Structural Studies on Bio-active Compounds. Part 2.[1] The Solid-state and Solution Conformations of *N*-Methyl-2-nitroethenamine and Related Compounds

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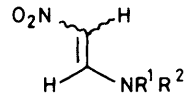
The ^{1}H n.m.r. spectra of *NN*-dimethyl-2-nitroethenamine, *N*-methyl-2-nitroethenamine, and 2-nitroethenamine in several solvents have been analysed. In the case of the monomethyl compound, the proportions of different rotamers about the C=C and C–N bonds are found to be solvent dependent. An *X*-ray crystallographic study of this compound indicates inter- rather than intra-molecular hydrogen bonding in the solid; molecular orbital calculations predict three of the possible four conformers about these bonds to be of similar and much lower energy than the fourth.

As part of a continuing study on analogues of the antitumour agent *N*-methylformamide (**2b**) (NMF), we have prepared a short series of 2-nitroethenamines (**1a**—**c**) for biological evaluation. A previous n.m.r. study undertaken by us[2] has shown (**2b**) to exhibit restricted rotation about the amide C–N bond, as for most amides, owing to delocalisation of the non-bonding pair of electrons on nitrogen into the carbonyl π-bonding system; (**2b**) shows a ratio of rotamers of *ca.* 9:1 *Z*:*E* which is almost independent of solvent. As *NN*-dimethylformamide (**2a**) and formamide (**2c**) can only exist as single 'rotamers' about this bond, it is interesting to speculate as to whether the ability of (**2b**) to change conformation has any bearing on the fact that of compounds (**2a**—**c**) only (**2b**) has significant antitumour activity in murine models,[3] has shown activity against human tumour xenografts and is currently in Phase 2 clinical trial. In this paper, we present the results of our studies on the conformations adopted by the analogous compounds (**1a**—**c**) particularly with reference to the closest analogue of NMF (**2b**), *i.e.* *N*-methyl-2-nitroethenamine (**1b**).

Rajappa[4] has recently reviewed the current state of knowledge concerning the synthesis, utility, and structure of 2-nitroenamines, stating that most examples of this class of compounds exist as the enamine tautomer with only two examples reported[5] to have the 2-nitroimine structure. Our results show that all three 2-nitroenamines (**1a**—**c**) follow the general rule in being true enamines in solution in nonacidic solvents and (**1b**) being so in the solid state.

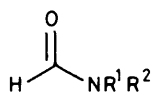
Compounds (**1a**—**c**) were synthesized generally according to known procedures. The dimethylenamine (**1a**) was obtained by condensation of dimethylformamide dimethylacetal with nitromethane.[6] The methylamino (**1b**) and amino (**1c**) compounds were prepared by transamination of *N*-methyl-*N*-phenyl-2-nitroethenamine with methylamine and ammonia, respectively.[7] Repeated recrystallisation of (**1b**) from deuterium oxide gave the N-D species (**1d**).

Two main points can be inferred from the ^{1}H n.m.r. spectra of (**1a**): geometrical isomerism about the olefinic bond and restriction of rotation about the N–C(1) bond. The C(1)H–C(2)H coupling constant is 11 Hz in both $CDCl_3$ and $(CD_3)_2SO$ solution, a value which is of little diagnostic value in determining the stereochemistry about that bond, as noted by Büchi.[8] In $(CD_3)_2SO$, the signals due to the methyl groups appear as sharp singlets at δ 2.85 and 3.20 indicating the non-equivalence reported by Büchi[8] and by Rajappa[9] for this compound. Thus, the charge-separated canonical forms (**I**)—(**III**) of (**1a**) make a contribution, *i.e.* there is significant delocalisation of the non-bonding lone pair at N(1) into the π-system of the remainder of the molecule. In $CDCl_3$, also at



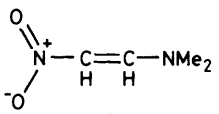
(1)

a; $R^1 = R^2 = Me$
b; $R^1 = Me$, $R^2 = H$
c; $R^1 = R^2 = H$
d; $R^1 = Me$, $R^2 = D$

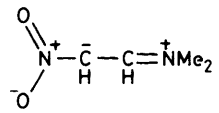


(2)

a; $R^1 = R^2 = Me$
b; $R^1 = Me$, $R^2 = H$
c; $R^1 = R^2 = H$



(I)



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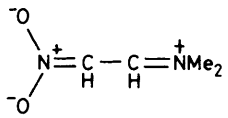

(III)

29 °C, these resonances are significantly broadened, implying that the coalescence temperature is higher in $(CD_3)_2SO$ than in $CDCl_3$. (Mannschreck[10] gives a coalescence temperature of 52 °C in $CDBr_3$.) The origins of this effect are unclear but it may arise from the greater viscosity of dimethyl sulphoxide or from such factors as the dielectric constant or dipole moment of the solvent.

Krowczynski and Kozerski[7] report a 60:40 *Z*:*E* ratio of geometrical isomers about the olefinic bond in (**1b**) in chloroform solution. We observed only one conformer to be present in solution in $CDCl_3$ at 34 °C. The magnitudes of the C(1)H–C(2)H coupling constant (5.5 Hz) and of $J_{C(1)H-NH}$ (14.0 Hz) are consistent with *Z* and *E* configurations respectively. This arrangement is stabilised by an intramolecular hydrogen bond between the NH and the nitro group, which is confirmed by the immutability of the chloroform solution i.r. spectrum upon dilution.

A mixture of three rotamers is observed in $(CD_3)_2SO$ in the ratio 23.5:7.7:68.8, as shown in Table 1. Now, three-quarters of the total population of solute adopt an *E* conformation about C(1)–C(2), reflecting the facility of hydrogen-bonding to solvent. However, of these C(1)–C(2)*E* species, the majority adopt the *Z* arrangement about the C(1)–N bond. Assign-

Table 1. Relative isomer populations of (**1b**) in various solvents

Solvent	C(1)–C(2)*Z*/C(1)–N*E*	C(1)–C(2)*E*/C(1)–N*E*	C(1)–C(2)*E*/C(1)–N*Z*	(**1ba**)	(**1bb**)
$CDCl_3$	100				
$(CD_3)_2SO$	23.5 ± 1.0	7.7 ± 0.7	68.8 ± 1.7		
D_2O	63 ± 3	37 ± 3			
CF_3CO_2H				47.5 ± 0.5	52.5 ± 0.5

Table 2. ^1H N.m.r. data for compounds (**1a—d**)

Compound	Solvent	C(1)–C(2) Stereochemistry	C(1)–N Stereochemistry	Chemical shift δ C(1)H	C(2)H	NH	CH_3
(**1a**)	$CDCl_3$	*E*		8.20 (d, *J* 11 Hz)	6.65 (d, *J* 11 Hz)		2.90br (s) 3.25br (s)
(**1a**)	$(CD_3)_2SO$	*E*		8.30 (d, *J* 11 Hz)	6.80 (d, *J* 11 Hz)		2.85 (s) 3.20 (s)
(**1b**)	$CDCl_3$	*Z*	*E*	6.79 (dd, *J* 14, 5.5 Hz)	6.54 (d, *J* 5.5 Hz)	9.1br	3.21 (d, *J* 5 Hz)
(**1b**)	$(CD_3)_2SO$	*Z*	*E*	7.22 (dd, *J* 15, 6 Hz)	6.48 (d, *J* 6 Hz)	9.4br	3.09 (d, *J* 6 Hz)
(**1b**)	$(CD_3)_2SO$	*E*	*E*	8.29 (d, *J* 10.5 Hz)	6.80 (d, *J* 10.5 Hz)	8.15br	3.03 (d, *J* 4.5 Hz)
(**1b**)	$(CD_3)_2SO$	*E*	*Z*	8.24 (dd, *J* 7.5, 10.5 Hz)	6.82 (d, *J* 10.5 Hz)	8.15br	2.74 (d, *J* 4.5 Hz)
(**1b**)	D_2O	*Z*		7.55	6.81 (d, *J* 6 Hz)		3.28 (s)
(**1b**)	D_2O	*E*		8.51 (d, *J* 10.5 Hz)	7.08 (d, *J* 10.5 Hz)		2.96 (s)
(**1b**)	CF_3CO_2H	Adduct (**1ba**)		5.06 (m)	5.27 (dd, *J* 5.5, 16 Hz) 5.48 (dd, *J* 7, 16 Hz)		3.10 (t, *J* 5.5 Hz)
(**1b**)	CF_3CO_2H	Protonated species (**1bb**)		7.90 (d, *J* 15 Hz)	8.2 (m)	8.2br	3.49 (*J* 5.5 Hz)
(**1c**)	$(CD_3)_2SO$	*Z*		7.20 (m)	6.45 (d, *J* 6 Hz)	8.1br	
(**1c**)	$(CD_3)_2SO$	*E*		6.80br (d, *J* 11 Hz)	8.25 (*J* 11 Hz)	8.1br	
(**1d**)	$(CD_3)_2SO$	*Z*	*E*	7.20 (m)	6.46 (*J* 6 Hz)		3.08 (s)
(**1d**)	$(CD_3)_2SO$	*E*	*E*	8.24 (d, *J* 10 Hz)	6.79 (*J* 10 Hz)		3.02 (s)
(**1d**)	$(CD_3)_2SO$	*E*	*Z*	8.22 (d, *J* 11 Hz)	6.83 (d, *J* 11 Hz)		2.73 (s)

ments of structure are derived from the coupling constants $J_{C(1)H,C(2)H}$ and $J_{C(1)H,NH}$ $J_{C(1)H,C(2)H_2}$ is 5.5 Hz for the *Z* and *ca.* 11 Hz for the *E* isomers about C(1)–C(2); values lower than those generally accepted for olefinic *cis* and *trans* vicinal coupling, owing to reduction of the double bond character in 2-nitroenamines. By analogy, the uncertainty of the stereochemistry of (**1a**) is resolved, the 11 Hz coupling being shown to be *trans*-vicinal $J_{C(1)H,C(2)NH}$. Similarly, having identified *Z* and *E* isomers about C(1)–N giving chemical shifts of δ 2.74 and 3.03 for NCH_3 protons, it is possible to assign the resonances due to the $N(CH_3)_2$ methyl protons in (**1a**) [in $(CD_3)_2SO$ solution] as δ 2.85 for the CH_3 *syn* to C(2) and as δ 3.20 *anti* to C(2). Orientation about C(1)–N was also established using coupling constant information (7.5 and 15 Hz for *Z* and *E*, respectively); Fetell and Feuer[11] give $J_{C(1),NH}$ 14 Hz for an *E*-C–N bond in a related molecule. Hence, of those molecules of (**1b**) that are *E* about C(1)–C(2), the *E*:*Z* ratio about C(1)–N is 1:8.9, a proportion that is remarkably similar to the 1:9 ratio of *E*:*Z* rotamers for the archetypal compound in our antitumour investigations, *N*-methylformamide (**2b**). Perhaps the factors involved are similar for (**1b**) and for (**2b**). In D_2O, however, owing to exchange with the solvent, the C(1)H–NH coupling is not observed and confident assignment of stereochemistry about C(1)–N is not possible. Two isomers about C(1)–C(2) are shown by $J_{C(1)H,C(2)H}$ analysis. The proportion of the *Z* (*i.e.* intramolecularly hydrogen-bonded) isomer is 63%, between the amounts present in chloroform and dimethyl sulphoxide. This reflects, perhaps, a lesser stabilisation of the *E* form (with its hydrogen-bonding to solvent) in water (dipole moment μ 1.85 D)[12] than in the dipolar aprotic dimethyl sulphoxide (μ 3.96 D).[12] Slow hydrolysis is evident in D_2O, a significant amount of products tentatively identified as methylamine and nitroacetaldehyde being present after 1 h at 34 °C.

As it was considered, in view of the D_2O spectra, that addition of D_2O to a $(CD_3)_2SO$ solution of (**1b**) might perturb the equilibria between isomers, the N–D derivative was prepared and its ^1H n.m.r. spectrum in anhydrous $(CD_3)_2SO$ was examined. Analysis of this spectrum served to confirm our assignment of the corresponding (**1b**) spectrum.

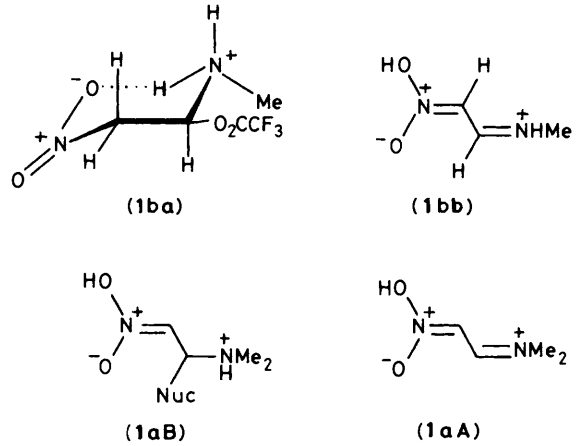

Figure 1. Proposed structures of products of (**1b**) and (**1a**) in trifluoroacetic acid. (**1ba**) and (**1bb**) are shown by n.m.r. in this study. (**1aA**) and (**1aB**) adapted from ref. 8

In trifluoroacetic acid, (**1b**) forms two distinct species in the ratio 47.5:52.5 which we denote as (**1ba**) and (**1bb**) (Figure 1). The spectrum of (**1ba**) contains an ABX system with J_{gem} of the prochiral methylene at C(2) being 16 Hz. The prochirality arises from the adjacent asymmetric centre at C(1) in the adduct (**1ba**). The N–CH_3 resonates as a triplet coupled now to two protons on N(1). Hence we put forward the structure (**1ba**) as representing this adduct. The other species appears simply to be protonated (**1b**) having the structure (**1bb**) with protonation at N(1) followed by tautomerism to give the imine nitronic acid. *E*-Stereochemistry about C(1)–C(2) can be inferred from

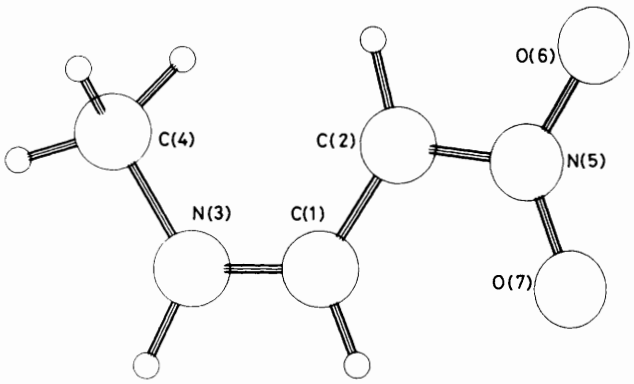

Figure 2. Structure of (**1b**) in the crystal with crystallographic numbering scheme

$J_{C(1)H,C(2)H}$ 15 Hz, clearly a *trans*-coupling constant. Büchi[8] reports the dimethyl compound (**1a**) to be unstable to aqueous acid and both he and Colonna[13] show that (**1a**) reacts with aromatic carbon nucleophiles under acidic conditions. Two intermediates (**1aA**) and (**1aB**), shown in Figure 1, are proposed in ref. 8. Whereas we concur in that (**1b**) does indeed hydrolyse very rapidly in wet trifluoroacetic acid, in anhydrous trifluoroacetic acid in the absence of a good nucleophile we observe the monomethyl analogue of (**1aA**) [*i.e.* (**1bb**)] but not that of (**1aB**). Rather, the nitro tautomer (**1ba**) of the adduct is formed.

The analysis of the i.r. spectra of (**1b**) and its deuterio-analogue (**1d**) is straightforward. In the solid phase as a KBr disc and as Nujol mull, one can observe a hydrogen-bonded N–H stretch band at 3 250 cm^{-1} which is moved to 2 370 cm^{-1} upon deuteriation (wavenumber ratio 1.37:1). A strong band is also observed at 1 615 cm^{-1}, interpretable as having contributions from C=C and C=N bonds. The spectrum in $CHCl_3$ solution was unchanged on dilution confirming the intramolecularly hydrogen-bonded structure determined by ^1H n.m.r. in $CDCl_3$ to be *Z* about C(1)–C(2) and *E* about C(1)–N. The demethyl analogue (**1c**) is virtually insoluble in chloroform; in $(CD_3)_2SO$, the ^1H n.m.r. spectrum shows it to be a mixture of the expected two stereoisomers about C(1)–C(2). The *Z* isomer ($J_{C(1)H,C(2)H}$ 6 Hz) comprises 68% of the mixture and the *E* ($J_{C(1)H,C(2)H}$ 11 Hz) represents 32%.

Crystal Structure of N-*Methyl*-2-*nitroethenamine* (**1b**).—The numbering scheme used in the crystallographic determination is shown in Figure 2. The crystal was grown from ethyl acetate and had dimensions 0.35 × 0.15 × 0.15 mm. The data were collected from an Enraf–Nonius CAD4 diffractometer with monochromated Mo-K_α radiation, λ = 0.710 69 Å.

Crystal data. $C_3H_6N_2O_2$, *M* = 102.09, monoclinic, *a* = 3.915(3), *b* = 12.009(7), *c* = 10.271(7) Å, β = 95.46(6)°, *V* = 480.7 $Å^3$, *Z* = 4, D_m = 1.412(5) g cm^{-3}, D_x = 1.411 g cm^{-3}, *F*(000) = 216.00, μ = 0.78 cm^{-1}, space group $P2_1/c$. Intensity data were collected by the ω–2θ scan technique. The 1 829 reflections were measured for $+h \pm k \pm l$ in the range $2° < \theta < 24°$ and were merged to give 760 independent reflections of which 384 were deemed observed with $F > 3\sigma$. The structure was determined by the EEES direct methods procedure in SHELX.[14] An *E*-map was produced in which all the non-hydrogen atoms were located. After least-squares refinement of positions and isotropic temperature factors, a difference Fourier synthesis located the hydrogen atoms. Further refinement of co-ordinates and anisotropic temperature factors for non-hydrogen atoms, and co-ordinates and isotropic temperature factors for hydrogen atoms, was carried out with SHELX, with the methyl C–H, H ··· H, and H ··· N distances constrained by the DFIX procedure in SHELX. In the final stages of refinement, reflections were weighted according to: $W = k/[\sigma^2(F_o) + g F_o^2] = 1.5164/[\sigma^2(F_o) + 0.000\,157\,F_o^2]$. The final discrepancy indices were $R = 0.0622$ and $R_g = \Sigma[w(|F_o| - |F_c|)^2/wF_o^2]^{\frac{1}{2}} = 0.0490$. No feature on the final difference electron density map exceeded ± 0.23 e$Å^{-3}$.

The structure and numbering scheme[15] are presented in Figure 2 and the atomic co-ordinates and equivalent isotropic temperature factors are listed in Table 3. Anistropic thermal parameters and torsion angles are given in Supplementary Publication No. SUP 56125 (3 pp.).* Bond lengths, bond angles, and selected torsion angles are shown in Tables 4—6,

Table 3. Atom positional parameters (fractional co-ordinates × 10^4 for non-hydrogen atoms; × 10^3 for hydrogen atoms) and equivalent isotropic temperature factors (× 10^3)

Atom	*x*	*y*	*z*	U_{iso}/$Å^2$
C(1)	1 565(17)	1 746(5)	2 765(6)	48(2)
C(2)	3 130(16)	1 302(4)	3 881(5)	42(2)
C(4)	−868(21)	11(5)	1 868(8)	59(3)
N(3)	−208(13)	1 201(4)	1 834(5)	49(2)
N(5)	5 044(14)	1 971(4)	4 764(5)	50(2)
O(6)	6 331(13)	1 541(3)	5 805(4)	69(2)
O(7)	5 501(12)	2 974(3)	4 535(3)	66(2)
H(1)	178(11)	250(4)	261(4)	34(13)
H(2)	312(11)	53(3)	417(4)	32(13)
H(3)	−142(18)	161(4)	108(5)	100(23)
H(4A)	−210(15)	−20(4)	105(4)	83(24)
H(4B)	145(14)	−44(4)	187(5)	98(24)
H(4C)	−188(18)	−23(5)	272(5)	126(29)

Table 4. Bond distances for (**1b**) with standard deviations in parentheses

Bond	Distance (Å)
C(1)–C(2)	1.356(7)
C(1)–N(3)	1.303(7)
C(2)–N(5)	1.378(6)
C(4)–N(3)	1.453(7)
N(5)–O(6)	1.250(5)
N(5)–O(7)	1.243(6)

Table 5. Bond angles of (**1b**) for non-hydrogen atoms with standard deviations in parentheses

Bond	Angle (°)
N(3)–C(1)–C(2)	126.1(6)
N(5)–C(2)–C(1)	120.0(5)
C(4)–N(3)–C(1)	124.0(6)
O(6)–N(5)–C(2)	118.2(5)
O(7)–N(5)–O(6)	120.6(5)
O(7)–N(5)–C(2)	121.3(5)

Table 6. Selected torsion angles of (**1b**)

Bonds	Torsion angle (°)
N(3)–C(1)–C(2)–N(5)	177.4
N(3)–C(1)–C(2)–H(2)	−1.9
C(2)–C(1)–N(3)–C(4)	1.8
C(1)–C(2)–N(5)–O(6)	177.1
C(1)–C(2)–N(5)–O(7)	−3.2
C(1)–N(3)–C(4)–H(4A)	−176.4
C(1)–N(3)–C(4)–H(4B)	−64.6
C(1)–N(3)–C(4)–H(4C)	52.1

* For details of Supplementary Publications see Instructions for Authors in *J. Chem. Soc., Perkin Trans. 2*, 1985, Issue 1.

Table 7. Calculated ground-state energies for conformers of (**1b**)

C(1)–C(2) Stereochem.	C(1)–N Stereochem.	Electronic component (a.u.)	Nuclear component (a.u.)	Total (a.u.)	Energy above lowest isomer (kJ mol^{-1})
E	*Z*	−669.0832	298.4275	−370.6558	10.2
E	*E*	−665.3905	294.7350	−370.6555	11.0
Z	*Z*	−698.2881	327.9118	−370.3763	744.3
Z	*E*	−677.0514	306.3918	−370.6597	0

respectively. Torsion angles show that the molecule is virtually planar. Thus the amine nitrogen atom, N(3), is trigonal and this is confirmed in that the sum of the H(3)–N(3)–C(4), C(4)–N(3)–C(1), and C(1)–N(3)–H(3) bond angles is 359.7°. The nitro and methylamino groups are disposed *trans* about the carbon–carbon double bond, as reported[16] for the solid-state conformation of the dimethyl analogue (**1a**). Simple steric considerations would predict the stereochemistry about the C(1)–N(3) bond to be *E*, but it is found to be *Z* in the crystal. However, the C(1)–C(2)–H(2) bond angle is 128(2)°, bending H(2) slightly towards the nitro group and away from the *N*-methyl. Torsion angles involving the methyl hydrogens show that they are also disposed so as to relieve steric strain.

Bond lengths and angles are largely similar to those reported[16] for the dimethyl analogue (**1a**). Two main exceptions are evident; in the dimethyl compound the C(1)–N(3) bond length is 1.334(4) Å and the C(2)–N(5) distance is 1.394(4) Å. In (**1b**), these are significantly shorter at 1.303(7) and 1.378(6) Å; moreover, the C(1)–C(2) bond length is concomitantly markedly longer than a simple carbon–carbon double bond.[17] These data would indicate delocalisation throughout the $NCCNO_2$ system of (**1b**) to an even greater extent that in (**1a**). Probably there is a contribution from a charge-separated canonical form, the so-called 'push–pull' effect.

Intermolecular hydrogen bonding, as suggested by the solid-state i.r. spectra, is found to be present. Molecules in the unit cell (Figure 3), related by a screw axis, are linked by intermolecular N(3)–H(3)···O(7) bonds with an N(3)–O(7) bond distance of 2.937 Å and a N(3)–H(3)···O(7) bond angle of 164°.

Molecular Orbital Calculations for (**1b**).—Calculations of energies of the four isomers considered (*E*/*Z*, *E*/*E*, *Z*/*Z*, and *Z*/*E*) were performed by the GAUSSIAN 70 program using STO-3G. The geometry of the *E*/*Z* form was taken from the *X*-ray crystal structure determination and that of other isomers taken to be obtained by altering the appropriate torsion angles by 180°. The results are shown in Table 7. Three conformers have calculated energies within 11 kJ mol^{-1} whereas the fourth is *ca.* 744 kJ mol^{-1} higher. This prediction correlates well with the observation that, in n.m.r. experiments, judicious choice of solvent can produce these three isomers whereas we have never observed the fourth (high energy) isomer.

In two parameters, we can now test the analogy between (**1b**) and the antitumour archetype (**2b**): populations of the rotamers about the C(1)–N bond and the bond order of that bond with respect to the amide or 'pro-amide' C(1)–N bond. First, as previously noted, there is observed a 9:1 preference of *Z* over *E* for both compounds about C(1)–N as indicated by n.m.r. This is corroborated by a calculated energy difference for this isomerism of 0.8 kJ mol^{-1} in the case of (**1b**), difference of 1.3 kJ mol^{-1} calculated using STO-3G for (**2b**).[18] Secondly, comparison of the C(1)–N bond lengths determined here for the crystal of (**1b**) and calculated[18] for (**2b**) (1.303 and 1.405 Å respectively) shows that the double bond character of this formal single σ-bond is much greater in the nitroethenamine (**1b**) than in the formamide (**2b**).

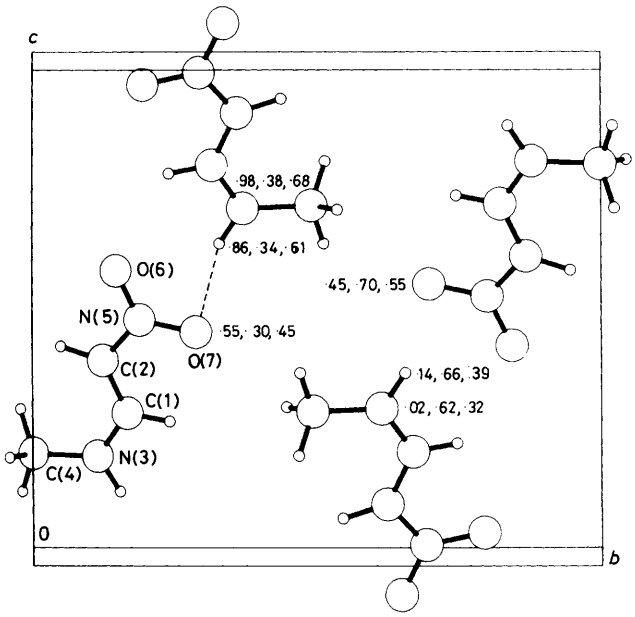

Figure 3. The unit cell of a crystal of (**1b**)

Experimental

^{1}H N.m.r spectra were obtained at 220 MHz using a Perkin-Elmer R34 spectrometer and at 60 MHz using a Varian EM360A instrument. M.p.s are uncorrected.

NN-*Dimethyl*-2-*nitroethenamine* (**1a**).—This material was prepared by the method of Meerwein[6] from nitromethane and *N*-(dimethoxymethyl)dimethylamine in 75% yield and had m.p. 104—105 °C (lit.,[6] 104 °C), $\nu_{max.}$(KBr) 3 100w, 3 030w, 2 920w, 2 820w, and 1 630 cm^{-1}.

N-*Methyl*-2-*nitroethenamine* (**1b**).—Transamination of *N*-methyl-2-nitro-*N*-phenylethenamine with methylamine according to the method of Krowczynski[7] gave (**1b**) in 87% yield. The orange-brown crystals had m.p. 121—123 °C (lit.,[7] 114—116 °C) (Found: C, 35.0; H, 5.8; N, 27.3. Calc. for $C_3H_6N_2O_2$: C, 35.3; H, 5.9; N, 27.4%); $\nu_{max.}$(KBr) 3 250, 3 100w, 3 040w, and 1 615 cm^{-1}; $\nu_{max.}$(Nujol) 3 250 and 1 615 cm^{-1}.

2-*Nitroethenamine* (**1c**).—N-*Methyl*-2-*nitro*-N-*phenylethenamine* was transaminated with ammonia as for (**1b**) above to give 2-nitroethenamine (**1c**) in 88% yield as orange-brown needles, m.p. 102—104 °C (lit.,[7] 101 °C); $\nu_{max.}$(KBr) 3 370, 3 150, and 1 625 cm^{-1}.

N-*Deuterio*-N-*methyl*-2-*nitroethenamine* (**1d**).—*N*-Methyl-2-nitroethenamine (150 mg, 1.5 mmol) was dissolved in warm deuterium oxide (99%+; Aldrich; 750 μl) followed by evaporation of the solvent under reduced pressure. The process was repeated and the residue was recrystallised from deuterium

oxide to give the *N*-deuterio compound (**1d**) as brown needles (100 mg, 0.97 mmol, 65%), m.p. 119—120 °C; $\nu_{max.}$(KBr) 3 100w, 3 050w, 2 370, and 1 620 cm^{-1}; $\nu_{max.}$(Nujol) 2 370 and 1 610 cm^{-1}.

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