Spectral Properties and Isomerism of Nitroenamines. Part 3.†

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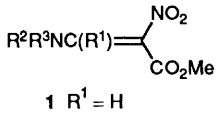
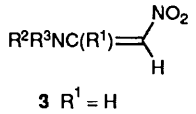
Vibrational, NMR and dynamic NMR spectra, considered together with the results of theoretical studies, provide a complete and fairly accurate quantitative picture of the isomerism affecting the nitroenamines R^2R^3N–C(1)R^1=C(2)H–NO_2 (R^1 = H, Me). The compounds with primary or secondary amino groups (R^2 and/or R^3 = H) exist as solvent-dependent equilibrium mixtures of the intramolecularly hydrogen-bonded *Z*-form and the *E*-form; the latter isomer can adopt the *Z* and/or the *E* conformation around the C(1)–N single bond when $R^2 \neq R^3$. The compounds with a tertiary amino group exist solely in the *E*-form. Vibrational couplings occur inside the mesomeric system leading to an IR strong (medium or weak Raman) 'enamine' band at 1650–1550 cm^{-1}, the result of the asymmetrical coupling of the C=C and C(1)–N stretching modes, and when R^1 and R^2 = H, with contributions of the in-plane N–H and C(1)–H bending modes. The N–O stretchings do not contribute to the enamine band, but couple with other vibrations to give a weak IR and Raman band at 1530–1480 cm^{-1}, with a main contribution of the $\nu_a(NO_2)$, and a strong IR (medium or weak Raman) band, mainly $\nu_s(NO_2)$, at 1280–1230 cm^{-1}. The energy barriers to rotation around the C(1)=C(2) and C(1)–N bonds, and the $\Delta G^{\ddagger}$ values for the ionization of the N–H group, indicated that the $E \rightleftharpoons Z$ isomerization takes place by a thermal mechanism with dipolar transition state, with the contribution, in some of the compounds with an NH group, of an anionic mechanism.

Nitroenamines[2] have attracted interest because of their potential use in organic synthesis[3] and their biological activity.[4] A knowledge of the isomerism and electron distribution inside these mesomeric systems is of paramount importance in understanding their properties and reactivity. As in similar push–pull ethylenes, spectroscopic techniques combined with theoretical studies can provide information on these matters, and we have previously reported on the NMR and vibrational spectra of 3-amino-2-nitroacrylic[5] (**1**) and 3-amino-2-nitro-

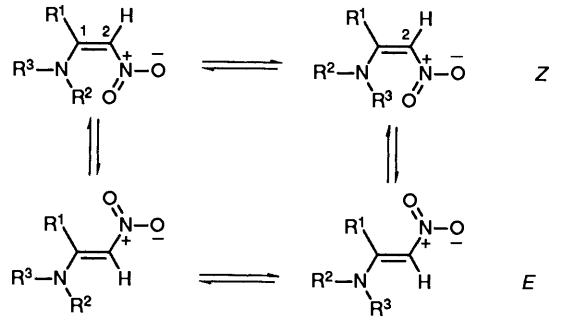


1 R^1 = H
2 R^1 = Me



3 R^1 = H
4 R^1 = Me

crotonic[1] esters (**2**) as well as semiempirical and *ab initio* studies[6,7] on the stability and theoretical vibrational spectra of their different isomeric forms and the energy barriers separating them. We turn now to the parent 1-amino-2-nitroethenes (**3**) and 2-amino-1-nitropropenes (**4**)‡ and report herein on the NMR and vibrational spectra of a set (see Table 1) of compounds **3** and **4**. We present a combined discussion of the results thus obtained and those derived from our theoretical studies.[6–8] Compounds **3** and **4** can exist in the four isomeric forms indicated in Scheme 1. In the derivatives with R^2 and/or R^3 = H, the *Z*-isomer can form an intramolecular hydrogen bond. According to the literature[10,15–22] these compounds show weak IR and Raman $\nu_a(NO_2)$, and strong IR and weak Raman $\nu_s(NO_2)$ bands, both displaced to low frequencies, and a strong IR (weak Raman) band at *ca.* 1630 cm^{-1} attributable to ν(C=C) or to ν(C=N) of C–N with high bond order.



Scheme 1

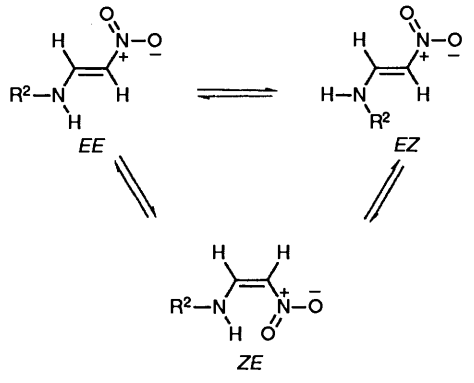
N-Deuteriation of compounds with primary or secondary amino groups affects considerably these frequencies,[10,15,16] which points to extensive mechanical coupling. On the basis of the anomalous intensities of the bands and a structural analogy with amino enones the mixed character of the vibrations affecting the NO_2, C=C and C–N bonded units has been proposed.[13,15] While the vibrational frequencies seem to be rather insensitive to isomerism and no assignment of bands to a particular isomer has been attempted,[15] the reported[4d,9,10,15,21–24] ^{1}H NMR spectra show that compounds **3** with primary or secondary amino groups exist in solution as equilibrium mixtures of the *E*- and *Z*-isomers, and that similar compounds **4** exist solely in the *Z*-configuration.[13] Compounds **3** and **4** with a tertiary amino group appear to exist exclusively in the *E*-configuration,[15] though a compound **4**, 2-piperidino-1-nitropropene, has been reported[13] to be a *Z*-isomer. A barrier to rotation around the C(1)–N bond of $\Delta G^{\ddagger}$ = 69.3 kJ mol^{-1} (325 K, in $CDBr_3$) has been measured for 1-dimethylamino-2-nitroethene (**3d**).[24,25] There are discrepancies concerning the isomeric equilibria of 1-methylamino-2-nitroethene (**3b**) in solution: while some authors[4d] only observed the *Z*-isomer in $CDCl_3$, others[23] found that, under these conditions, the *Z* and *E* isomers were in the ratio *ca.* 3:2; in $(CD_3)_2SO$, this compound showed the presence of the *ZE*, *EE* and

† For Part 2, see ref. 1.
‡ For comparative purposes, the numbering system for compounds **3** has been preserved in the formula of compounds **4**.

Table 1 Physical data for compounds **3** and **4**

Compound	R^1	R^2	R^3	Yield (%)	Solvent	M.p. (°C) Observed	M.p. (°C) Literature
3a	H	H	H	55	$CHCl_3$	101–102	101[a]
3b	H	H	Me	59	EtOH	119–120	114–116[a]
3c	H	H	*cyclo*-C_6H_{12}	72	EtOH	81–82	81–82[b]
3d	H	H	Ph	10	EtOH	94–95	94–95[c]
3e	H	Me	Me	60	EtOH	103–104	104[d]
4a	Me	H	H	65	C_6H_6	97–98	98–99[e]
4b	Me	H	Me	73	CCl_4	65–66	65–66[e]
4c	Me	H	Bn	80	CCl_4	85–86	86–87[e]
4d	Me	H	Ph	80	EtOH	85–86	85–86[e]
4e	Me	Me	Me	70	CCl_4	80–81	84–85[f]
4f	Me	$CH_2(CH_2)_2CH_2$		82	CCl_4	110–111	111–112[g]

[a] Refs. 9 and 10. [b] Ref. 26. [c] Ref. 11. [d] Ref. 12. [e] Ref. 13. [f] Ref. 14. [g] Ref. 15.



Scheme 2

*EZ** isomers (Scheme 2, R^2 = Me), the *EZ* being the predominant form for Gate *et al.*,[4d] and the *EE* for Krówczynsky and Kozerski.[23] An X-ray crystallographic study[4d] showed that the compound exists in the solid state in the *EZ* form.

The purpose of this investigation has been to obtain a reasonably complete and fairly accurate quantitative picture of the isomerism affecting **3** and **4**, to measure the energy barriers around the C(1)=C(2) and C(1)–N bonds for some representative compounds, and to establish the mechanism(s) of the $E \rightleftharpoons Z$ isomerization. Another objective has been to characterize spectroscopically the different isomeric forms, and in the light of the substituent and isotopic effects observed and the theoretical studies performed,[6–8] to gain a deeper insight into the vibrational couplings affecting these molecules and a better understanding of the electron distribution inside them.

Experimental

General spectroscopic measurements[5] and dynamic NMR experiments[1] were performed as described. Solutions of concentration 0.001–0.3 mol dm^{-3} depending on the solvent (40–0.03 mm cells) were used for IR measurements and 0.1–0.2 mol dm^{-3} solutions were used for NMR spectroscopy. Relative intensities of IR and Raman bands are indicated by the usual abbreviations (see Table 4); overlapping of bands, due in most cases to the presence of isomers, precluded measurements of the extinction coefficients. Secondary deuterium isotope effects on ^{13}C chemical shifts, $^2\Delta^{13}C(^{2/1}H)$, were measured on partially-deuteriated samples prepared by the addition of a calculated amount of EtOD to a 0.2 mol dm^{-3} solution of the compound in $CDCl_3$, so that the H:D ratio would be slightly >1.[27] The estimated error in the $^2\Delta^{13}C(^{2/1}H)$ values is ± 15 ppb.

Preparation of Compounds.—Compounds **3a–e**, **4d** and **4f** were prepared according to the literature (see Table 1). Compounds **4a–c** and **4e** were synthesized by the transamination reaction of 2-anilino-1-nitropropene (**4d**) with an excess of ammonia or the appropriate amine in ether solution.[28] Solid samples of the *N*-deuteriated derivatives of **3b** and **4b** were prepared by repeated recrystallization of the compounds from EtOD until monitoring by IR spectroscopy indicated the absence of ν(NH) absorption. *N*-Deuteriation of samples in solution was performed by shaking with D_2O and, in the case of IR spectra, separating the organic phase, filtering it, and transferring it to the IR cell.

Results and Discussion

The main spectral features of compounds **3** and **4** appear in Tables 2–4. As shown in the following discussion, consideration of these data provides a fairly complete picture of the isomeric equilibria.

Straightforward evidence for the configurational assignment was provided by the NMR spectra (Tables 2 and 3). The presence of a strong intramolecular hydrogen bond in the *Z*-isomer and the *cis*-deshielding effect of the NO_2 group,[1,5,15] allowed us to distinguish the configuration on the basis of the chemical shift of the amino proton (δ 8.4–11.6 and 8.0–9.7 for the *Z* and *E* isomer, respectively) and of 1-H of compounds **3** (δ 6.8–8.2 and 8.1–9.2 for the *Z* and *E* isomers, respectively), or of the protons of the C(1)–Me group of compounds **4** (δ 1.9–2.1 and 2.4–2.6 for the *Z* and *E* isomers, respectively). In compounds **3** the assignment was further supported by the $^3J_{1\text{-H},2\text{-H}}$ coupling (5.5–6.0 Hz for the *Z*-isomer and 10.0–10.8 Hz for the *E*-isomer); in compounds **4** confirmation was obtained from the value of $^3J_{C,H}$ for the $CH_3C(1)$=C(2)–*H* grouping: the values measured for 2-methylamino-1-nitropropene (**4b**) in $(CD_3)_2SO$ (2.5 Hz for the predominating isomer and 4.2 Hz for the minor isomer) confirmed the *Z* configuration of the main isomer. The value found (3.9 Hz in $CDCl_3$) for this coupling in 2-pyrrolidino-1-nitropropene (**4f**) and comparison with the values found for **4b** indicated the *E*-configuration of the former compound; this result is at variance with the reported,[13] most likely erroneously, *Z*-configuration for the analogous 2-piperidino derivative.

From the population of *Z*-isomer shown in Table 2 it follows that, for compounds **3** and **4** with primary and secondary amino groups, the *Z*-isomer is the most favoured (by ΔG° of at least 7.2 kJ mol^{-1}) in $CDCl_3$ and is the only isomer observed in this solvent by NMR spectroscopy. In the more polar $(CD_3)_2SO$,

* The symbols indicate, in the order shown, the configuration around the C(1)=C(2) bond and the conformation around the C(1)–N single bond.

Table 2 ^{1}H NMR spectral data [δ(ppm); J/Hz] for compounds **3** and **4**

Compd.	Solvent[a]	% Z-isomer	NH		R^1		2-H		Other
			Z	*E*	*Z*	*E*	*Z*	*E*	
3a	$CDCl_3$	>95	8.44br 5.73br	—	6.83ddd *J* 14.2 *J* 8.4 *J* 6.0	—	6.49d *J* 6.0	—	—
	$(CD_3)_2SO$	60	8.76br 8.55br	8.00br 7.67br	7.08dd *J* 15.9 *J* 5.7	8.07br	6.40d *J* 5.7	6.80d *J* 10.0	—
	$(CD_3)_2SO$–D_2O	62	—	—	7.09d *J* 5.6	8.15d *J* 10.7	6.46d *J* 5.6	6.87d *J* 10.7	—
	$(CD_3)_2NCDO$	70	9.70br 9.53br	8.96br 8.66br	8.21dd *J* 15.8 *J* 5.5	9.24br	7.46d *J* 5.7	7.91d *J* 10.7	—
	$(CD_3)_2NCDO$[b]	67	10.29d *J* 15.9 10.09d *J* 4.9	9.52dd *J* 16.0 *J* −3.7 9.25dd *J* 8.8 *J* −3.7	8.37ddd *J* 15.9 *J* 5.6 *J* 4.9	9.40m *J* 16.0 *J* 10.7 *J* 8.8	7.56d *J* 5.6	7.95d *J* 10.7	—
	CD_3OD	77	—	—	7.07d *J* 5.6	8.24br	6.46d *J* 5.6	6.95d *J* 10.5	—
3b	$CDCl_3$	>95	9.06br	—	6.75dd *J* 14.0 *J* 5.8	—	6.48d *J* 5.8	—	3.18d *J* 5.1
	$(CD_3)_2SO$	23	9.40br	8.16br	7.15dd *J* 14.6 *J* 5.8	8.16d (*EZ*) *J* 10.8	6.41d *J* 5.8	6.78d (*EZ*) *J* 10.8 6.74d (*EE*) *J* 10.8	3.05d (*ZE*) *J* 5.0 2.99s (*EE*) 9% 2.71s (*EZ*) 68%
	$(CD_3)_2NCDO$[c]	22			7.35dd *J* 14.6 *J* 5.8	8.2–8.5m	6.56d *J* 5.5	6.91d (*EZ*) *J* 10.2 6.87d (*EE*) *J* 9.8	3.16d (ZZ) *J* 4.9 3.12d (*EZ*) *J* 4.8 2.82d (*EE*) *J* 4.8
	$(CD_3)_2SO$–D_2O	28	—	—	7.16d *J* 5.7	8.20d (*EZ*) *J* 10.8 8.22d (*EE*) *J* 10.8	6.45d *J* 5.7 *J* 10.8	6.81d (*EZ*) *J* 10.8 6.77d (*EE*)	3.02s (*ZE*) 2.96s (*EE*) 2.68s (*EZ*)
3c	$CDCl_3$	>95	9.1br	—	6.83dd *J* 14.0 *J* 5.8	—	6.47d *J* 5.8	—	3.2br, 1.7br
3d	$CDCl_3$	>95	9.0br	—	*d*	—	6.63d	—	7.2m
	$(CD_3)_2SO$	24	10.88d *J* 13.9	10.56d (*EE*) 71% *J* 12.3 10.19s (*EZ*) 5%	7.81d *J* 14.0 *J* 6.2	8.61dd *J* 12.4 *J* 11.8	6.66d *J* 6.2	7.11d *J* 10.7	7.05–7.61m
3e	$CDCl_3$	<5	—	—	—	8.12d *J* 10.7	—	6.54d *J* 10.7	3.2br, 2.8br
4a	$CDCl_3$	>95	9.22br 6.72br	—	2.05s	—	6.53d *J* 1.3	—	
	$(CD_3)_2SO$	>95	9.16br 8.74br	—	1.93s	—	6.50d *J* 0.8	—	
4b	$CDCl_3$	>95	10.20br	—	2.01s	—	6.59s	—	3.11d *J* 5.4
	$(CD_3)_2SO$	91	10.10br	8.09br	1.99s	2.37s	6.62s	—	3.01d (*Z*) *J* 5.3 2.68d *J* 4.8
4c	$CDCl_3$	>95	10.44br	—	2.01s	—	6.59s	—	4.60d, 7.3m *J* 6.6
	$(CD_3)_2SO$	93	10.48br	8.46br	2.00s	2.46s	6.67s	—	4.65d (*Z*) *J* 6.4 4.34d (*E*) *J* 6.2 7.2–7.5m

Table 2 (*continued*)

Compd.	Solvent[a]	% Z-isomer	NH Z	NH E	R^1 Z	R^1 E	2-H Z	2-H E	Other
4d	$CDCl_3$	>95	11.91br	—	2.00s	—	6.69s	—	7.2–7.5m
	$(CD_3)_2SO$	88	11.52br	9.70br	1.97s	2.54s	6.84s	6.74s	7.2–7.5m
4e	$CDCl_3$	<5	—	—	—	2.62s	—	6.76s	3.08s
	CD_2Cl_2	<5	—	—	—	2.60s	—		3.01s, 3.19s
4f	$CDCl_3$	<5	—	—	—	2.63s	—	6.70s	3.57m, 3.25m, 2.03m

[a] At 293 K, unless otherwise indicated. [b] At 218 K. [c] At 227 K. [d] Hidden under the multiplet due to the aromatic protons.

Table 3 ^{13}C NMR spectral data [δ(ppm); J/Hz] for compounds **3** and **4**

Compd.	Solvent	C-1 Z	C-1 E	C-2 Z	C-2 E	$\Delta\delta$[a] Z	$\Delta\delta$[a] E	Other
3a	$(CD_3)_2SO$	146.9 $^1J_{1-H}$ 167.8 $^2J_{2-H}$ 9.4	151.1 $^1J_{1-H}$ 168.4 $^2J_{2-H}$ 5.2	109.4 $^1J_{2-H}$ 192.1 $^2J_{1-H}$ 7.8	113.7 $^1J_{2-H}$ 186.8	37.5	37.4	
3b	$(CD_3)_2SO$	149.6 (*ZE*) $^1J_{1-H}$ 171.0	149.8 (*EZ*) $^1J_{1-H}$ 155.9 $^2J_{2-H}$ 3.9 154.1 (*EE*)	108.3 (*ZE*) $^1J_{2-H}$ 182.8	111.5 (*EZ*) $^1J_{2-H}$ 160.3 111.8 (*EE*)	41.3 (*ZE*)	38.3 (*EZ*) 42.3 (*EE*)	36.2, $^3J_{1-H}$ 4.5 (*ZE*) 30.5, $^3J_{1-H}$ 7.9 (*EZ*) 35.0 (*EE*) N–CH_3
3d	$CDCl_3$	138.2	—	112.4	—	25.8	—	138.2 (C_i), 129.7 (C_m) 125.3 (C_p), 116.9 (C_o)
3e	$CDCl_3$	—	150.9 $^1J_{1-H}$ 169.8 $^2J_{2-H}$ 4.3	—	110.8 $^1J_{2-H}$ 188.0	—	40.1	44.6, $^3J_{1-H}$ 4.6 (N–CH_3, *anti*) 37.1, $^3J_{1-H}$ 6.3 (N–CH_3, *syn*)
4a	$CDCl_3$	158.3	—	110.4	—	47.9	—	20.0 (C-1–CH_3)
	$(CD_3)_2SO$	159.3	—	109.0 $^1J_{2-H}$ 191.4	—	50.3	—	19.2 (C-1–CH_3)
4b	$CDCl_3$	159.6	—	110.2 $^1J_{2-H}$ 192.0	—	49.4	—	30.2 (N–CH_3) 17.0 (C-1–CH_3)
	$(CD_3)_2SO$	163.3	*b*	110.0	*b*	53.3	*b*	21.9, $^3J_{2-H}$ 4.2 (*E*) 17.6, $^3J_{2-H}$ 2.5 (*Z*) (C-1–CH_3)
4c	$CDCl_3$	158.4	—	110.6	—	47.8	—	17.2 (C-1–CH_3)
4d	$CDCl_3$	156.3	—	111.7	—	44.6	—	18.0 (C-1–CH_3) 136.4 (C_i), 129.5 (C_m) 127.6 (C_p), 125.4 (C_o)
4e	$CDCl_3$	—	160.6	—	112.3	—	48.3	40.5 (N–CH_3) 15.8 (C-1–CH_3)
4f	$CDCl_3$	—	158.3	—	112.4 $^1J_{2-H}$ 159.3	—	46.1	17.8 (C-1–CH_3) $^3J_{2-H}$ 3.9

[a] $\Delta\delta = \delta_{C-1} - \delta_{C-2}$. [b] Not measured.

the *Z*-isomer of **4** is still the favoured state (by $\Delta G°$ 4.5–23 kJ mol^{-1}), while in compounds **3**, (with the exception of **3a**) the *E*-form is more stable by $\Delta G°$ *ca.* 2.7 kJ mol^{-1}. The stabilization of the *Z*-form produced by the introduction of a Me group at C(1) is ascribed to two effects: (*i*) the C(1)–Me strengthens the intramolecular hydrogen bond of the *Z*-isomer by a buttressing effect as can be deduced from a decrease in the ν(N–H) frequencies ($\Delta\nu$ 30–95 cm^{-1}) and an increase in the δ values ($\Delta\delta$ 0.7–1.6 ppm) of the amino proton on passing from compounds **3** to their homologous **4**, and from the larger isotopic effect $^2\Delta\,^{13}C(^{2/1}H)$ of the latter compounds (see Table 6 and the discussion below); (*ii*) the steric interaction between the C(1)–Me and the NO_2 groups in the *E*-isomer hinders planarity and destabilizes this isomer. The geometries predicted theoretically for **3a** and **4a** (Table 5) bear this out: the introduction of the C(1)–Me group causes a decrease in the N–C(1)=C(2) bond angle and of the length H···O of the hydrogen bond in the *Z*-isomer, and, consequently, a stronger hydrogen bond interaction; on the other hand, geometry distortion and destabilization occur in the *E*-isomer, as shown by the decrease of the N–C(1)=C(2) bond angle and the increase of the C(1)=C(2)–N bond angle. For compounds **3** and **4**, with tertiary amino groups, the *E*-isomer is the most stable (by $\Delta G°$ of at least 23 kJ mol^{-1}) under all the conditions used and is the only isomer observed.

The vibrational spectra (Table 4) of compounds **3** with a secondary amino group show in $CDCl_3$ a band at 1645 cm^{-1}, very strong in the IR, medium or weak in Raman, which because of its position and the above considerations can be assigned to, or must have a large contribution of, ν(C=C) due to the *Z*-isomer. A second band appears in $(CD_3)_2SO$ at lower frequency ($\Delta\nu$ −20 to −30 cm^{-1}), attributed to the same mode of the *E*-

Table 4 IR and Raman (*in italics*) frequencies cm^{-1} for compounds **3**, **4** and their *N*-deuteriated derivatives

		ν(N–H)		ν(N–D)		ν(C=C) + ν(C–N) + δ(N–H)		ν(C=C) + ν(C–N)[a]		$\nu_a(NO_2)$[b]		$\nu_s(NO_2)$[b]	
Compound	Medium	*c*	*d*	*c*	*d*	*Z*	*E*	*Z*	*E*	*Z*	*E*	*E*	*Z*
3a	CCl_4	3520m[e,f]	3355w[f]			*g*				*g*			*g*
	$CDCl_3$	3500m	3350w			1645vs 1568w				1453s			1265vs
	a			2635w	2450vw			1623vs		1443s			1300s
	$CHCl_3$		*h*			*1645*w *1563*w				*1452*w			*1266*m
	$[^2H_6]Me_2SO$		*g*			1648vs 1605sh	1630vs			1441vs		1272vs	1250vs
	KBr		3372s[i] 3190s			1650vs 1598s 1582s				1435vs			1250vs
	Solid		*3365*w[i] *3185*vw			*1668*w *1650*w				*1448w*			*1255*vw
3b	$CDCl_3$[j]	3460w[k]	3315w			1645vs 1582vw	1632m			1463m		1267m	1246vs
	a			2560w[k]	2450w			1631vs	1622sh	1440m			1296vs
	$CHCl_3$	*3450vw*[k]	*3300*vw			*1650*vw				*1452*vw			*1250*w
	$[^2H_6]Me_2SO$		3252w-m[l]			1640sh	1623vs 1543vw			1460sh	1452m	1272vs	1250sh
	KBr		3255s[i,k]		2360s[i,k]		1622vs 1562w		1618vs		1440m	1263vs	
	Solid		*3255*w[i,k]				*1624*w *1546*vw				*1450*w	*1250*vw	
3c	$CDCl_3$	3430vvw[k]	3308vw			1641vs	1625sh			1465m			1243s-vs
	a			2545vvw[k]	2450vw			1626vs		1463m-s			1292vs
	$[^2H_6]Me_2SO$		3220w			1640vs	1615vs 1550vw			1460sh	1450m	1246vs	1262vs
	KBr		3258s[i,k]				1613vs 1558m				1452m	1230vs	
	Solid		*3256*vw[i,k]				*1615*w *1551*w				*1450*sh	*1235*w	
3d	CCl_4	3430sh[f,m] 3418vw[f,n]	3300vw[f]			1647vs	1635sh			*g*			1257vs
	$CDCl_3$	3410vvw	3305vw			1644vs				1485sh			1265vs
	a				2457vw			1629vs		1476s			1290vs
	$CHCl_3$		*h*			*1647*vw				*1490*sh			*1270*w
	$[^2H_6]Me_2SO$		3188w			1648vs	1620s			1493m[o]	1473w	1275sh	1260vs
	KBr		3220w			1650vs 1563vw	1632m[p]			1486m	*q*	1265sh[p]	1248vs
	Solid		*h*			*1650*vw *1562*vw	*1632*vw			*1490*sh	*1452*w	*1260*w	*1243*w

Table 4 (*continued*)

Compound	Medium	ν(N–H)		ν(N–D)		ν(C=C) + ν(C–N) + δ(N–H)		ν(C=C) + ν(C–N)[a]		$\nu_a(NO_2)$[b]		$\nu_s(NO_2)$[b]	
		c	*d*	*c*	*d*	*Z*	*E*	*Z*	*E*	*Z*	*E*	*E*	*Z*
3e	CCl_4								1636vvs		1498w-m	1267vs	
	$CDCl_3$								1635vvs		1498w-m	1265vs	
									*1635*w		*1500*m	*1262*s	
	$[^2H_6]Me_2SO$								1632vs		1498w	1256vs	
	KBr								1632vs		1500w	1245vs	
	Solid								*1635*w		*1506*w	*1250*vw	
4a	CCl_4	3505m	3400vw[i]			1621vs				1462s			1295vs
			3330w										
	$CDCl_3$	3500m	3400vw[i]			1621vs				1449s			1297vs
			3330w			1567m							
						1547w							
	a			2620w	2450vw			1598s		1442m			1303vs
	$CDCl_3$					*1629*w		*1600*w		*1460*m			*1296*s
						*1567*w							
						*1551*w							
	$[^2H_6]Me_2SO$		*g*			1620s				1440m			1288vs
						1592vs							
						1575sh							
						1545sh							
	KBr		3403m[i]			1634s		1593s		1465m			1275vs
			3348m[i]			1620s							
			3295m			1568m							
			3215m			1546w							
	Solid		*3405*vw[i]			*1635*w				*1465*w			*1290*w
			*3350*vw[i]			*1575*vw							
			*3295*vw			*1550*vw							
			*3215*vw										
4b	CCl_3		3245vw			1613vs				1497m			1255vs
	a				2410vw-w			1580s-vs		1492m-s			1297vvs
	$CDCl_3$		*3235*vw			*1618*w				*1503*m			*1260*m
	$[^2H_6]Me_2SO$		3240w			1612vs	1588s			1493s	*q*	1303vs	1258vs
	a				2405w				1583vs	1493s			1300vvs
	KBr		3245w			1615vs				1503m			1247vs
	a				2410w			1582vs		1490s			1295vs
	Solid		*h*			*1610*w-m				*1485*m			*1239*m
						*1602*sh							
	a				*2423*vw			*1581*w-m		*1489*m			*1276*w
4c	$CDCl_3$		3240vw			1604vs				1489m			1240s
	KBr		3220vw			1603vs				1495m			1230s
													1216vs
	Solid		*3220*vw			*1605*sh				*1495*sh			*1234*m
													*1215*vw

Table 4 (*continued*)

Compound	Medium	ν(N–H)		ν(N–D)		ν(C=C) + ν(C–N) + δ(N–H)		ν(C=C) + ν(C–N)[a]		$\nu_a(NO_2)$[b]		$\nu_s(NO_2)$[b]	
		c	*d*	*c*	*d*	*Z*	*E*	*Z*	*E*	*Z*	*E*	*E*	*Z*
4d	$CDCl_3$		3210vw			1609vs				1477m			1280vs
	$[^2H_6]Me_2SO$		*h*			1606s	1570s			1480s	*q*	1295sh	1287vs
	KBr		3195vw			1604vs				1474m			1275vs
	Solid					*1603*w				*1478*m			*1276*s
4e	CCl_4								1575s		1504w	1293vs	
	$CDCl_3$								1568s		1504w	1278vs	
									*1566*w		*1503*w	*1278*vs	
	$[^2H_6]Me_2SO$								1563s		1503w	1274vs	
	KBr								1563vs		1509m	1248vs	
	Solid								*1565*s		*1509*m	*1245*w	
4f	CCl_4								1561s		1472m	1272vs	
									1556s				
									1530sh				
	$CDCl_3$								1562s		1476m	1272vs	
									1555s				
									1535w				
	$CHCl_3$								*1557*w		*1479*s	*1274*m-s	
									*1528*vw				
	$[^2H_6]Me_2SO$								1554s		1478m	1270vs	
									1532sh				
	KBr								1565s		1480m	1276vs	
									1542m			1254vs	
	Solid								*1545*w		*1488*m-s	*1257*vw	
									*1524*vw				

[a] Measured in the *N*-deuteriated derivative. [b] Tentative assignment. [c] Assigned to the free NH (or ND) group. [d] Assigned to the intramolecularly bonded NH (or ND) group unless otherwise indicated. [e] s, strong; m, medium; w, weak; sh, shoulder; v, very. In the case of isomeric mixtures, the actual relative intensities are indicated. [f] Measured at very dilute solution. [g] Not measured. [h] Not detected. [i] Intermolecularly bonded NH group. [j] Freshly prepared solution. [k] *E*-form. [l] Assigned to the NH group associated with the solvent. [m] Tentatively assigned to the *EZ*-conformation. [n] Tentatively assigned to the *EE*-conformation. [o] Possible contribution of aromatic ν(C=C). [p] Some samples showed only the bands corresponding to the *Z*-isomer. [q] Not assigned.

Table 5 AM1 geometrical parameters of the *Z* and *E* isomers of compounds **3a** and **4a** (distances in Å and angles in degrees)

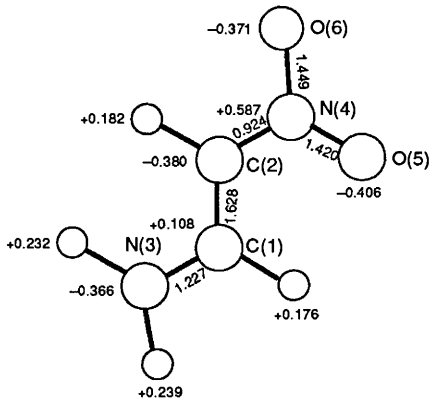
Compound	Isomer	C(1)=C(2)	C(1)–N	C(2)–N	H···O	N–C(1)=C(2)	C(1)–C(2)–N
3a[a]	*Z*	1.371	1.348	1.448	2.195	127.7	125.4
	E	1.371	1.353	1.453		124.1	121.3
4a[a]	*Z*	1.380	1.357	1.445	2.151	125.3	126.0
	E	1.378	1.370	1.447		118.9	127.5

[a] Data from ref. 6. [b] Data from ref. 8.

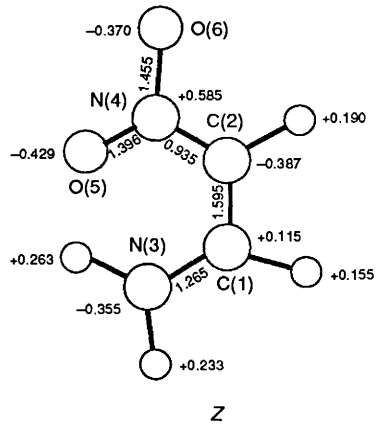
Table 6 Two-bond deuterium isotope effects [$^2\Delta C(1)$/ppb] on C-1 chemical shifts, and calculated[a] hydrogen bond energies (E_H/kJ mol^{-1}) for compounds **3a, b, d** and **4a, b, d**

Compound	Solvent	$^2\Delta C(1)$ *Z*	$^2\Delta C(1)$ *E*	$E_H(Z)$
3a	$(CD_3)_2SO$	146	0	26.0
3b	$(CD_3)_2SO$	170	0	27.8
3d	$CDCl_3$	259	—	32.8
4a	$CDCl_3$	180	—	28.5
4b	$CDCl_3$	236	—	31.7
4d	$CDCl_3$	272	—	33.4

[a] $\ln(^2\Delta C) = 2.817 + 0.084\,E_H$ [ref. 27(*b*)].



E



Z

Fig. 1 AM1 calculated total charge distribution and bond orders for the *E*- and *Z*-isomer of 1-amino-2-nitroethene (**3a**)

isomer, also present in this solvent. The frequency of this band is very near to that shown by compounds with a tertiary amino group, thus supporting the *E*-configuration assigned to these compounds on the basis of the NMR spectra. All the compounds **3** and **4** with primary and secondary amino groups examined here (with the exception of **3b–d**) showed only the band of higher frequency in the solid state spectra, thus indicating that they crystallize in the *Z*-isomeric form. Compounds **3b** and **3c**, which showed only the lower frequency band, crystallize in the *E*-isomeric form. The configuration of **3b** has also been established by X-ray crystallography.[4d]

Joint consideration of the theoretical results,[6–8] the isotopic and substituent effects and the band intensities provides an insight into the complexity of the C=C band (referred to hereafter and in Table 4 as the 'enamine' band). The isotopic frequency shift ($\Delta\nu$ *ca.* -14 and -28 cm^{-1} for the *Z*- and *E*-isomer, respectively) of this band calculated[7] for the C(1)-deuteriated isotopomer of **3a**, and the still larger frequency shift caused by methyl substitution at C(1) ($\Delta\nu$ -30 to -36 cm^{-1}; *c.f.* compounds **3** and **4** in Table 4) are indicative of mechanical coupling between the in-plane δ[C(1)–H] bending mode and the C=C stretching mode. *N*-Deuteriation of the *Z*-isomer of compounds **3** with primary or secondary amino groups also produced a frequency drop ($\Delta\nu$ -14 to -16 cm^{-1}), and the effect was still larger ($\Delta\nu$ -28 to -35 cm^{-1}) in the same isomer of the stronger chelated compounds **4**; on the other hand, this isotopic effect is almost nil in the *E*-isomer of both kinds of compound. In agreement with this, the effect of *N*-deuteriation on the frequency of the enamine band has been predicted[7] to be almost negligible for the *E* isomer, but considerable ($\Delta\nu$ up to -43 cm^{-1}) for the *Z* isomer, especially when the substituted hydrogen is that involved in the intramolecular hydrogen bond. Therefore, coupling also occurs between the in-plane δ(N–H) and ν(C=C) modes, the magnitude of which is related to the presence and strength of the intramolecular hydrogen bond and, therefore, non-existent in the *E*-isomer. As a consequence, the frequency of the enamine band of the *N*-deuteriated *Z*-isomers has practically the same value as the corresponding non *N*-deuteriated *E*-isomer and the nearest similar compound with a tertiary amino group. It seems, therefore, that *N*-methylation and *N*-deuteriation have similar effects on the enamine band, as previously observed in these compounds[15] and the related amino enones,[29] and that the ν(C=C) component of the enamine band is not much affected by the isomerism.

In accordance with the theoretical studies,[7] the observed enamine band of **3** and **4** is characterized by its rather high frequency when compared with the related amino enones [*e.g.* 1641 cm^{-1} for (*Z*)-**3c** and 1570 cm^{-1} for (*Z*)-3-(cyclohexylamino)acrolein **5**].[30] We consider this to be due to a difference in the electron distribution in both kinds of compounds and the concomitant difference in couplings. The AM1 calculations[8] of the total charge distribution and bond orders for the two configurational isomers of **3a** (Fig. 1) indicate an accumulation of negative charge at the amino nitrogen and C(2), an increased bond order of the C(1)–N bond, and reduced bond order of the C(1)=C(2) and C(2)–N bonds, the effect being larger in the *Z*-isomer. The 3-21G calculated[7] $F_{C(1)=C(2)}$ and $F_{C(1)-N}$ stretching force constants are very similar thus reflecting the strong conjugation of the amino group and the double bond. As a consequence, both internal coordinates strongly interact, and indeed the enamine mode is described[7] as an asymmetric combination of the C(1)=C(2) and C(1)–N stretching motions,

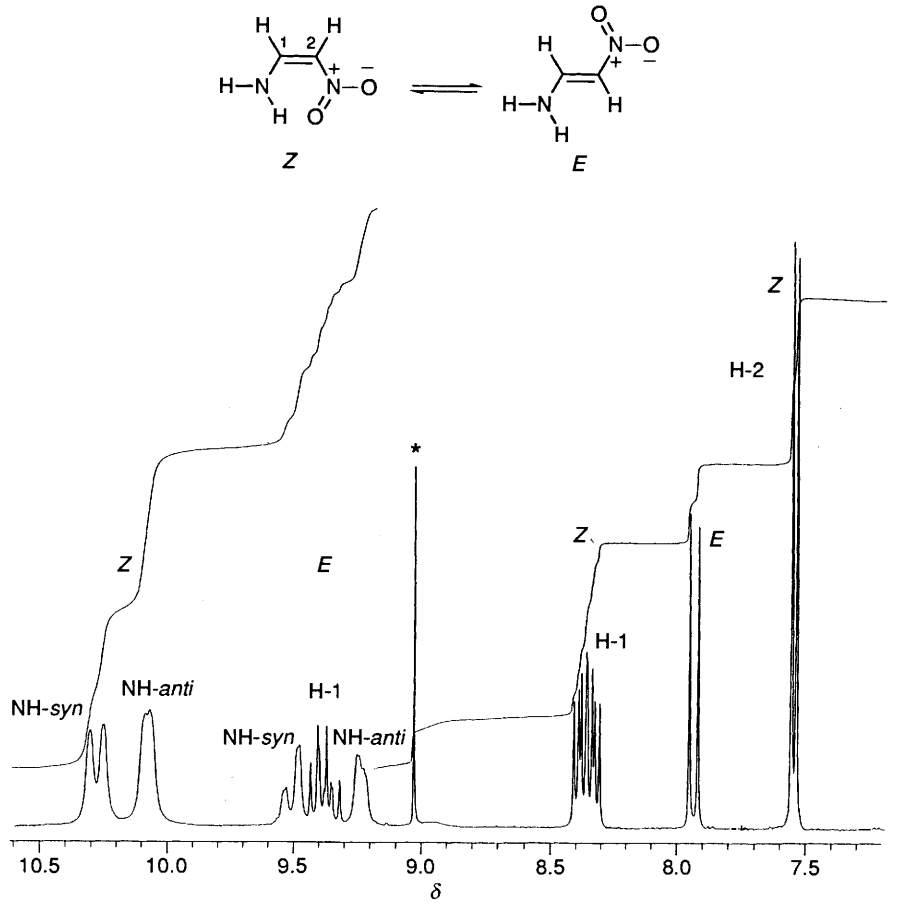


Fig. 2 ^{1}H NMR spectrum (300 MHz) of 1-amino-2-nitroethene (**3a**) in $(CD_3)_2NCDO$ at 218 K

with contribution of the δ[C(1)–H] and δ(N–H) modes when the two groups are present. Furthermore, the frequency of the enamine mode of the *E*-isomer is also calculated to be 18 cm^{-1} lower than that of the *Z*-isomer (see above for comparison with the experimental results). The opposing dipoles associated with the C(1)=C(2) and C(1)–N bonds results in a large change of the dipole moment during the asymmetric vibration and a high IR intensity. In the related amino enones, the much more effective charge transfer from the N–C=C-group to the carbonyl group by through-resonance results in a large dipole moment, but also in a different pattern of bond orders and associated mechanical couplings and frequencies. Therefore, in spite of its structural analogy, both kinds of compound must show significant spectral differences, as observed. The observed medium or weak Raman intensity, in accordance with the calculated[7] Raman activity, of the enamine band can be associated with the low polarizability of these strongly polarized molecules, as suggested.[15]

Compounds **3a** and **4a** with a primary amino group showed more complex absorptions in the double-bond region, due to the intrusion of the in-plane bending of the NH_2 group. The IR spectrum of **3a** showed (in $CDCl_3$ solution in which only the *Z*-isomer is present) two bands, sensitive to *N*-deuteriation, the strongest of which, at 1645 cm^{-1}, is considered to have the largest contribution of ν(C=C), ν[C(1)–N] and δ(NH_2) modes (*i.e.*, the enamine band), because of its similarity to the IR frequency (1635 cm^{-1}), intensity and Raman activity calculated[7] for the enamine band using the 3-21G split-valence basis. The weaker band at 1568 cm^{-1} is considered, in accordance with these calculations,[7] to have a much larger δ(NH_2) component. On *N*-deuteriation, the δ(NH_2) component of the enamine band is lost, and the new band which then appears, due to ν(C=C) + ν(C–N), has approximately the same frequency and intensity as the similar band of the *N*-deuteriated derivatives of compounds **3** with secondary amino groups. In $(CD_3)_2SO$ solution (containing the *Z*- and *E*-isomers in the ratio *ca.* 3:2) another strong, *N*-deuteriation-sensitive band appears at 1630 cm^{-1} which can be assigned as the enamine band of the *E*-isomer, again because of its similarity in frequency to the 3-21G-calculated[7] enamine band of the *E*-isomer. The corresponding band with the largest δ(NH_2) component of this isomer has been calculated[8] to have a higher frequency than the enamine band and is most likely overlapped by the strong enamine band of the co-existing *Z*-isomer. Compound **4a**, which according to the ^{1}H NMR spectra exists solely in the *Z*-configuration in both solvents, showed strong bands at 1592–1625 cm^{-1}, which, by analogy, are assigned to the C=C–NH_2 group.

By analogy with compounds **1** and **2**, it was anticipated that **3** and **4** would show ν(NO_2) bands in the ranges 1520–1470 and 1315–1240 cm^{-1}. These are very populated regions, the ν(NO_2) bands being usually distinguished by their strong intensity. The split-valence 3-21G basis set calculations for **3a** predict[7] bands at 1464 and 1489 cm^{-1}, of medium IR intensity, for $\nu_a(NO_2)$ of the *Z*- and *E*-isomer, respectively, and at 1331 and 1310 cm^{-1}, of strong intensity for $\nu_s(NO_2)$. These are complex modes with contributions of other coordinates such as the C=C–H and C(1)–N–H in-plane bendings, and with no contribution of C(1)=C(2) stretching. The compound exhibits $CDCl_3$ bands at 1453 and 1265 cm^{-1}, strong in the IR and weaker in the Raman, that can be assigned to these complex modes. Both bands are sensitive to *N*-deuteriation, and the one at lower frequency is split into two bands on passing from $CDCl_3$ to Me_2SO due to the presence of the two geometrical isomers. Compound **4a** and the compounds with secondary and tertiary amino groups behave similarly, the frequency of the $\nu_a(NO_2)$ band being displaced to higher frequency by the

introduction of the methyl group at C(1) and by increasing the substitution degree at the nitrogen (see Table 4). In most cases, one or more medium to strong bands also appear in the 1450–1300 cm^{-1} region, probably related to the ν[C(1)–N] vibration.

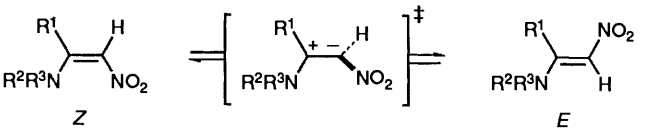
The assignment of the ^{13}C NMR spectra was made on the basis of the coupled spectra, the relative intensities of the signals and their comparison with those of the corresponding ^1H NMR spectra. For compounds **3a**, **b**, **d** and **4a**, **b**, **d** the assignment was supported by the data of the isotopic effect, $^2\Delta^{13}C(^{2/1}H)$, since only the C(1) signal of the intramolecularly-bonded *Z*-isomer showed a measurable effect (see Table 6 and below for discussion). The electron delocalization produces a large chemical shift, $\Delta\delta = \delta_{C(2)} - \delta_{C(1)}$, between the olefinic carbons, the value of which increases with the donor capacity of the R^2R^3N group and the polarity of the medium, and is almost independent of the configuration. Comparing the data in Table 3 for the *Z*-isomer of compounds **3a** and **3b** with a primary amino group and methylamino group, respectively, with those of their homologous compounds **4a** and **4b**, it can be seen that the introduction of C(1)–Me produces a deshielding of the signal of C–1 of 12.4 and 13.7 ppm, respectively, as well as a small deshielding of the signal of C-2 of 0.4 and 1.7 ppm, respectively. On the other hand, comparison of the two homologous compounds with an anilino group, **3d** and **4d**, shows a still larger deshielding effect (18.1 ppm) on C(1), but a shielding effect of 0.7 ppm for the signal of C(2). This difference is attributed to the loss of the coplanarity of the phenyl group with the nitroenamine moiety in **4d** due to its steric interaction with C(1)–Me; the result is an increase of the electron-donating capacity of the amino proton and a larger accumulation of negative charge at C(2). The same conclusion is reached by considering the isotopic effects, $^2\Delta^{13}C(^{2/1}H)$, on C(1) of these compounds (see below). From the ^1H and ^{13}C NMR spectra it was deduced that the proportion of *E*-isomer increases with the polarity of the medium; *e.g.*, in the case of **3a**, the *E*:*Z* ratio increased in the order $CDCl_3 < CD_3OD < (CD_3)_2NCDO < (CD_3)_2SO$. This stabilization of the *E*-isomer is attributed to two effects: (*i*) the larger dipolar moment of the more extended *E*-isomer relative to that of the intramolecularly bonded *Z*-isomer,[6,8] and (*ii*) the formation of intermolecular hydrogen bonds between the *E*-isomer and the solvent. The latter effect also explains that, for a given solvent, the proportion of *E*-isomer increases with the hydrogen bond donor capacity of the R^2NH group, *i.e.*, in the order $H_2N < MeNH \simeq BnNH <$ PhNH.

Consideration of the coupling constants measured provided a further insight into the geometry of the compounds under study. The $^3J_{NH,1-H}$ value (14.0–16.0 Hz) measured for the *Z*-isomer of compounds **3** indicated the rigid *E*-disposition of 1-H and the amino proton imposed by the chelation. The ^1H NMR spectrum of **3a** in $(CD_3)_2NCDO$ at 218 K showed well-resolved signals for each proton in both geometric isomers (Fig. 2). The 1-H proton of each isomer is coupled with 2-H and with each of the protons of the NH_2 group. In the *E*-isomer there is a geminal coupling ($^2J_{NH,NH}$ −3.7 Hz) between the two amino protons of the same order of magnitude as that observed[31] in primary amides (−2.2 to −2.5 Hz), thus indicating the sp^2 character of the amino proton of the nitroenamines; this geminal coupling was not observed in the *Z*-isomer. From the values of the couplings between 1-H and the amino protons (4.9 and 15.9 Hz for the *Z*-isomer, and 8.8 and 16.0 Hz in the *E*-isomer) it was established that, in both isomers, the NH proton in a *syn* disposition with respect to the C=C appears at lower field than the one in the *anti*-disposition. In compound **4a**, a long-range (^4J) coupling can be observed between 2-H and the amino proton *anti* with respect to the double bond.

1-Methylamino-2-nitroethene (**3b**) showed in its ^1H and ^{13}C NMR spectra in $(CD_3)_2SO$ solution the presence of the *ZE*, *EZ* and *EE* isomeric forms (Scheme 2) in the ratios *ca.* 23:68:9, thus confirming the results of Gate *et al.*[4d] and at variance with the results of Kozerski and Krówczynski.[23] The assignments were made using the coupling $^3J_{C,1-H}$ between 1-H and the carbon of the NMe group (Table 3). 1-Anilino-2-nitroethene (**3d**) also exists in $(CD_3)_2SO$ solution as an equilibrium mixture of the *ZE*, *EZ* and *EE* isomers in the approximate ratios 24:5:71 as deduced from ^1H NMR spectroscopy in this solvent, which showed three NH signals, two of them doublets due to $J_{1-H,NH}$ coupling (13.9 Hz for the signal at lowest field, attributed to the *ZE*-isomer and 12.3 Hz for the major *EE*-rotamer); in this compound the *EZ*-form is probably destabilized because of the large steric interaction between the phenyl group and 2-H.

The presence of a strong intramolecular hydrogen bond in **3** and **4** was further evidenced, and the corresponding energies estimated, by the large two-bond isotope effect, $^2\Delta^{13}C(^{2/1}H)$, observed on the C(1) chemical shift in partially *N*-deuteriated samples of a selected set of the compounds (Table 6). Deuteriation of an amino group involved in an intramolecular hydrogen bond produces a relatively large upfield isotope effect on the resonance of the carbon bearing the group, the magnitude of which correlates with the hydrogen bond energy by a simple relationship.[1,5,27] From the $^2\Delta$ values, and the corresponding energies which appear in Table 6, it can be seen that the energy of the hydrogen bond increases in the order $NH_2 <$ MeNH < PhNH. The introduction of C(1)–Me increases the energy by 2.5 kJ mol^{-1} for the compound with NH_2, and by 3.9 kJ mol^{-1} in the compound with a MeNH group, but by only 0.6 kJ mol^{-1} for the compound with a PhNH group. The last value is indicative of a non-planar disposition of the phenyl ring with the nitroenamine moiety in **4d**, as deduced above from the $\Delta\delta$ values. The *E*-isomers did not show any measurable isotopic effect on C(1) due to the absence of intramolecular hydrogen-bonding.

Dynamic ^1H NMR studies have been performed on compounds **3a**, **3b**, **4b** and **4d** in order to determine the activation parameters for the $Z \rightleftharpoons E$ equilibrium. The activation energies, $\Delta G^{\ddagger}$, for the exchange of the amino proton have also been determined for compounds **3a**, **3b** and **4b**, by measuring the temperatures at which the couplings due to this proton are lost. A similar study has been performed for 2-dimethylamino-1-nitropropene (**4e**) to obtain the activation parameters to rotation around the C(1)–N bond. The values obtained are collected in Table 7, together with the values of the free energy, ΔG°, for the equilibrium $Z \rightleftharpoons E$. In 2-methylamino-1-nitropropene (**4b**), the couplings of the amino proton were observed even at the highest temperature (425 K) reached, thus indicating that the isomerization process $Z \rightleftharpoons E$ takes place without ionization of the NH, *i.e.*, the barrier measured [$\Delta G^{\ddagger}$ 91.3 ± 0.6 kJ mol^{-1}, in $(CD_3)_2NCDO$] is the one corresponding to the thermal mechanism with a dipolar transition state[32] (Scheme 3). From the coupling constants observed at 425 K the



Scheme 3

lowest limit (included in Table 7) for $\Delta G^{\ddagger}$ for exchange of the amino proton could be obtained using the Gutowsky–Holm equation.[33] The rate constant given by this equation was statistically corrected for the fact that, after the exchange, the new proton may have the same spin as the starting one.

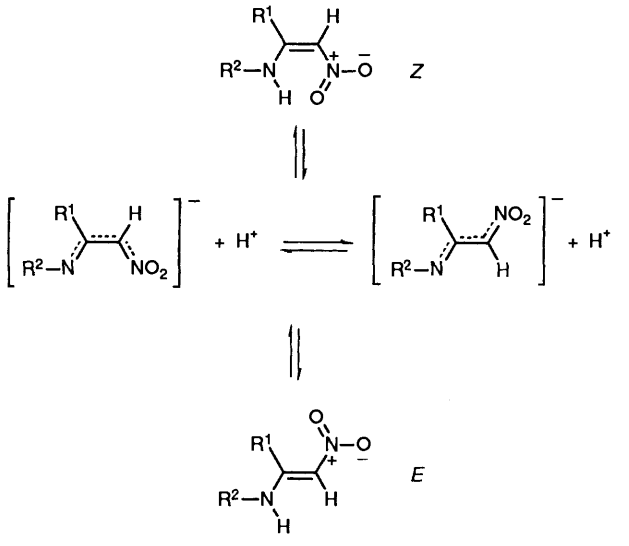
For 1-amino-2-nitroethene (**3a**) and 1-methylamino-2-nitroethene (**3b**), $\Delta G^{\ddagger}$ values obtained for the exchange of the NH proton were lower than those for the $Z \rightleftharpoons E$ isomerization, thus

Table 7 Thermodynamic and activation parameters (ΔG, ΔH/kJ mol^{-1}, ΔS/J mol^{-1} K^{-1}) for compounds **3a**, **b**, **d** and **4b**, **d**, **c**

Compound	Solvent	T/K	$\Delta G^{\circ}_{Z\rightleftharpoons E}$	N–C-1 Rotation			$Z\rightleftharpoons E$ interconversion	NH ionization $\Delta G^{\ddagger}$	
				$\Delta G^{\ddagger}$	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	$\Delta G^{\ddagger}$	Z	E
3a	$(CD_3)_2NCDO$	398.8	0.9	—	—	—	89.0 ± 0.6	70.2 ± 0.5[a] (338 K)	—
3b	$(CD_3)_2NCDO$	376.8	−1.7	—	—	—	80.2 ± 0.5 (316 K)	69.4 ± 0.5 (262 K)	57.4 ± 0.5
3e	CH_2Cl_2	298.2	—	69.0 ± 2.1[b]	59.4 ± 2.1[b]	−32.6 ± 6.3[b]	—	—	—
4b	$(CD_3)_2NCDO$	390.4	6.8	—	—	—	91.3 ± 0.6	>94.3 (425 K)	—
4d	$(CD_3)_2NCDO$	402.5	6.7	—	—	—	96.2 ± 0.6	—	—
4e	CD_2Cl_2	298.2	—	54.0 ± 0.4	68.3 ± 4.2	48.3 ± 15.3	—	—	—
		261.0	—	55.7 ± 0.4	—	—	—	—	—

[a] NH intramolecularly bonded. [b] Ref. 25.

suggesting the contribution of an anionic mechanism[34] (Scheme 4) to the process. Assuming that C(1)–Me substitution



Scheme 4

causes a decrease in $\Delta G^{\ddagger}_{Z\rightleftharpoons E}$ of the same order of magnitude as that observed in the 3-amino-2-nitrocrotonic esters **2** ($\delta\Delta G^{\ddagger}_{Z\rightleftharpoons E} \sim -40$ kJ mol^{-1}),[1] $\Delta G^{\ddagger}_{Z\rightleftharpoons E}$ anticipated for the thermal isomerization of compound **3b**, calculated from the value corresponding to its homologous compound **4b**, is $\Delta G^{\ddagger}_{Z\rightleftharpoons E}$ 91.3 + 40 = 131.3 kJ mol^{-1}, a value 51 kJ mol^{-1} higher than the experimental value, thus confirming the contribution of the anionic mechanism in the isomerization.

Compounds **3** and **4** show restriction to rotation around the C(1)–N bond, as indicated by the chemical shift anisochrony of the protons of the R^2R^3N group in the *E*-isomer of compounds **3a**, **3e**, **4e** and **4f** with $R^2 = R^3$ (in the last two compounds only in the low-temperature spectra), and by the observation of rotamers in the C(1)–N bond in compounds **3b** and **3d** possessing a secondary amino group. The barrier, $\Delta G^{\ddagger}_{298.2}$, to rotation around the C(1)–N bond of 2-dimethylamino-1-nitropropene (**4e**) is 15 kJ mol^{-1} lower than that reported[25] for its lower homologue **3e** (see Table 7). This decrease in the barrier is most likely due to the destabilization of the ground state of **4e** due to the steric interaction between the C(1)–Me and the Me_2N group. The positive value of $\Delta S^{\ddagger}$ is attributed to the decrease of the molecular dipole moment on passing from the ground state to the transition state, and the consequent decrease in the order of the solvent molecules surrounding the molecule of the compound. Therefore, the negative value of $\Delta S^{\ddagger}$ reported[25] for **3e** in the same solvent, is unlikely. Furthermore, the $\Delta H^{\ddagger}$ value determined for **4e** is 9 kJ mol^{-1} larger than that reported[25] for **3e**, which was unexpected. By contrast to that observed for the C(1)=C(2) barrier, the C(1)–N barrier increases with the polarity of the solvent, as deduced from the broadening of the ^{1}H NMR Me_2N signal of **4e** on passing from $CDCl_3$ to $(CD_3)_2SO$.

Conclusions

The vibrational, NMR and dynamic NMR spectra, considered together with the results of theoretical studies, provide a complete and fairly accurate quantitative picture of the isomerism affecting nitroenamines. The simplest compound of this class, 1-amino-2-nitroethene, exists as a solvent-dependent equilibrium mixture of the intramolecularly-bonded *Z*-form and the *E*-form, the proportion of the latter increasing with the polarity of the solvent. Methylation at C(1) causes an increase in the stability of the *Z*-form, while alkylation or arylation at the amino nitrogen stabilizes the *E*-form. In polar solvents, the proportion of *E*-form in the compounds with a secondary amino group increases with the hydrogen bond donor capacity of the amino function; this isomer can exist in the *Z* and/or the *E* conformation around the C(1)–N single bond, the proportion of the rotamers being dependent on the steric requirement of the R^2NH group. The energy of the intramolecular hydrogen bond of the *Z*-form of those compounds with primary or secondary amino groups increases in the order NH_2 < MeNH < PhNH, and with the methyl substitution at C(1). The energy barrier to rotation around the C=C bond decreases by increasing the π-donor capacity of the substituent at the amino function and by the introduction of the C(1)–Me group; comparison of these barriers with the free energy of activation for the exchange of the amino proton indicates that, in 2-methylamino-1-nitropropene, the $Z\rightleftharpoons E$ isomerization takes place by a thermal mechanism with a dipolar transition state, while in the more acidic 1-amino-2-nitroethene and its *N*-methyl derivative, both the thermal mechanism and an anionic mechanism contribute to the isomerization process. The compounds with a tertiary amino group exist exclusively in the *E*-form; in these compounds, the energy barrier to rotation around the C(1)–N bond decreases with the introduction of the C(1)–Me group and increases with the polarity of the solvent.

The different isomeric forms of the nitroenamines can be easily distinguished by their vibrational and NMR spectra. The vibrational properties characteristic of the nitroenamine system are as follows.

(*a*) A band (the 'enamine band') at 1650–1550 cm^{-1}, strong in the IR and medium or weak in the Raman, assigned as the asymmetric combination of the C(1)=C(2) and C(1)–N stretching modes, with contribution of the in-plane C(1)–H and N–H bending modes when these groups are present. The frequency of this band is displaced to low frequencies by the

introduction of the C(1)–Me group, and by the deuteriation and persubstitution of the amino function. Its frequency is higher in the *Z*-form than in the *E*-form. The two isomers can be more easily distinguished by the much better separated enamine bands of the *N*-deuteriated derivatives.

(*b*) A displacement to low frequency of the $\nu_a(NO_2)$ and $\nu_s(NO_2)$ bands (appearing at 1530–1480 and 1280–1230 cm^{-1}, respectively) relative to the ranges observed in simple nitroalkenes. These are complex bands with contribution of the C=C–H and C(1)–N–H in-plane bendings; however, at variance with the analysis of previous authors, no significant coupling between the $\nu(NO_2)$ modes and the $\nu(C{=}C)$ mode is considered to exist. The $\nu_a(NO_2)$ mode is usually of medium or weak intensity in the IR, and weak in the Raman, while the $\nu_s(NO_2)$ mode is strong both in the IR and in the Raman.

The NMR spectra provide a very straightforward way of distinguishing, and quantifying, the different isomeric and rotameric forms of the nitroenamines studied.

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