3 (*E*)	
	$(CD_3)_2SO$	49.6	29.6		107.0	168.9	
7	$CDCl_3 + (CD_3)_2SO$	47.0	18.8	29.8	103.5 (*Z*)	161.0	
8	$(CD_3)_2SO$	55.6	20.0	34.3	108.1 (*E*)	164.4	33.7 (NMe)
9	$CDCl_3 + (CD_3)_2SO$	43.2	43.2	–	96.1 (*E*)	160.6	
13	$CDCl_3$	48.5	–	–	107.0 (*E*)	[a])	14.6 (SMe)
	$(CD_3)_2SO$	47.5	–	–	106.7 (*E*)	164.7	13.9 (SMe)
14	$CDCl_3$	59.3			113.3 (*Z*?)	166.7	17.9 (SMe) 41.9 (NMe)

[a]) Not observed.

The decreased interaction of the N-atom with the double bond in (*Z*)-**3** is supported by the ^{13}C-NMR spectral data (*Table 2*). The spectrum of **3** could not be run in $CDCl_3$ alone, but a study of the spectrum in $(CD_3)_2SO$ and in a $CDCl_3/(CD_3)_2SO$ mixture enabled us to assign the signals in (*E*)-**3** and (*Z*)-**3** using relative intensities of proton signals as a guideline. The data show that in (*Z*)-**3** the olefinic C-atoms are deshielded, the α-C-atom is shielded and the β-C-atom unaffected compared to the situation in (*E*)-**3**.

In (*E*)-**3**, but not (*Z*)-**3**, the N-atom may be forced to be nearly planar to permit H-bonding, with a consequent upfield shift of the olefinic proton. However, the net energy difference between the (*E*)-isomer with a planar N-atom and the (*Z*)-isomer with a pyramidal N-atom must be small enough to allow a solvent like $(CD_3)_2SO$ to disrupt the former in favour of the latter. A possible explanation for the second point raised earlier would be that in the case of **7**, **10**, **11** and **13** the H-bonded structures are considerably more stable than the alternative ones with NH and NO_2 in a *trans*-relation and are, therefore, unperturbed by solvents of high dielectric constant[7]).

3. ^{15}N-NMR Studies of 3. – In a carefully dried solvent mixture of $(CD_3)_2SO/CDCl_3$ (1:2, v/v) at 25°, 40.5 MHz (9.4 T), and under conditions of gated ^{1}H-decoupling, **3** shows two ^{15}N-signals of comparable intensities at –264.1 and –275.4 ppm. The signals are inverted, *i.e.* NOE-enhanced, and their chemical shifts are in very good agreement with enaminic C=C–NH N-atoms [5] [20]. These signals support the conclusions drawn from the ^{1}H-NMR spectrum in the same solvent mixture (*cf. Table 1*) and prove the presence of (*Z*)-**3** and (*E*)-**3**. While signals for the NO_2-group did not appear under these experimental conditions, they were observed, however, when inverse-gated decoupling for NOE suppression was applied, as two resonances of comparable intensities at –11.7 and –11.3 ppm (29°), typical shielding values for NO_2-groups [21]. In $(CD_3)_2SO$-solution at 20.3 MHz one NO_2-signal at –11.0 ppm and one NH-signal at –271 ppm were observed allowing an assignment to isomer (*Z*)-**3**, the major component (80%) in this solvent.

It is important to note that signals for a biligant N-atom (–N=), as required for the nitronic-acid form **6** or the nitromethyleneimine **5**, have never been observed in the expected range between –60 and –120 ppm. This result rules out structures **5** and **6** and confirms the enaminic structure **3**.

4. Discussion of X-Ray Structure Analyses. – The X-ray data of **3** (*Fig. 1, Tables 3–6*) show (*Z*)-configuration, and those of compound **8** (*Fig. 2, Tables 7–9*) show (*E*)-configuration in the solid state. The former is preserved to the extent of nearly 80% in $(CD_3)_2SO$-solution; but evidently the switchover to (*E*)-**3** is very fast and complete when dissolved in $CDCl_3$, because NMR spectra run within minutes of dissolution show no detectable level of (*Z*)-**3**.

Data on **3** and **8** show that in both the conformation of the five-membered ring is essentially the same with C_2-symmetry passing through C(2) and the midpoint of the C(4)–C(5) bond (*Tables 5* and *9*). In **3**, the plane through C(4), C(2) and H(1) shows N(3) to be off by –0.153 Å. This is significant, although the position of H(1) is less precisely determined than that of the other atoms. A more reliable indication of pyramidal character is obtained from the fact that from the plane through C(4), N(3) and C(2), H(1) is off by 0.372 Å. In **8**, from the plane through C(5), C(2) and C(6), N(1) is off by –0.074 Å. It is difficult to decide whether in fact there is significantly more pyramidality at N(3) in **3** compared to N(1) in **8**, although this would explain qualitati-

---

[7]) It can be argued that in the case of **7**, **10**, **11**, and **13**, diastereomeric isomers are indeed formed in $(CD_3)_2SO$ but are not perceived because chemical shifts of olefinic and other protons are totally or almost completely coincidental. This can be ruled out by the fact that their ^{13}C-NMR spectra (more sensitive to (*E*)/(*Z*)-isomerism) in mixtures of $CDCl_3$ and $(CD_3)_2SO$ showed only one set of signals and thus the presence of only one species.

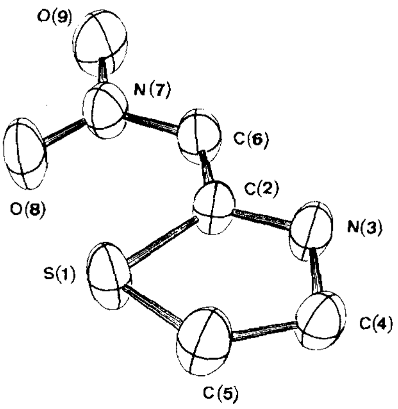


Fig. 1. *A perspective view of the molecule* **3** *viewed down* 'a'*-axis*

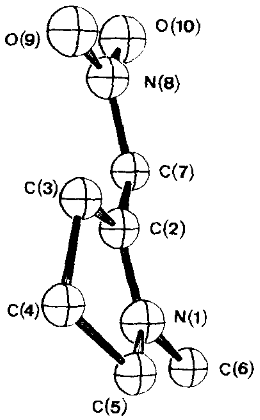


Fig. 2. *A perspective view of the molecule* **8** *viewed down* 'a'*-axis*

vely the ^{1}H-NMR observations (see above). In **3**, C(6) is essentially in the plane through S, C(2) and N(3) while in **8**, C(7) is out of the plane through N(1), C(2) and C(3) by about 0.064 Å.

In **3**, the C(2)=C(6) bond (1.405(5) Å) and in **8** the C(2)=C(7) bond (1.357(8) Å) are both significantly longer than the normal C=C bond of ethylene (1.336(2) Å) [22] [23] indicating that there is some degree of delocalization. The lengths of the C(2)–N(3) (1.317(4) Å) and C(6)–N(7) (1.342(5) Å) bonds in **3** and the N(1)–C(2) (1.318(7) Å) and C(7)–N(8) (1.377(7) Å) bonds in **8** are considerably shorter than the normal values for such bonds [24].

While we have not been able to obtain unequivocal facts to explain the NMR data of **3** in $(CD_3)_2SO$ *vis-a-vis* **8** and other enamines in this study, it does appear possible that in polar solvents N(3) in **3** does indeed have some pyramidal nature. Another difference between the structures of **3** and **8** can be observed in the significant out-of-plane torsion (7°) of the NO_2-group in **3** (*cf. Tables 5* and *9*). If this torsion, reflecting the steric interaction between the NO_2-group and the S-atom, persists in the solution structure, an influence on the chemical shift of the olefinic proton in **3** may also be expected.

H-atom positions for **8**, anisotropic temperature factors for **3** and **8**, and structure-factor tables can be obtained from one of the authors on request *(K. V.)*.

We are thankful to Mrs. *S. J. Shenoy* for the synthesis of some enamines. This work has been supported by the *Swiss National Science Foundation*.

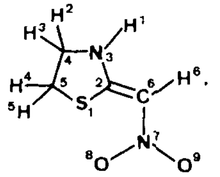
Experimental Part

General. The ^{1}H- and ^{13}C-NMR spectra were measured on a *Bruker WH-90 Fourier*-transform NMR spectrometer using 10–20% w/v solutions at a probe temperature of 30 ± 1°; resonances were measured at 90 MHz for ^{1}H and 22.63 MHz for ^{13}C using the broad-band decoupling technique. Chemical shifts are quoted in ppm downfield from TMS internal reference and ^{13}C-values are correct to ±0.06 ppm. ^{15}N-NMR spectra were measured on a *Varian XL-200* (20.2 MHz) and a *Bruker AM-400-wb* spectrometer (40.5 MHz). Chemical shifts are referred to CH_3NO_2 as an external standard in a capillary.

X-Ray Structure Analysis of **3**. Suitable crystals of the compound were grown from EtOH-solution[8]). *Crystal data:* $C_4H_6N_2O_2S$, space group *C2/c*, $a = 8.821(2)$, $b = 10.884(2)$, $c = 12.870(2)$ Å, $\beta = 95.6(1)°$, $V = 1229.7$ Å^3, $D_x = 1.40$ Mg/m^3 (KI/H_2O), $D_c = 1.44$ Mg/m^3, $Z = 8$, Cu$K\alpha$, $\lambda = 1.5418$ Å. A crystal of size 0.2 × 0.4 × 0.5 mm was used for data collection. Preliminary *Weissenberg* photographs indicated the crystal to be monoclinic, space group either *C2/c* or *Cc*. Intensity measurements and accurate cell parameters were obtained by least squares from the settings of 23 reflections measured on an *Enraf-Nonius CAD-4* automatic four circle diffractometer with Ni-monochromated Cu$K\alpha$ ($\lambda = 1.5418$ Å) radiation. The distribution of E-values showed clearly a centric distribution. 841 reflections were considered observed ($I \geq 3\sigma(I)$) and corrected for *Lorentz* and polarization effects. The structure was solved by direct methods using *MULTAN-80* [25]. All H-atoms were located from a difference *Fourier* synthesis. Weighted anisotropic (isotropic for H-atoms) full matrix least-squares refinement using *SHELX-76* system [26] converged at $R = 0.071$; $W(|F_o|-|F_c|)^2$ minimized where $W = 11.4923/(\sigma^2(F) + 0.0002|F_o|^2)$. The atom H(6) was not refined in the final stages of refinement. The shift/e.s.d. was of the order of ≈ 0.005 Å. A final difference map showed no significant residual electron density.

Final positional and thermal parameters are given in *Table 3*, bond distances and angles in *Table 4*, and the torsion angles in *Table 5*. The crystal structure is stabilized by intermolecular H-bonding of N–H···O. There is also a weak C–H···O interaction *(Table 6)* [27]. Some of the significant intra- and intermolecular contacts (less than 3.5 Å) are also given in *Table 6*. There is a short intramolecular contact S···O of 2.685 Å [28]. *Fig. 1* shows the perspective view of the molecule down '*a*'-axis [28].

Table 3. *X-Ray Structure Analysis of* **3**: *Final (Fractional) Coordinates* (× 10^4) *for Non-H-Atoms and* (× 10^3) *for H-Atoms, Isotropic Equivalent Temperature Factors* (× 10^2) *for Non-H-Atoms of the Form* U_{eq} [Å^2] = $\frac{1}{3}\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*a_i \cdot a_j$, *and Isotropic Temperature Factors* (× 10^2) U_{iso} *for H-Atoms* (E.S.d's in parenthesis)



(*Z*)-**3**

Atom	*x/a*	*y/b*	*z/c*	U_{eq} [Å^2]
S(1)	9178 (1)	1041 (1)	5698 (1)	5.04 (0.05)
C(2)	8608 (4)	2217 (3)	6466 (2)	3.81 (0.10)
N(3)	9148 (3)	3299 (2)	6231 (2)	4.51 (0.09)
C(4)	9989 (4)	3366 (3)	5313 (3)	4.57 (0.12)
C(5)	10391 (5)	2073 (4)	5032 (4)	5.77 (0.15)
C(6)	7672 (4)	2068 (3)	7280 (2)	4.32 (0.11)
N(7)	7179 (4)	961 (2)	7558 (2)	4.50 (0.10)
O(8)	7414 (4)	25 (2)	7051 (2)	6.42 (0.09)
O(9)	6469 (4)	872 (3)	8360 (2)	6.62 (0.11)

	x/a	*y/b*	*z/c*	U_{iso} [Å^2]
H(1)	855 (5)	404 (3)	656 (3)	5.5 (1.1)
H(2)	946 (5)	355 (4)	475 (4)	8.5 (1.6)
H(3)	1082 (13)	307 (10)	573 (8)	34.9 (7.0)
H(4)	1056 (5)	200 (4)	435 (3)	6.3 (1.2)
H(5)	1129 (8)	206 (6)	535 (5)	11.8 (2.2)
H(6)	733 (0)	284 (0)	783 (0)	9.3 (0.0)

---

[8]) A sample crystallized from a large volume of CH_2Cl_2 was found to be identical with the one from EtOH: m.p., mixed m.p., IR (Nujol), NMR (fresh $(CD_3)_2SO$ solution).

Table 4. *Bond Lengths* [Å] *and Angles* [°] *for Non-H-Atoms and H-Atoms in* **3** (E.S.d.'s in parenthesis)

S(1)–C(2)	1.722 (3)	N(7)–O(8)	1.239 (4)
C(2)–N(3)	1.317 (4)	N(7)–O(9)	1.263 (4)
N(3)–C(4)	1.457 (4)	N(3)–H(1)	1.08 (4)
C(4)–C(5)	1.504 (5)	C(4)–H(2)	0.85 (4)
S(1)–C(5)	1.823 (4)	C(4)–H(3)	0.93 (9)
C(2)–C(6)	1.405 (5)	C(5)–H(4)	0.91 (4)
C(6)–N(7)	1.342 (5)	C(5)–H(5)	0.85 (6)
		C(6)–H(6)	1.15 (3)
C(5)–S(1)–C(2)	91.7 (2)	H(1)–N(3)–C(2)	112 (2)
S(1)–C(2)–N(3)	113.6 (2)	H(1)–N(3)–C(4)	126 (2)
C(2)–N(3)–C(4)	117.1 (3)	H(2)–C(4)–N(3)	115 (4)
N(3)–C(4)–C(5)	107.4 (3)	H(2)–C(4)–C(5)	98 (3)
C(4)–C(5)–S(1)	107.4 (3)	H(3)–C(4)–N(3)	87 (7)
C(2)–C(6)–N(7)	122.2 (3)	H(3)–C(4)–C(5)	68 (7)
C(6)–N(7)–O(8)	121.5 (3)	H(2)–C(4)–H(3)	157 (8)
C(6)–N(7)–O(9)	119.2 (3)	H(4)–C(5)–C(4)	112 (3)
O(8)–N(7)–O(9)	119.3 (3)	H(4)–C(5)–S(1)	124 (3)
N(3)–C(2)–C(6)	121.8 (3)	H(5)–C(5)–S(1)	109 (4)
S(1)–C(2)–C(6)	124.6 (2)	H(5)–C(5)–C(4)	97 (4)
		H(5)–C(5)–H(4)	103 (5)
		H(6)–C(6)–C(2)	126 (3)
		H(6)–C(6)–N(7)	112 (3)

Table 5. *Some Important Torsion Angles* [°] *in* **3**

C(5)–S(1)–C(2)–N(3)	4.1 (3)	N(3)–C(2)–C(6)–N(7)	−176.6 (3)
S(1)–C(2)–N(3)–C(4)	6.2 (4)	C(2)–C(6)–N(7)–O(8)	−6.5 (5)
C(2)–N(3)–C(4)–C(5)	−15.5 (4)	C(2)–C(6)–N(7)–O(9)	173.0 (3)
N(3)–C(4)–C(5)–S(1)	16.9 (4)	C(5)–S(1)–C(2)–C(6)	−175.2 (3)
C(4)–C(5)–S(1)–C(2)	−12.3 (3)	C(6)–C(2)–N(3)–C(4)	−174.5 (3)
S(1)–C(2)–C(6)–N(7)	2.6 (5)		

Table 6. *H-Bond Parameters in* **3** *and Intramolecular Contact* (< 3.5 Å)

H-Bond	D···A [Å]	H···A [Å]	D–H [Å]	H–D···A [°]	D–H···A [°]	Symmetry code
N(3)–H(1)···O(9)^{I}	2.911 (4)	1.99 (4)	1.08 (4)	26 (2)	141 (3)	I: ½ − x ½ + y ½ − z
C(6)–H(6)···O(8)^{I}	3.331 (4)	2.39 (2)	1.15 (3)	30 (2)	137 (3)	I: ½ − x ½ + y ½ − z

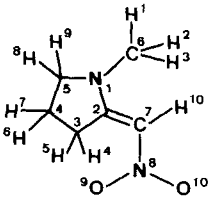
Intramolecular contact

S(1)···O(8) 2.68 (5) [Å]

X-Ray Structure Analysis of **8**. Suitable crystals of the compound were grown from EtOH-solution. The X-ray structure determination is based on the data collected on a three-circle diffractometer designed and constructed at the *Bhabha Atomic Research Centre,* Bombay. *Crystal data:* $C_6H_{10}N_2O_2$, space group, $P2_1/c$, $Z = 4$, $a = 6.023(4)$ Å, $b = 15.851(6)$ Å, $c = 7.447(4)$ Å, $\beta = 106.9(3)°$, $V = 680.2$ Å^3, $D_x = 1.36$ Mg/m^3 (KI/H_2O), $D_c = 1.39$ Mg/m^3, Mo$K\alpha$, $\lambda = 0.7107$ Å.

The study was carried out essentially as on compound **3**. The structure was solved by direct methods using *MULTAN-80* [25]. Refinement of non-H-atoms anisotropically (isotropic for H-atoms) with 809 observed reflections ($I \geq 3\sigma(I)$) using unit weights through *SHELX-76* [26] gave an R-value of 0.1100. The parameter shift/e.s.d. was of the order of ≈ 0.001 Å. A final difference map showed no significant residual electron density.

Final positional and thermal parameters are given in *Table 7*. Bond distances and angles are given in *Table 8* and torsion angles in *Table 9*. A perspective view of the molecule viewed down '*a*' axis is shown in *Fig. 2* [29].



(*E*)-**8**

Table 7. *X-Ray Structure Analysis of* **8**: *Final (Fractional) Coordinates* ($\times 10^4$) *for Non-H-Atoms and Isotropic Equivalent Temperature Factors* ($\times 10^2$) *for Non-H-Atoms of the Form*

U_{eq} [Å^2] $= \frac{1}{3}\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* a_i \cdot a_j$ (E.S.d.'s in parenthesis)

Atom	*x/a*	*y/b*	*z/c*	U_{eq} [Å^2]
N(1)	5390 (9)	−1539 (3)	1795 (7)	5.03 (0.18)
C(2)	5333 (10)	−740 (4)	2264 (8)	4.51 (0.20)
C(3)	7699 (11)	−471 (4)	3469 (9)	5.28 (0.24)
C(4)	8984 (13)	−1313 (5)	3977 (11)	6.36 (0.27)
C(5)	7685 (12)	−1914 (5)	2474 (12)	5.98 (0.28)
C(6)	3588 (14)	−1995 (5)	498 (12)	6.21 (0.28)
C(7)	3398 (10)	−261 (4)	1600 (9)	4.83 (0.21)
N(8)	3338 (9)	578 (3)	2063 (7)	5.18 (0.19)
O(9)	5043 (8)	956 (3)	3067 (7)	6.88 (0.20)
O(10)	1495 (8)	954 (3)	1371 (7)	6.61 (0.18)

Table 8. *Bond Lengths* [Å] *and Angles* [°] *in* **8** (E.S.d.'s in parenthesis)

N(1)–C(2)	1.318 (7)	N(1)–C(6)	1.422 (8)
C(2)–C(3)	1.507 (8)	C(2)–C(7)	1.357 (8)
C(3)–C(4)	1.534 (9)	C(7)–N(8)	1.377 (7)
C(4)–C(5)	1.504 (10)	N(8)–O(9)	1.235 (6)
C(5)–N(1)	1.453 (8)	N(8)–O(10)	1.232 (6)
C(5)–N(1)–C(6)	119.3 (6)	C(2)–C(3)–C(4)	102.9 (6)
C(5)–N(1)–C(2)	113.3 (5)	C(3)–C(4)–C(5)	104.5 (5)
C(6)–N(1)–C(2)	126.5 (6)	C(4)–C(5)–N(1)	103.7 (6)
N(1)–C(2)–C(3)	109.6 (5)	C(2)–C(7)–N(8)	122.1 (6)
N(1)–C(2)–C(7)	121.8 (5)	C(7)–N(8)–O(9)	122.8 (5)
C(3)–C(2)–C(7)	128.4 (6)	C(7)–N(8)–O(10)	116.7 (5)
		O(10)–N(8)–O(9)	120.5 (6)

Table 9. *Some Important Torsion Angles* [°] *in* **8** (E.S.d.'s in parenthesis)

C(5)–N(1)–C(2)–C(3)	2.9 (7)	C(7)–C(2)–C(3)–C(4)	171.7 (7)
C(6)–N(1)–C(2)–C(3)	−172.2 (6)	N(1)–C(2)–C(7)–N(8)	−179.0 (6)
C(5)–N(1)–C(2)–C(7)	173.3 (6)	C(3)–C(2)–C(7)–N(8)	−3.6 (10)
C(6)–N(1)–C(2)–C(7)	4.0 (10)	C(2)–C(3)–C(4)–C(5)	22.0 (7)
C(2)–N(1)–C(5)–C(4)	17.3 (8)	C(3)–C(4)–C(5)–N(1)	−23.7 (7)
C(6)–N(1)–C(5)–C(4)	−172.6 (6)	C(2)–C(7)–N(8)–O(9)	1.9 (10)
N(1)–C(2)–C(3)–C(4)	−12.4 (7)	C(2)–C(7)–N(8)–O(10)	179.6 (6)

REFERENCES

[1] *S. Rajappa & B.G. Advani*, Proc. Indian Acad. Sci. *91*, 463 (1982).

[2] *K. Nagarajan & S. Rajappa*, Tetrahedron Lett. *1969*, 2293.

[3] *S. Rajappa & K. Nagarajan*, J. Chem. Soc., Perkin Trans. 2 *1978*, 912.

[4] *D. Tourwé, G. Van Binst, S.A.G. De Graaf & U.K. Pandit*, Org. Magn. Reson. *7*, 433 (1975).

[5] *W. Schwotzer & W. von Philipsborn*, Helv. Chim. Acta *60*, 1501 (1977).

[6] *R. Stradi, P. Trimarco & A. Vigevani*, J. Chem. Soc., Perkin Trans. 1 *1978*, 1.

[7] *A.I. Fetell & H. Feuer*, J. Org. Chem. *43*, 497 (1978).

[8] *H. Hamberger, H. Reinshagen, G. Schulz & G. Sigmund*, Tetrahedron Lett. *1977*, 3619.

[9] *F.A. Bovey*, 'NMR data tables for organic compounds', Vol. 1, Interscience, New York, 1967, p. 70.

[10] See [9], p. 96.

[11] *A.G. Sánchez, M.T. Aldave & U. Scheidegger*, J. Chem. Soc. (C) *1968*, 2570.

[12] *Yu. V. Baskov, T. Urbànski, M. Witanowski & L. Stefaniak*, Tetrahedron *20*, 1519 (1964).

[13] *B.-Th. Gröbel & D. Seebach*, Synthesis *1977*, 357.

[14] *L.M. Jackman & S. Sternhell*, 'Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry', 2nd edn., Pergamon Press, New York, 1969, p. 202.

[15] *F.P. Colonna, G. Distefano, J. Sandström & U. Sjöstrand*, J. Chem. Soc., Perkin Trans. 2 *1978*, 279; *J. Sandström, U. Sjöstrand & I. Wennerbeck*, J. Am. Chem. Soc. *99*, 4526 (1977).

[16] *W.L.F. Armarego*, 'Stereochemistry of Heterocyclic Compounds', Part 2, Wiley-Interscience, New York, 1977, p. 305.

[17] *R. Osman, A. Zunger & Y. Shvo*, Tetrahedron *34*, 2315 (1978); *R. Osman & Y. Shvo*, ibid. *34*, 2321 (1978).

[18] *I. Ernest, J. Gosteli, C.W. Greengrass, W. Holick, D.E. Jackman, H.R. Pfaendler & R.B. Woodward*, J. Am. Chem. Soc. *100*, 8214 (1978).

[19] *K.L. Brown, L. Damm, J.D. Dunitz, A. Eschenmoser, R. Hobi & C. Kratky*, Helv. Chim. Acta *61*, 3108 (1978).

[20] *L. Kozerski, K. Kamienska-Trela, L. Kania & W. von Philipsborn*, Helv. Chim. Acta *66*, 2113 (1983).

[21] *B.C. Chen, W. von Philipsborn & K. Nagarajan*, Helv. Chim. Acta *66*, 1537 (1983).

[22] *L.S. Bartell, E.A. Roth, C.D. Hollowell, K. Kuchitsu & J.E. Young, Jr.*, J. Chem. Phys. *42*, 2683 (1965).

[23] *K. Kuchitsu*, J. Chem. Phys. *44*, 906 (1966).

[24] International Tables for X-ray Crystallography, Vol. III, Kynoch Press, Birmingham, 1968, p. 276.

[25] *P. Main, S.J. Fiske, S.E. Hull, L. Lessinger, G. Germain, J.P. Declerq & M.M. Woolfson* (1980). MULTAN. A System of computer programs for the automatic solution of crystal structures from X-ray diffractometer data, Univs. of York, England & Louvain, Belgium.

[26] *G.M. Sheldrick*, 'SHELX-76', Program for crystal structure determination, Univ. of Cambridge, England, 1976.

[27] *F.H. Allen, O. Kennard & R. Taylor*, Acc. Chem. Res. *16*, 146 (1983).

[28] *T.R. Lynch, I.P. Mellor & S.C. Nyburg*, Acta Crystallogr., Sect. B *27*, 1948 (1971).

[29] *C.K. Johnson*, 'ORTEP ORNL-3794', Oak Ridge National Laboratory, Tennessee, USA, 1965.

[30] *H. Feuer & J.P. Lawrence*, J. Org. Chem. *37*, 3662 (1972). This compound has been wrongly described as 2-nitromethyl-4,5-dihydrothiazole, Chem. Abstr. *78*, 16129 (1973).

[31] *J.E. Powell* (Shell Oil Co.), U.S. Pat. 4,006,156 (1977).

[32] *A. Etienne & Y. Correia* (Produits Chimiques Péchiney – Saint-Gobain), Brit. Pat. 1,167,809 (1969).

[33] (Société d'Etudes Scientifiques et Industrielles de L'Ile-de-France), Brit. Pat. 1,236,842 (1971).

[34] *R. Gompper & H. Schaefer*, Chem. Ber. *100*, 591 (1967).

[35] *C.H. Tieman, W.D. Kollmeyer & S.A. Roman* (Shell International) Ger. Offen. 2,445,421 (1975).

[36] *S. Rajappa, B.G. Advani & R. Sreenivasan*, Indian J. Chem. *10*, 323 (1972).