Spectral properties and isomerism of nitroenamines. Part 4.[1] β-Amino-α-nitro-α,β-unsaturated ketones

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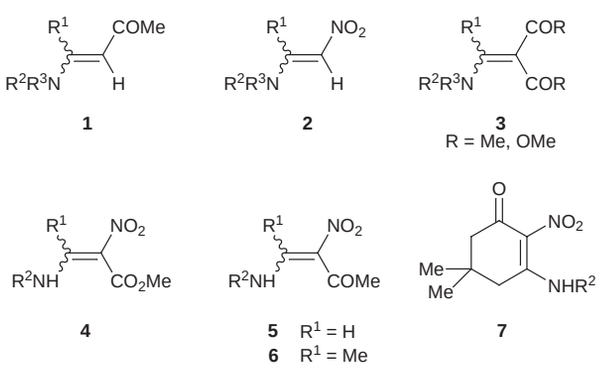
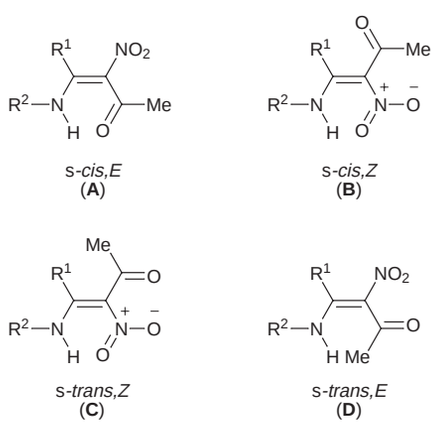
A set of 4-alkyl(aryl)amino-3-nitrobut-3-en-2-ones (5), 4-ethylamino-3-nitropent-3-en-2-one (6), the related 3-alkyl(aryl)amino-2-nitro-2-cyclohexenones (7) with fixed geometry, and the *N*-deuteriated derivatives of some of them, were prepared and studied by vibrational (IR, Raman), NMR and, for some of the compounds, dynamic NMR spectroscopy. The spectra, considered together with the results of theoretical studies, provide a fairly accurate quantitative picture of the isomerism affecting 5 and 6. These compounds exist in solution as a mixture of the *Z*-isomer, having a strong hydrogen bond between the *cis*-related NO_2 and the NH groups, in equilibrium with the *E*-isomer having a still stronger hydrogen-bond between the *cis* C=O and NH groups. The proportions of the two isomers depend on concentration, solvent polarity, number of substituents around the C=C bond and temperature, though the *E*-isomer is always the predominant one. The CH_3CO group of the *Z*-isomers adopts, in the case of compounds 5, a planar s-*cis* conformation around the (C=)C–C(=O) single bond; in the case of the more sterically crowded compound 6, adopts a non-planar quasi-s-*cis* conformation. A low energy barrier between the configurational isomers was measured for compound 6 by dynamic ^1H NMR spectroscopy. Vibrational couplings occur inside these strongly electron-delocalised systems, the extent of which depends on the molecular geometry, affecting mainly the ν(C=C) and ν(C–N) modes, δ(N–H), and to a lesser extent ν(C=O) and $\nu_a(NO_2)$. The two isomeric forms can be readily distinguished and quantified by the spectra, and the energies of the intramolecular hydrogen bonds estimated by the large two-bond isotope effect, $^2\Delta^{13}C(^{2/1}H)$, observed on the C(1) chemical shifts on partially *N*-deuteriated samples. The spectral results for these compounds are discussed in comparison with those obtained for the simpler enaminones 1, nitroenamines 2, as well as for the related β-amino-α-nitro-α,β-unsaturated esters 4.

Introduction

β-Amino-α,β-unsaturated esters and ketones (enaminones, **1**) and 1-amino-2-nitroalkenes (nitroenamines, **2**) are typical push-pull ethylenes which can exist in several configurational and conformational isomeric forms, and, in some cases, tautomeric forms. These structures are well suited for spectral and theoretical studies, and have been the subject of extensive investigation.[1–3] The IR and NMR spectra enable, in most cases, an easy recognition of the different isomers as well as the investigation of the isomeric equilibria and the energy barriers separating the isomers. The IR spectra of **1** and **2** also show characteristic features attributed to mechanical couplings between the functional groups which form these strongly electron-delocalised systems; the groups involved in the couplings and the degree of these couplings depend on the nature of the electron-attracting group (COMe, CO_2R or NO_2) at C(2) and the geometry of the unsaturated system. The spectra and isomerism of enamines having two acyl groups (**3**),[4] or a nitro and an alkoxycarbonyl group (**4**)[3a,5] at C(2), have also been investigated. We extend now these studies to the related 2-acetyl-1-amino-2-nitroalkenes (nitroenaminones, **5** and **6**), and report herein on the vibrational and NMR spectra of a set (see Table 1) of these compounds and, for some of them, dynamic NMR studies. We present a combined discussion of the results thus obtained and those derived from theoretical studies.[5b,c,7] Compounds **5** and **6** can exist in the four isomeric forms **A**–**D**,‡





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‡ For comparative purposes, the numbering system for compounds **2** has been preserved in the formulae of the remaining compounds.

Table 1 Physical and analytical data for compounds **5**–**7**

Compound (Formula)	R^2	Yield (%)	Mp/°C[a]		Found (%) (Required)			
			Observed	Literature	C	H	N	Cl
5a ($C_5H_8N_2O_3$)	Me	70	145–146		41.9 (41.7)	5.6 (5.6)	19.5 (19.4)	
5b ($C_6H_{10}N_2O_3$)	Et	70	95–96		45.3 (45.6)	6.1 (6.4)	17.6 (17.7)	
5c ($C_8H_{14}N_2O_3$)	Bu^n	60	60–61		51.9 (51.6)	7.7 (7.6)	15.3 (15.0)	
5d ($C_{10}H_{16}N_2O_3$)	*cyclo*-C_6H_{11}	85	120–121		56.6 (56.6)	7.6 (7.6)	13.3 (13.2)	
5e ($C_{11}H_{12}N_2O_3$)	Bn	56	124–125		60.0 (6.0)	5.6 (5.5)	12.6 (12.7)	
5f ($C_{10}H_{10}N_2O_3$)	Ph	50	118–119	118–119[b]				
5g ($C_{11}H_{12}N_2O_4$)	*p*-MeO-C_6H_4	55	152–153		55.8 (55.9)	4.9 (5.1)	11.7 (11.9)	
5h ($C_{11}H_{12}N_2O_3$)	*p*-Me-C_6H_4	50	130–131		60.1 (60.0)	5.5 (5.5)	12.7 (12.7)	
5i ($C_{10}H_{12}N_2O_3$)	*p*-Cl-C_6H_4	60	169–170		49.8 (49.9)	3.8 (3.8)	11.7 (11.6)	15.0 (14.7)
5j ($C_{11}H_{12}N_2O_3$)	*o*-Me-C_6H_4	83	123–124		60.1 (60.0)	5.5 (5.5)	12.7 (12.7)	
5k ($C_{10}H_8Cl_2N_2O_3$)	*o*,*p*-Cl_2-C_6H_3	82	167–168		43.9 (43.7)	2.7 (2.9)	10.4 (10.2)	26.0 (25.8)
6 ($C_7H_{12}N_2O_3$)	Et	52	32–33[c]		48.8 (48.8)	7.0 (7.0)	16.2 (16.3)	
7a ($C_9H_{14}N_2O_3$)	Me	75	165–166		54.5 (54.4)	7.0 (7.1)	14.0 (14.1)	
7b ($C_{14}H_{16}N_2O_3$)	Ph	45	135–136	135–136[b]				

[a] All the compounds were recrystallised from EtOH unless otherwise indicated. [b] Ref. 6. [c] Recrystallised from Et_2O.

the other four non-chelated isomers that would derive from a 180° rotation around the C(1)–N bond, as well as the possible tautomeric imino and nitronic acid forms, are expected to be much less stable and unlikely to be involved in the equilibria. Compounds **7** have been included in this study as model compounds for **6** with s-*trans*,*Z* geometry. There are data in the literature[8] on the IR spectra of 4-amino-3-nitropent-3-en-2-ones (**6**) with primary and secondary amino groups. The low values of the ν(N–H) and ν(C=O) frequencies (3170–3120 cm^{-1} and 1605–1568 cm^{-1}, respectively, in $CHCl_3$) and the large chemical shift of the aminic proton (δ 10.62–13.35, in $CDCl_3$) led to the conclusion that these compounds exist in the chelated s-*cis*,*E* form (**A**). To our knowledge there are no data on the spectra of **5** and **7**.

The results now reported show that compounds **5** and **6** exist in solution as equilibrium mixtures of isomers that have characteristic and readily distinguishable spectra. The energy barriers separating the isomers have been measured for some of the compounds, and the results compared with the theoretical predictions. As for the previously studied compounds **1**–**4**, these results also provide an insight into the vibrational couplings affecting **5**–**7**. ^1H and ^{13}C NMR spectral data for some of the compounds studied here were included and briefly discussed in a more general context.[9] A more detailed and thorough discussion considering also the vibrational spectra is presented now, as well as a comparison with the spectra and isomerism affecting enaminones **1**, nitroenamines **2** and the related β-amino-α-nitro-α,β-unsaturated esters **4**.

Experimental

Preparation of compounds

The anilino derivatives **5f** and **7b** were prepared following the literature procedures (see Table 1). Compounds **5a**–**e** were obtained by the transamination reaction (Marchetti and Passalacqua procedure[10]) of **5f** and an excess of the appropriate amine using ether as solvent. The arylamino derivatives **5g**–**k** were prepared following the procedure described for **5f**, using the corresponding arylamine instead of aniline. Compound **6** was obtained as described[8] for other compounds of type **6**. Compound **7a** was prepared by transamination[10] of **7b** with methylamine in diethyl ether. Physical properties, yields and analytical data for the new compounds are included in Table 1.

Solid samples of the *N*-deuteriated derivatives were prepared by repeated recrystallisation of the compounds from EtOD until the IR spectra indicated the absence of N–H absorption. *N*-Deuteriation of samples in solution was performed by shaking with D_2O and separating the organic phase, filtering it, and transferring to the measurement IR cell or NMR tube.

Spectra

General spectroscopic measurements[5a] and dynamic NMR experiments[5c] were performed as described in previous papers of this series. For compound **6**, the procedure of Anet and Baus[11] was applied to estimate the activation parameters for the rotation around the C=C double bond since a complete band-shape analysis was not feasible due to the large difference in population between its two geometrical isomers. Solutions of concentration 0.001–0.3 M depending on the solvent (40–0.03 mm cells) were used for IR measurements and 0.1–0.2 M solutions were used for NMR spectroscopy. Relative intensities of the IR and Raman bands are indicated by the usual abbreviations (see Table 2); overlapping of bands due in most cases to the coexistence of isomers, precluded measurements of extinction coefficients. The reported frequencies (wavenumbers) are estimated to be accurate to within ±3 cm^{-1}, the chemical shifts (δ values, referred to TMS) to within 0.01 ppm, and the coupling constants J to within 0.1 Hz. Secondary deuterium isotope effects on ^{13}C chemical shifts, $^2\Delta^{13}C(^{2/1}H)$, were measured as previously described.[1] The estimated errors in $^2\Delta^{13}C(^{2/1}H)$ values are ±15 ppb. The hydrogen-bond energies were calculated using the expression[12a] $\ln [^2\Delta^{13}C(^{2/1}H)] = 2.817 + 0.084 E_H$, where E_H is the energy of the hydrogen-bond measured in kJ mol^{-1}.

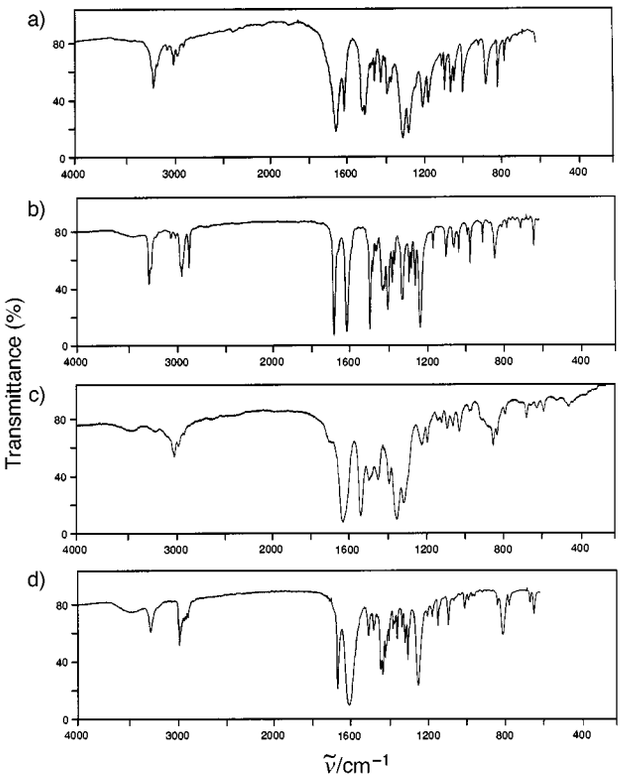


Fig. 1 IR spectra of compounds: (a) **5b**, (b) **5d**, (c) **6** and (d) **7a**, in the solid state (KBr)

Results

Vibrational spectra

Data of the IR and Raman spectra for compounds **5**–**7** and their *N*-deuteriated derivatives appear in Table 2. The spectra of 4-ethylamino-3-nitrobut-3-en-2-one (**5b**) and of 4-cyclohexylamino-3-nitrobut-3-en-2-one (**5d**) are particularly informative and will be considered first. The IR spectrum of **5b** in the solid state (Fig. 1) shows two bands in the double-bond region, at 1643 and 1600 cm^{-1}, assigned as a perturbed ν(C=O) and a vibration having a strong component of ν(C=C), respectively; a band at 3195 cm^{-1} is assigned as the ν(N–H) of the amino group involved in a strong hydrogen-bond. On the other hand, **5d** (Fig. 1) shows two bands in the double bond region, at 1673 and 1605 cm^{-1}, and a band at 3265 cm^{-1} which are assigned in the same manner.

Comparison of the frequency values suggests that the compounds crystallise in two different isomeric forms, **5b** having the C=O and NH groups in *cis*-disposition and strongly hydrogen-bonded (s-*cis*,*E* isomer, **A**), and **5d** having the NO_2 and NH *cis* and also hydrogen-bonded (s-*cis*,*Z* isomer or s-*trans*,*Z* isomer, **B** or **C**). On dissolving the samples, each of the bands appears split into two components (see Table 2), the relative intensities of which depend on concentration and on the polarity of the solvent, thus indicating that equilibria are established between the *E* and *Z* configurational isomers. Likewise, the IR spectra of solid samples (KBr pellets) of the *n*-butyl derivative **5c** already show the two sets of bands; those assigned to the *Z*-isomer predominate at room temperature; on heating the KBr pellet (1 h at 80 °C) an equilibrium is reached in which the bands attributed to the s-*cis*,*E* isomer have increased considerably at the expense of the other, and are the ones predominating. In solution, the spectra of this compound are similar to those of **5b** and **5d**. The spectra of the remaining compounds **5** (Table 2) indicate that they also crystallise as mixtures of the *E* and *Z* isomers, and that in solution they exist as solvent and concentration dependent equilibrium mixtures of the two forms.

The infrared ν(C=O) bands (at 1678–1665 cm^{-1}) of the *Z*-isomer of compounds **5** are of medium-weak intensity irrespective of the polarity of the medium, while those of the s-*cis*,*E* isomer (**A**) (at 1657–1635 cm^{-1}) are always very strong, thus suggesting that the latter is always the one predominating in solution. The corresponding mixed ν(C=C) bands appear rather close, at 1615–1595 cm^{-1} and 1602–1580 cm^{-1}, respectively, and are medium-weak. Increasing the polarity of the medium results in an increase of the bands assigned to the *Z*-isomer, which is therefore considered to be the most polar. *N*-Deuteriation affects the frequency of the ν(C=O) bands, generally more in the case of *Z*-isomer ($\Delta\nu$ 0 to −12 cm^{-1}) than in isomer **A** ($\Delta\nu$ 0 to −8 cm^{-1}), and still more the frequency of the C=C bands ($\Delta\nu$ −4 to −18 cm^{-1} for the *Z*-isomer and −24 to −40 cm^{-1} for isomer **A**). Thus, as in the parent compounds **1**, mechanical couplings between the ν(C=O), ν(C=C), δ(N–H), and probably the ν(C–N) vibrations occur in these compounds. In nitroenamines **2** and 3-amino-2-nitroacrylic esters **4** (R^1 = H), the magnitude of the isotope effect has been related to the presence and strength of the hydrogen-bond increasing with it,[1,5a] and on this basis the s-*cis*,*E* isomer (**A**) of **5** with the C=O···H–N bond is the strongest chelate, as suggested also by the ν(C=O) and ν(N–H) frequency values. For brevity, the mixed ν(C=C) band is referred to hereafter and in Table 2 as the 'enamine band', and the mixed carbonyl band simply as 'ν(C=O)'. Due to the different isotopic effect affecting the enamine band of the two isomers, the corresponding mixed bands of the *N*-deuteriated derivatives, mainly ν(C=C) + ν(C–N), appear well separated and readily distinguished. In the s-*cis*,*E* isomer (**A**) the ν(C=O) is stronger than the enamine band, while in the *Z*-isomer the two bands are of similar intensities; in the Raman spectra the enamine bands are generally medium-weak and stronger than the ν(C=O) bands.

The IR spectra of 4-ethylamino-3-nitropent-3-en-2-one (**6**) show in the solid state (Fig. 1) and in solution a very strong band at 1605–1603 cm^{-1} assigned as the ν(C=O) of the s-*cis*,*E* isomer, with a strong C=O···H–N hydrogen-bond, and a weak absorption at 1675–1665 cm^{-1} which is tentatively assigned as the ν(C=O) of a small amount of the more polar *Z*-isomer (see below), with a weaker NO···H–N hydrogen bond. The stronger band has two shoulders at 1590–1587 cm^{-1} and 1560 cm^{-1} (at 1590 and 1561 cm^{-1} in Raman), sensitive to the *N*-deuteriation, assigned as the enamine band of the *Z*- and *E*-isomers, respectively. In the *N*-deuteriated derivative, the infrared ν(C=O) band is much sharper and appears practically at the same frequency ($\Delta\nu$ −3 cm^{-1} in $CHCl_3$), and the shoulders are replaced by two weak ν(C=C) + ν(C–N) bands, at 1560 and 1518 cm^{-1} in $CHCl_3$ (at 1567 and 1527 cm^{-1} in Raman). The large isotope effect observed for the enamine band of the *E*-isomer, better measured in the Raman spectra ($\Delta\nu$ −33 to −42 cm^{-1}), is the one anticipated for the strongly hydrogen-bonded s-*cis*,*E* isomer (**A**) by comparison with that observed in compounds **5**.

The IR spectrum of model compound **7a**, with fixed s-*trans*,*Z* geometry, shows in the solid state the ν(C=O) as a sharp, medium intensity band at 1648 cm^{-1}, and the enamine band as a very strong, broad absorption, centred at 1588 cm^{-1} (Fig. 1). The ν(C=O) frequency is not appreciably affected by *N*-deuteriation, while the enamine band shows a fairly large displacement (−10 to −22 cm^{-1}) to lower frequency. As Fig. 1 shows, the pattern of IR absorption of **7a** is very different from that of the *Z*-isomer of **5d** and from that of *E*-**6**, thus indicating that the latter two compounds have a conformation (s-*cis*) around the (C=)C–C(=O) single bond different from that of **7**. The *Z*-isomer of compounds **5** should then be formulated as s-*cis*,*Z* (**B**).

The $\nu_a(NO_2)$ vibration of **5** and **6** appears as the band, very strong in IR and medium-weak in Raman, at 1518–1485 cm^{-1}. The splitting of this band into two close bands observed for some of the compounds is attributed to the coexistence of

Table 2 IR and Raman (*in italics*) frequencies (cm^{-1}) of compounds **5**–**7** and their *N*-deuteriated derivatives

		ν(N–H)[a]		ν(N–D)[a,b]		ν(C=O)		Enamine band		ν(C=C) + νC–N)[b]			
Compound	Medium	*Z*	*E*	*Z*	*E*	*Z*	*E*	*Z*	*E*	*Z*	*E*	$\nu_{as}(NO_2)$	$\nu_s(NO_2)$
5a	CCl_4	3285vw[c,d] 3260sh[e]	3180vw[d]			1674w	1648vs	1611w	1592w			~1510m	1312vs
	$CDCl_3$	3290vw	3185vw			1673m	1653vs	1610w	1596w			1511s	1308vs
	b			~2430vw	2350vw	1665w	1648vs			1603w	1568vw	1504s	1309vs
	$[^2H_6]$DMSO	3260sh	3195w			1665sh	1650vs	1609m	1597sh			1497s-vs	1304vs
	KBr	*f*	3193m			*f*	1657vs	1610sh[f]	1601s			1500vs	1290vs
	b				2385m		1654vs				1577m	1487vs	1310vs
	Solid		*3200*vw				*1657*w	*1612*vvw[f]	*1577*m			*1503*w	*1293*vs
	b				*g*		*1654*w			*1604*vw[f]	*1566*m	*g*	*1292*vs
5b	C_6H_{12}	*h*	*h*			1672w	1644vs	1610w	1590m			1513vs 1495sh	1312vs
	CCl_4	3285vw[d] 3255vw[e]	3195vw[d]			1672m	1645vs	1610w	1590m			1513vs 1495sh	1314vs
	b			2420vw	2345vw	1667w	1642vs			1595w	1553w	1509vs 1495sh	1311vs
	C_2Cl_4	3275vw	3195vw			1674w	1644vs	1610w	1593m			1514vs 1500sh	1314vs
	b			2420vw	2345vw	1670w	1643vs			1597w	1556w	1512vs 1500sh	1313vs
	$CDCl_3$	3280vw	3190vw			1670m	1645vs	1607w	1592w-m			1505s-vs	1311vs
	b			2420vw	2340vw	1662sh	1642vs			1595w	1558w	1503vs	1310vs
	$CHCl_3$	*g*	*g*			*1667*vw,p	*1644*w,p	*1605*sh,pp	*1587*w,pp			*i*	*1311*vs,pp
	b			*g*	*g*	*1659*vw,p	*1640*w,p			*1594*vw,pp	*1556*w,pp	*i*	*1307*vs,pp
	$[^2H_6]$DMSO	3260sh	3195vw			1665m	1646s	1603m	1593sh			1495s	1307vs 1275m
	b			*g*	2375w	1657sh	1644s			1599m	1570w	1493s	1307vs 1275sh
	KBr		3195m				1643vs		1600s			1507s 1491s	1295vs 1265vs
	b				2388m		1640vs				1573m	1500s 1487s	1294vs 1264vs
	Solid		*3220*vw				*1643*w	*1609*vvw[f]	*1577*m			*1507*vw *1484*vw	*1290*vs *1264*m
	b				*2395*vw		*1639*w			*1603*vvw[f]	*1561*m	*1501*vw *1481*vw	*1292*vs *1265*m
5c	C_6H_{14}	*h*	*h*			1676w 1668w[j]	1648vs	1610w	1596m			1518s 1504sh	1315vs 1290sh
	C_6H_{12}	*h*	3195vw			1674w 1663sh[j]	1644vs	1610w	1593m			1515s 1500sh	1312vs 1290sh
	CCl_4	3285vw 3250vw[c]	3195vw			1673w	1645vs	1610w	1592m			1513s 1500sh	1313vs 1290sh
	$CDCl_3$	3285vw	3195vw			1667m	1647vs	1603w,sh	1590w			1504s	1312vs 1295sh
	b			2425sh	2350vw	1661w	1640vs			1596w	1557w	1500s	1308vs 1295sh
	$CHCl_3$	*h*	*h*			*1669*vw,p	*1646*w,p	*1605*sh,pp	*1589*w,pp			*i*	*1311*vs,pp
	b			*h*	*h*	*1662*vw,p	*1641*w,p			*1597*vw,pp	*1557*w,pp	*i*	*1309*vs,pp
	$[^2H_6]$DMSO		3190vw			1665m	1649s	1603m	1592sh			1495s	1307vs 1297sh
	KBr[k]	3270m 3245m[e]	3205w			1669vs	1650s,sh	1595s	1605sh			1502s 1485s	1312sh 1295vs
	Solid[k]	*3265*vw				*1672*m	*g*	*1589*s	*1602*m			*1485*sh *1477*w	*1313*m *1287*m-s
5d	CCl_4	3280vw	3185vw			1671m	1644vs	1605sh	1590m			1512vs 1498sh	1312vs 1285sh
	b			2420vvw	2340vw	1666w-m	1639vs			1590m	1550m	1508vs 1483sh	1311vs 1290sh
	C_2Cl_4	3280vw[d]	3185vw[d]			1670w	1643vs	1605sh	1590m			1512vs	1313vs
	b				2340vw	1664w	1636vs			1587w	1550m	1504vs	1310vs
	$CDCl_3$	3280vw	3190vw			1666m	1644vs	1600sh	1590m			1505s	1309vs
	b				*h*	1659m	1636vs			1590m	1550w-m	1500s	1305vs
	$CHCl_3$	*h*	*h*			*1667*vw,p	*1645*w,p	*1600*sh,pp	*1590*w,pp			*i*	*1313*vs,pp
	b				*h*	*1663*vw,p	*1639*w,p			*1593*vw,pp	*1554*w,pp	*i*	*1310*vs,pp
	$[^2H_6]$DMSO	*g*	3185vw			1666m	1643vs	1602m	1593sh			1500s	1309vs
	KBr	3265m 3245w[e]				1673vs		1605vs				1486vs	1312s
	b			2420m		1661vs				1593vs		1463s	1292vs
	Solid	*3265*vw *3243*vw[e]				*1664*m		*1596*s				*1485*w	*1303*m
	b			*2420*vw		*1658*m				*1587*s		*1475*w	*1284*vs
5e	CCl_4	3285vw[d]	3190vw[d]			1673w	1642vs	1603w	1591m			1514s-vs 1498sh	1313vs 1293sh
	$CDCl_3$	3285vw	3190vw			1669m	1645vs	1605sh	1593m			1510vs	1312vs
	b			~2430vw	~2350vw	1665w	1640vs			1597m	1560w	1505vs	1309vs
	$[^2H_6]$DMSO	3280vvw	3195vw			1666m-s	1645s-vs	1603m	1590sh			1498s-vs	1306vs
	KBr[k]	3265w 3228w[e]	3198w			1665vs	1645vs	1603s	1584m			1499vs 1480s	1291vs
	Solid[k]	*h*	*h*			*1668*w	*1645*w	*1606*m	*1580*s			*1506*w *1486*w	

Table 2 (*Contd.*)

Compound	Medium	ν(N–H)[a]		ν(N–D)[a,b]		ν(C=O)		Enamine band		ν(C=C) + νC–N)[b]			
		Z	*E*	*Z*	*E*	*Z*	*E*	*Z*	*E*	*Z*	*E*	$\nu_{as}(NO_2)$	$\nu_s(NO_2)$
5f	CCl_4	*l*	<3100br[d]			1675w	1644vs	1605sh	~1600[m]			1517s	1296vs
	$CDCl_3$	*l*	~3100br			1670w-m	1642vs	1613sh	~1602[m]			1514s	1300vs
	b			*l*	*l*	1667w	1639vs			*m*	1547s	1512s	1298vs
	[$^2H_6$]DMSO		~3100br			1669m	1639s	1607sh	~1600[m]			1495s	1300vs
	KBr		*l*			1673sh	1650vs	1618sh	1605[n]			1503s	1305vs
5g	C_2Cl_4	*l*	*l*			1675w	1640vs	~1604[m]	~1582[m]			1512vs[n]	1295vs
	b			*g*	*g*	1673w	1636vs			~1582[m]	1546w	1512vs[n]	1294vs
	$CDCl_3$	*g*	*g*			1666w	1639vs	~1602[m]	~1581[m]			1503vs[m]	1297vs
	b			*g*	*g*	1664w	1634vs			1591w	1549m-s	1503vs[m]	1295vs
	$CHCl_3$	*g*	*g*			*1664*vw	*1636*w	*~1600*sh	*1583*w			*1500*vw	*l*
	b			*g*	*g*	*~1659*vw	*1629*w			*1591*vw-w	*1548*w	*1500*vw	*l*
	[$^2H_6$]DMSO	*h*	*h*			1666w	1639s	1603sh	~1580[m]			1499s	1298vs
	KBr		~3080br			1667sh	1637vs		1598s[n]			*m*	1294vs
	Solid		*g*			*1661*vvw	*1627*vs		*m*			*1499*vw	*1301*m
5h	$CDCl_3$	*g*	<3100			1669w	1640vs	~1604[m]	~1578[m]			1505s	1299vs
	b			*g*	*g*	1665w	1638vs			~1509sh	1549m	1504s	1299vs
	KBr		*l*				1634vs		1605s[n]			1497s	1294vs 1283vs
	Solid		*g*				*1635*m		*m*			*1495*w	*1295*vs
5i	C_2Cl_4	*g*	*g*			1678w	1639vs	1595sh	*m*			*n*	1292vs
	b			*g*	*g*	1677w	1639vs			1595sh[o]	1542w	*n*	1292vs
	$CDCl_3$		~3100vw			1671w	1640vs	1595sh	*m*			1493s[o]	1294vs
	b				*h*	1664w	1634vs			1583w[o]	1545s	1493s[o]	1295vs
	[$^2H_6$]DMSO		~3060br			1668m	1637s-vs	1595sh	*m*			1492vs	1298vs
	KBr	*g*	*g*			1665sh	1633vs		1604s[n]			1492vs	1295vs
	Solid	*g*	*g*			*g*	*1637*m		*1607*sh[m]			*m*	*1295*m
5j	C_2Cl_4	*g*	<3100			1676w	1638vs	1615w[o]	1583sh			1519s	1307vs 1284vs
	b			*g*	~2330vw	1673w	1637vs			1578sh	1543vs	1517s	1305vs 1295vs
	$CDCl_3$	*h*	*h*			1670w	1638vs	1615w[o]	1583sh			1511s	1308vs 1288vs
	b			*g*	*g*	1666w	1632vs			1575m	1545s	1510s	1305vs 1292vs
	[$^2H_6$]DMSO		<3100			1665w	1635vs	1612w	1580sh			1507s	1308vs 1292vs
	KBr		*g*				1639vs		1594s			1510s	1290vs
	Solid		*g*				*1635*w *1628*w		*m*			*1512*[n]	*1285*w
5k	$CDCl_3$		~3100vvw			1671sh	1639vs	*m*	1600[n]			1513m	1295vs[o]
	b				*g*	1671vw	1638vs			1590vvw	1545s	1513m	1302vs
	$CHCl_3$		*g*			*1672*vvw	*1636*w	*m*	*m*			*l*	*1319*s
	b				*g*	*1672*vvw	*1636*w			*m*	*1545*w	*l*	*l*
	[$^2H_6$]DMSO		*g*			1672vw	1636vs		1600s[n]			1512m-s	1302vs[o]
	KBr		3090vw[o]				1646vs		1606s[n]			1500s	1302vs[o]
	Solid		*3072*vw[o]				*1633*w		*1602*sh			*1505*sh	*1300*m
6	CCl_4		3200vw[e]			1665vw	1604vs	1590sh	1560sh			1514vs	1327vs
	b				2255vw,br	1665vw	1604vs			*i*	*g*	1502vs	1327vs
	$CDCl_3$		3195vw			1665vw	1603vs	1590sh	1560sh			1511vs	1322vs
	$CHCl_3$[b]				2255vw,br	1665vw	1600vs			1560sh[o]	1518sh[o]	1493vs	1322vs
	$CHCl_3$		*g*			*g*	*1601*w	1590sh	*1560*sh			*1510*w-m	*1326*vs
	b				*g*	*g*	*1599*w			*1567vw*	*1527m*	*1499*w	*1323*vs
	[$^2H_6$]DMSO		*g*			1675vw	1605vs	1590sh	1560sh			1510vs	1324vs
	KBr		3195vw			1665sh	1605vs	1587sh	1560sh			1511vs	1323vs
	Solid		*g*				*1611*w		*1561*w			*1500*w	*1323*vvs
7a	$CDCl_3$	~3220vw,br					1664m-s		1590vs			1503m	1200m-s
	b			2400w			1662m-s			1568vs		1467m	1277m-s
	[$^2H_6$]DMSO	3230w					1655m-s		1585vs			1494w	1217m
	b			2395vw			1655m-s			1570vs		1467w	1282m
	KBr	3255w					1648s		1588vs			1493m	1232s
	b			2420w			1645s			1578vs		1445m	1283s
	Solid	*~3240*vw					*1643*s		*1590*m			*1488*w	*1232*vs
	b			*2420*w			*1640*s			*1578*s		*1450*w	*1279*vs
7b	KBr	3150vw					1668s		1572vs			1487m	1282m

[a] Assigned to the intramolecularly bonded NH (or ND) group. [b] Measured in the *N*-deuteriated derivative. [c] Abbreviations: s, strong; m, medium; w, weak; sh, shoulder; v, very; br, broad; p, polarised; pp, partially polarised. [d] Measured at very dilute solution. [e] Probably a combination band with contribution of δ(N–H). [f] Small proportion of *Z*-form. [g] Not detected. [h] Not measured. [i] Overlapped by the medium. [j] Tentatively assigned to the s-*trans*,*Z*-conformation. [k] This compound generally crystallises as a mixture of both isomers. [l] Not assigned. [m] Overlapped by the ν(C=C) ring band. [n] Contribution of ring ν(C=C). [o] Tentative assignment.

forms **A** and **B** in the samples. Thus, the spectrum of the butylamino derivative **5c** in KBr pellets (mixture of the two isomers) shows bands at 1502 and 1485 cm^{-1} due to the **A** form and the **B** form, respectively, and on heating the sample the relative intensities varied in the same way as varied the relative intensities of the ν(C=O) bands of **A** and **B** described above. A

small isotope effect ($\Delta\nu$ 0 to -23 cm^{-1}) was observed on *N*-deuteriation, indicative that the coupling also affects this vibration.

The $\nu_a(NO_2)$ vibration of compounds **7** appears as a medium-weak band at 1503–1493 cm^{-1} and is more strongly affected by *N*-deuteriation ($\Delta\nu$ -27 to -48 cm^{-1}) than those of **5** and **6**, thus indicating the pattern of couplings is different in this compound than in their open-chain analogues (see above also).

NMR spectra

The ^{1}H and ^{13}C NMR spectra of **5** (Table 3) show, at room temperature, separated signals for two geometrical isomers in equilibrium. The *E*-configuration is assigned to the major isomer on the following basis: (*i*) the larger chemical shift of H(1) due to the stronger deshielding effect of the *cis*-NO_2 group as compared to the COMe group; (*ii*) the value of the ^3JC(=O),H(1) coupling constant across the carbon–carbon double bond which has been measured for compounds **5a** and **5f**, being larger for the major isomer (see Table 3) as expected for a *trans*-disposition of both nuclei. These results confirm the assignment made on the basis of the vibrational spectra.

Compound **6** shows a single set of signals in the ^{1}H NMR spectra (Table 3) at room temperature indicative of the presence of a single isomer in solution or a very low barrier to interconversion of the two configurational isomers. The ^{1}H NMR spectra in $CHCl_2F$–$CHClF_2$ (1 : 1) show dynamic behaviour at low temperatures, and splitting of the signals of the COMe and CH_3–C(1) groups is observed at temperatures below 152 K. Due to the partial overlapping of the signals, the relative abundance of the isomers (98 : 2) was calculated by adjusting Lorentzian lines to the experimental spectrum. The major isomer is assigned the s-*cis*,*E*-configuration (**A**) on the basis of the vibrational spectra. In accordance with that, the CH_3C(1) signal of this isomer appears at lower field than that of the s-*cis*,*Z* isomer due to the stronger deshielding effect of the *cis*-NO_2 group; the corresponding sharper CH_3–C(=O) signals appear at still lower fields and in the opposite order (see Table 3).

The ^{1}H NMR spectra of compounds **5** show that the amount of s-*cis*,*Z* isomer (9–32%; the lowest values corresponding to the two *ortho*-substituted anilino derivatives **5j**,**k**) increases with the polarity of the medium, thus confirming that it is the most polar isomer. The high chemical shift of the NH protons (δ 9.16–12.68) and the value of the ^3JNH,H(1) coupling constants (13.3–16.0 Hz) are indicative of the rigid *trans*-disposition of H(1) and the amino proton and the presence of a strong intramolecular hydrogen-bond in both isomers. The higher δ_{NH} value observed for the s-*cis*,*E* isomer, in spite of the larger *cis*-deshielding effect of the NO_2 group on the aminic proton operating in the s-*cis*,*Z* isomer, indicates that the former has the strongest intramolecular hydrogen-bond. The average chemical shift of the aminic proton of **6** is higher than those of the two geometrical isomers of its lower homologue **5b** (see Table 3). This fact shows that methyl substitution at C(1) increases the strength of the intramolecular hydrogen-bond due to a buttressing effect, as previously observed for nitroenamines **2** (R^1 = H, Me)[1] and for **4** (R^1 = H, Me).[5e] Cyclic compounds **7** (Table 3), with fixed s-*trans*,*Z* geometry, have δ_{NH} values lower than that of their acyclic analogue **6**, a result in agreement with the fact that the two compounds differ in configuration and conformation.

The ^{13}C NMR spectra of compounds **5** were assigned on the basis of the J_{CH} couplings and the relative intensities of the signals, which parallel those in the corresponding ^{1}H NMR spectra. As for other enamines, $\Delta\delta = \delta_{C(1)} - \delta_{C(2)} > 0$ and large (Table 3) as a consequence of the strong polarisation of the C=C double bond typical of push-pull ethylenes.[9] The $\Delta\delta$ values are larger for the *E* than for the *Z* configurational isomers, and increase with the electron donor character of the amino group, being higher for the alkylamino than for the arylamino derivatives; they increase also with the polarity of the solvent, being higher in [$^2H_6$]DMSO than in $CDCl_3$ (see compound **5a**, Table 3).

The ^{13}C NMR spectrum of **6** shows single signals for each type of carbon, assigned to the s-*cis*,*E* isomer in fast equilibrium with a small amount of the s-*cis*,*Z* isomer. The $\Delta\delta$ value is larger than that of its lower homologue **5b** as a consequence of the different deshielding effect introduced by the methyl group at C(1) on the signals of the two olefinic carbons. By contrast, in model compounds **7** (fixed s-*trans*,*Z* geometry) the value of $\Delta\delta$ is larger than that of **6** (mainly s-*cis*,*E*), *i.e.* the opposite to that observed for the lower homologues **5** (see above). An explanation for this apparent inconsistency is the different configuration and conformation around the (C=)C–C(=O) single bond of both compounds.

As for other nitroenamines,[1,5a,b,9,12c–e] the relative strengths and energies of the intramolecular hydrogen-bond in the *E* and *Z* isomers of **5** and **6**, and in compound **7**, can be conveniently estimated by means of the two-bond isotope effect on the ^{13}C chemical shift, $^2\Delta^{13}C(^{2/1}H)$, produced on C(2) upon *N*-deuteriation.[12a] The values of this parameter for **5**–**7** and the calculated energies of the hydrogen-bonds are shown in Table 4. The data in Table 4 show that the hydrogen-bond is stronger in the *E*-isomer than in the *Z*-isomer, with an energy difference of 0.3–4.2 kJ mol^{-1}. The difference between the isotopic effects observed for **6** and **7** clearly indicates the different configuration of both compounds. There is a reasonably good linear correlation between the $^2\Delta^{13}C(^{2/1}H)$ values and the chemical shifts of the aminic proton, eqn. (1). In this equation, *r* is the correlation

$$^2\Delta^{13}C(^{2/1}H) = 4.07 \times 10^{-2}\,\delta_{NH} - 0.222 \qquad (1)$$
$$n = 25,\ r = 0.933,\ \text{sd} = 0.04,\ F = 155$$

coefficient, *n* is the number of data points, sd is the standard deviation of the estimate and *F* is the Fisher *F*-statistic. A good linear correlation could also be found for **5f** and *para*-substituted anilino derivatives **5g**–**i** between $^2\Delta^{13}C(^{2/1}H)$ and the $\Delta\delta$ values, eqn. (2).

$$^2\Delta^{13}C(^{2/1}H) = 1.056 - 3.67 \times 10^{-2}\,\Delta\delta \qquad (2)$$
$$n = 4,\ r = 0.997,\ \text{sd} = 0.01,\ F = 302$$

Compounds **6** and **7a** show a three-bond isotopic effect for the C(2) signal. A small long-distance isotopic effect, $^4\Delta^{13}C(^{2/1}H)$, was also observed for the carbonyl group carbon of the *E* isomers of compounds **5**.

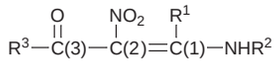
A dynamic ^{1}H NMR study for compounds **5a** and **6** gave the energy activation parameters for the conversion of the *Z*-isomer into the *E*-isomer. For **5a** in *o*-dichlorobenzene solution, a complete bandshape analysis (Fig. 2) gave the following activation parameters at the standard temperature 298.2 K: $\Delta G^{\ddagger}$ 79.4 ± 0.6 kJ mol^{-1}, $\Delta H^{\ddagger}$ 55.5 ± 2.7 kJ mol^{-1} and $\Delta S^{\ddagger}$ -80 ± 5.9 J mol^{-1}. The free-energy of activation, $\Delta G^{\ddagger}$, found for **6** in $CHCl_2F$–$CHClF_2$ (1 : 1), at the coalescence temperature 189 ± 2.5 K, was 42.8 ± 2.5 kJ mol^{-1}. For both compounds the couplings with the NH proton were observed even at the highest temperatures studied (447 K for **5a** and 303 K for **6**) thus indicating that the isomerisation takes place without the ionisation of this proton, *i.e.* it follows a thermal mechanism.[13]

Theoretical calculations

It is instructive to compare the empirical spectral results with those of theoretical studies. For the sake of simplicity, the calculations have been performed on the simplest compounds having a primary amino group, *i.e.* **5** and **6**, R^2 = H. The results are still significant for the purpose of the present discussion as it has been shown[5b] that the relative energies of the isomers remain unchanged upon *N*-methyl substitution.

Table 5 shows the relative *ab initio* 3-21G calculated energy of the three most stable s-*cis*,*E* (**A**), s-*cis*,*Z* (**B**) and s-*trans*,*Z* (**C**)

Table 3 ^{13}C and ^{1}H NMR data for compounds **5**–**7** at 293 K



Compound	Solvent	Isomer (%)	$\delta_C(J_{CH})$ C(1)	C(2)	C(3)	R^3	$\Delta\delta$	$\delta_H(J_{HH})$ R^1	R^3	NH
5a	$CDCl_3$	*Z* (18)	154.3 (173.3)[a]	126.0 (1.4)[b]	190.9	30.6	28.3	8.21 (15.4)[c]	2.61[d]	9.77[e]
		E (82)	158.0 (169.3)[a]	126.8 (5.0)[b]	194.6	31.0	31.2	8.59 (13.8)[c]	2.61[d]	10.68[c]
	$[^2H_6]$DMSO	*Z* (27)	154.2	125.2	190.4	31.2[d]	29.0	8.27[e]	2.45[d]	10.50[d,e]
		E (73)	158.0	126.0	192.7	31.2[d]	32.0	8.54[e]	2.45[d]	10.50[d,e]
5b	C_6D_6	*Z* (10)						7.72 (15.3)[c]	2.60	9.16[e]
		E (90)						7.96 (14.2)[c]	2.56	10.32[e]
	$CDCl_3$	*Z* (19)	152.8 (172.2)[a]	125.6	191.2	30.7	27.2	8.25 (15.3)[c]	2.61	9.88[e]
		E (81)	156.4 (171.0)[a]	126.4	194.6	31.3	30.0	8.63 (14.3)[c]	2.62	10.87[e]
5c	$CDCl_3$	*Z* (20)	153.2	125.5	191.5	30.8	27.7	8.22 (15.3)[c]	2.61	9.81[e]
		E (80)	156.9	126.5	195.0	30.8	30.4	8.60 (14.4)[c]	2.62	10.84[e]
5d	$CDCl_3$	*Z* (19)	151.2	125.5	191.6	30.8	25.7	8.27 (15.3)[c]	2.61	9.89[e]
		E (81)	154.9	126.5	194.9	31.5	28.4	8.65 (15.6)[c]	2.62	10.91[e]
5e	$CDCl_3$	*Z* (19)	153.0	*f*	191.5	30.8	—	8.30 (15.6)[c]	2.60[d]	10.00[e]
		E (81)	156.8	127.0	195.1	31.4	29.8	8.66 (14.1)[c]	2.60[d]	11.03[c]
	$[^2H_6]$DMSO	*Z* (32)						8.38[e]	2.46[d]	10.90[d,e]
		E (68)						8.84[e]	2.46[d]	10.90[d,e]
5f	$CDCl_3$	*Z* (14)	145.5 (169.8)[a]	*f* (1.8)[b]	191.0	30.8	—	8.67 (16.0)[c]	2.66	11.34[e]
		E (86)	149.1 (168.4)[a] (2.6)[g]	128.2 (5.4)[b]	195.3	31.5	20.9	9.04 (13.8)[c]	2.69	12.49[e]
	$[^2H_6]$DMSO	*Z* (30)						8.42 (15.2)[c]	2.54[d]	11.56[e]
		E (70)						8.99 (14.0)[c]	2.54[d]	12.18[e]
5g	$CDCl_3$	*Z* (16)	145.8	*f*	191.4	30.9	—	8.48 (15.0)[c]	2.66	11.43[h]
		E (84)	149.4	127.9	195.4	31.5	21.5	8.96 (13.7)[c]	2.68	12.54[h]
5h	$CDCl_3$	*Z* (14)	145.7	*f*	191.4	30.9	—	8.64 (14.8)[c]	2.66	11.38[h]
		E (86)	149.3	128.1	195.5	31.5	21.2	9.01 (13.8)[c]	2.68	12.45[h]
5i	$CDCl_3$	*Z* (15)	145.4	*f*	191.2	30.8	—	8.60 (14.8)[c]	2.66	11.30[h]
		E (85)	149.1	128.5	195.7	31.5	20.6	8.99 (13.7)[c]	2.68	12.46[h]
5j	$CDCl_3$	*Z* (11)	146.2	*f*	191.4	30.8	—	8.66 (14.7)[c]	2.67	11.55[h]
		E (89)	149.6	*f*	195.7	31.5	—	9.06 (13.6)[c]	2.71	12.68[h]
5k	$CDCl_3$	*Z* (9)	144.0	*f*	191.1	30.5	—	8.58 (14.4)[c]	2.67	11.57[h]
		E (91)	147.9	*f*	195.6	31.2	—	8.99 (13.3)[c]	2.71	12.81[h]
6	$CDCl_3$	*E*/*Z*[i]	164.7	130.0	192.4	28.6	34.7	2.30	2.38	12.08
	$CHClF_2$–$CHCl_2F$[j]	*Z* (2)						2.21[e]	2.45[e]	
		E (98)						2.31[e]	2.41[e]	
7a	$CDCl_3$	*Z* (100)	165.5	123.6	185.6		41.9			10.66
7b	$CDCl_3$	*Z* (100)	163.2	124.2	186.0		39.0			11.81

[a] $^1J_{CH}$. [b] $^3J_{C(=O),H(1)}$. [c] $^3J_{H(1),NH}$. [d] Averaged signal for both configurational isomers. [e] Broad singlet. [f] Not found. [g] $^2J_{C(2),H(1)}$. [h] Doublet. [i] Averaged spectrum of *E* (major) and *Z* configurational isomers in rapid equilibrium. [j] At 152 K.

Table 4 Deuterium isotope effects on ^{13}C nuclear shieldings for compounds **5**–**7**[a] in $CDCl_3$

Compound	Isomer	$^2\Delta C(1)$	$^3\Delta C(2)$	$^4\Delta CO$	E_H[b]
5a	*Z*	0.188			29.0
	E	0.193			29.3
5b	*Z*	0.176			28.2
	E	0.204			30.0
5c	*Z*	0.183			28.7
	E	0.212		0.033	30.4
5d	*Z*	0.183			28.7
	E	0.209		0.040	30.4
5e	*Z*	0.172			27.9
	E	0.245		0.037	32.1
5f	*Z*	0.241			31.9
	E	0.291			34.2
5g	*Z*	0.223			31.0
	E	0.267		0.042	33.1
5h	*Z*	0.257			32.7
	E	0.280		0.041	33.7
5i	*Z*	0.278			33.6
	E	0.300		0.043	34.5
5j	*Z*	0.274			33.4
	E	0.292		0.052	34.2
5k	*Z*	0.250			32.4
	E	0.301		0.068	34.6
6	*E*/*Z*[c]	0.265	0.029		33.1
7a	*Z*	0.209	0.026		30.2
7b	*Z*	0.243			32.0

[a] Isotope effects produced by *N*-deuteriation, defined as $^n\Delta X = \delta X(N\text{-}H) - \delta X(ND)$ (in ppm), *n* being the number of intervening bonds between the deuterium and the observed nucleus, X. [b] Hydrogen bond energies calculated according to the expression[12c] $\ln [^2\Delta^{13}C(^{2/1}H)] = 2.817 + 0.084\ E_H$. [c] Averaged spectrum of *E*- (major) and *Z*-configurational isomers in rapid equilibrium.

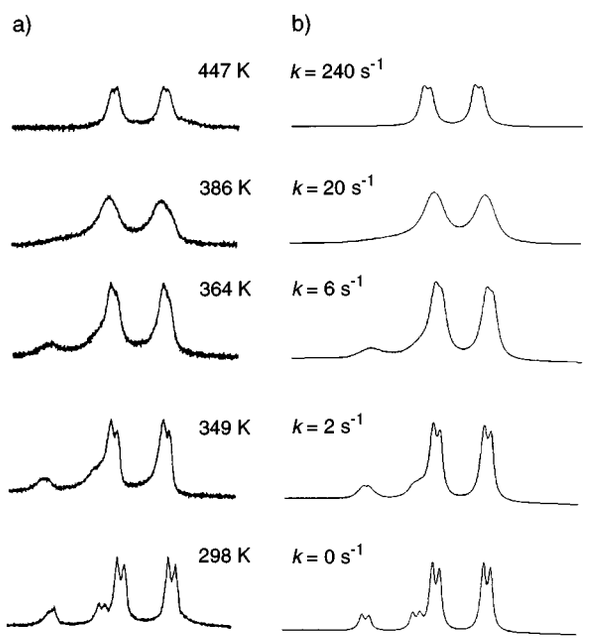


Fig. 2 (a) Temperature dependence of the ^1H NMR signal of the N–CH_3 group (1.6–1.5 ppm region) of compound **5a** in *o*-$C_6H_4Cl_2$ at 100 MHz, and (b) calculated lineshape. The observed splittings are due to coupling with the NH (^3J = 5.3 Hz) and H(1) (^4J = 0.8 Hz) protons in both geometrical isomers.

isomers of **5** (R^2 = H). For purposes of comparison, the energies obtained[5b] by the semiempirical AM1 and MNDO/H methodologies have also been included in Table 5. It can be seen that the order of stability predicted by the *ab initio* calculations (isomer **A** > isomer **B** >>> isomer **C**) agrees quite well with that deduced from the spectra. On the other hand, the MNDO/H method gives nearly the same stability for **A** and **B**, and AM1 predicts that **B** is more stable than **A** (by 6.81 kJ mol^{-1}). In all cases, the s-*trans*,*E* isomer (**D**) is, by far, the least stable.

It has been previously shown[5b,7] that, while the energy differences between the most stable isomers are within the intrinsic error (*ca.* 8 kJ mol^{-1}) of the calculations, the predicted geometries are more accurate and in better accordance with the experimental results. The AM1 calculations[7] for **5** (R^2 = H) predict that **A** and **B** are planar, while the unstable s-*trans*,*Z* form (**C**) has the acetyl group twisted 37° with respect to the rest of the conjugated system. The MNDO/H and AM1 values for **6** (R^2 = H) (Table 5) indicate that the introduction of a methyl group at C(1) strongly destabilises the s-*trans*,*Z* isomer (**C**) in such a way that **A** and **B** are the only forms involved in the equilibrium; for this compound AM1 also predicts that isomer **A** has the acetyl and the nitro groups rotated out of the enamine plane by 15° and 25°, respectively,[5b,7] and isomer **B** has the acetyl group rotated 35°.

The spectral measurements were obtained in different solvents and the theoretical calculations were made for the gas phase. As the compounds under study are highly polar, the solvent dependence of the conformational equilibrium should be included in the calculations. Thus, solvent effects were taken into account by means of the inclusion of a continuum model of solvation. The AM1 calculated[5b,7] dipole moments and the relative free-energies of the different isomers of **5** and **6** (R^2 = H) at relative permittivities ε 1.0, 4.8 ($CHCl_3$) and 46.7 (DMSO) appear in Table 5. The results show that, for a given solvent, the predicted relative order of stability of the **A** and **B** isomers is the opposite to the one observed, and that the solvation free-energy does not follow the same trend as the dipole moments. This suggests that multiple moments of orders higher than two contribute significantly to the total value of the solvation free-energy. In accordance with this, the 3-21 G relative gas-phase and solvation energies,[7] included in Table 5, allow a more satisfactory comparison with the experiments. For compound **5** (R^2 = H), the calculation of the contribution to the solute–solvent interaction energy of the first four terms of the multipole development shows[7] that the isomers with the acetyl group in the s-*cis* conformation (*i.e.* **A** and **B**) present the greatest energy contribution for the quadrupole moment and that the overall solvation energy of the **B** isomer outweighs that of the **A** isomer.

The AM1 calculated[7] free-energy barriers to rotation, $\Delta G^{\ddagger}$, around the C(1)=C(2) bond, by a thermal mechanism, for compounds **5** and **6** (R^2 = H) are 71.1 kJ mol^{-1} (at relative permittivity 9.9, *o*-dichlorobenzene) and 51.0 kJ mol^{-1} (at relative permittivity 4.8, $CHCl_3$; similar to that of $CHCl_2F$–$CHClF_2$ 1 : 1), respectively, which compares well with the experimental values found for their *N*-methyl derivatives **5a** and **6** (see above). As the *N*-methyl substitution only lowers the barrier of the thermal mechanism by *ca.* 4–8 kJ mol^{-1},[5b,14] this correction does not modify the conclusions of the analysis.

Discussion and conclusions

The vibrational and NMR spectra (Tables 2 and 3) conclusively show that **5** and **6** exist in solution as equilibrium mixtures of the *Z* and *E* configurational isomers. The spectra also show that the *Z*-isomer of **5** adopts the s-*cis* conformation around the (C=)C–C(C=O) single bond (**B**), and this is strongly supported by the theoretical calculations (Table 5) which indicate that this conformation is much more stable than the alternative s-*trans* conformation (**C**). The s-*cis* conformation (**A**) of the *E*-isomer of **5** is imposed by the strong hydrogen-bond between the C=O and N–H groups and is confirmed by the calculations. The ^1H NMR measurements show that, in $CHCl_3$ solution, isomer **A** of **5** is more stable than isomer **B** by $\Delta G°$ 2.0 to 5.5 kJ mol^{-1}; the highest values correspond to the NHAryl derivatives where the C=O···H–N hydrogen-bond is the strongest as follows from the ν(C=O) and ν(N–H) frequency values, the chemical shifts of the aminic proton, and the two-bond isotopic effects, $^2\Delta C(1)$ (Table 4). The larger stability of **A** and **B** relative to **C**, of com-

Table 5 Calculated gas-phase relative energies, dipole moments and relative free-energies in solution at different permittivities for the isomers of compounds **5** and **6** (R^2 = H)

		E_{rel}/kJ mol^{-1}			Dipole moment/D	G_{rel}/kJ mol^{-1}			H_{rel}/kJ mol^{-1}	
	Method:	3-21G	MNDO/H	AM1	AM1	AM1			3-21G	
Compound	Isomer					ε: 1.0	4.8	46.7	1.0	4.7
5 (R^2 = H)	s-*cis*,*E* (**A**)	0.00	0.00	6.81	5.3	5.85	6.67	6.69	0.00	0.00
	s-*cis*,*Z* (**B**)	0.58	0.08	0.00	4.8	0.00	0.00	0.00	3.34	2.51
	s-*trans*,*Z* (**C**)	59.3	3.85	25.41	8.6	21.32	13.79	11.29	64.37	56.01
	s-*trans*,*E* (**D**)		65.08	52.17						
6 (R^2 = H)	s-*cis*,*E* (**A**)		0.00	2.22	5.5	2.93	2.96	2.93	0.00	0.00
	s-*cis*,*Z* (**B**)		0.59	0.00		0.00	0.00	0.00	15.05	4.63
	s-*trans*,*Z* (**C**)		16.05	44.98						
	s-*trans*,*E* (**D**)		90.37	54.17						

pounds **5** is attributed to the planarity of the former two forms, and to the larger steric hindrance which prevents planarity and effective electron-delocalisation operating in the latter. In **C**, the interaction through space between the parallel C=O and N^+–O^- groups by a dipolar field effect can also result in further destabilisation. The still larger steric hindrance prevailing in compounds **6** only allows the existence of an overwhelmingly predominant s-*cis*,*E* isomer (**A**) in equilibrium with the s-*cis*,*Z* isomer (**B**), both of them lacking planarity. Another main factor governing the isomeric equilibria of **5** and **6** is the strength of the intramolecular hydrogen-bond involving the N–H group which, as a function of the acceptor group, diminishes in the order COMe > NO_2, and as function of the donor, in the order ArylNH > AlkylNH. This is the same order observed for the proton acceptor and donor ability of these groups in intermolecular hydrogen bonds.[15] The *E*-isomer is therefore the one prevailing in solution, especially in the NHAryl derivatives, as indicated above.

Compounds **5** and **6** are sterically more constrained than the analogous compounds **4** (R^1 = H, Me) with a CO_2R group. Thus, 3-amino-2-nitroacrylic esters (**4**, R^1 = H) exist in solution as equilibrium mixtures of three planar forms similar to **A**, **B** and **C**, and, in $CDCl_3$ solution, the *E* and *Z* configurational isomers (**A** and **B** + **C**) are almost in the same proportion,[5a,b] and separated by an energy barrier $\Delta G^{\ddagger}$ 7.1–84 kJ mol^{-1}.[13] In 3-amino-2-nitrocrotonic esters (**4**, R^1 = Me), the isomers in equilibrium are a planar s-*cis*,*E* form (similar to **A**) and a predominating non-planar form similar to **B**, separated by a barrier $\Delta G^{\ddagger}$ 49 kJ mol^{-1} (at 206 K). The differences observed can be attributed to the smaller steric requirements of the CO_2R group relative to the COMe group, the additional steric strain introduced by the CH_3–C(1) group when present, and to the larger capability of the ketone C=O group to act as a hydrogen-bond acceptor relative to the ester C=O group. It follows also from the above that in nitroaminoenones **4**–**6** the capability of the electron-withdrawing group to act as a hydrogen-bond acceptor decreases in the order COMe > NO_2 > CO_2R. This result, as noted previously,[16] is at variance with the order observed for the intermolecular hydrogen-bond basicity of these groups, where CO_2R is a better hydrogen-bond acceptor than NO_2 even in similar systems (Me_2NCH=$CHCO_2Et$, Me_2NCH=$CHNO_2$), although in these cases the intermolecular hydrogen-bond is greatly reinforced.§[15c–f] The reason for this discrepancy could be the greater electron-withdrawing character of the nitro group compared to the ester group. Thus, a synergistic reinforcement of hydrogen bonding and electron delocalisation would be specially efficient in the case of the nitro group. This synergetic effect, previously observed in enolic systems, has been dubbed resonance assisted hydrogen bonding (RAHB).[17] The total charge distribution calculated with the AM1 semiempirical method for model compounds **2** (R^1 = R^2 = R^3 = H),[1] **4** (R^1 = H, Me; R^2 = H),[5c] and 3-aminoacrylate and -crotonate[5c] supports this view.

The shifts of the vibrational frequencies produced by *N*-deuteriation (Table 2) reveal the presence of vibrational couplings, the groups involved and the extent of the couplings being dependent on the configuration and conformation of the compounds. In **5**, ν(C=O), the enamine band, and $\nu_a(NO_2)$ are affected both in the **A** and **B** isomers, though the effect is particularly noticeable in the enamine band of **A** due to the stronger hydrogen-bond present in this form. The ν(C=O) stretching of isomer **A** of **6** is little disturbed, and the coupling affects mainly the enamine and, to a lesser extent, $\nu_a(NO_2)$. In compounds **7** (s-*trans*,*Z* geometry), the coupling affects mainly $\nu_a(NO_2)$ and to a lesser extent the enamine band; the ν(C=O) vibration, that shows a negligible effect, does not seem to be coupled to δ(N–H). The results of the *ab initio* 3-21G theoretical calculations[18] for compound **5** (R^1 = H) are in accordance with these observations and also indicate that, in the strongest coupled isomer **A**, the enamine mode can be described as the symmetric combination of the C=O, C=C and C(1)–N stretching motions, with contribution of the C(1)–H and the N–H bending modes. The frequency shift ($\Delta\nu$ −32 cm^{-1} in $CDCl_3$) of the enamine band of *E*-**6** relative to the same band of *E*-**5b** can be attributed to the lack of the δ[C(1)–H] mode in the composition of the band in the former compound, though the electronic effects introduced by the methyl group may also contribute. The same effect caused by methyl substitution at C(1) has been observed when comparing the spectra of compounds *Z*-**2** (R^1 = Me, R^2 = H) with those of their lower homologous *Z*-**2** (R^1 = R^2 = H),[1] and the spectra of 3-amino-2-nitrocrotonic esters (**4**, R^1 = Me) with those of 3-amino-2-nitroacrylic esters (**4**, R^1 = H).[5c]

Enaminones with a secondary amino group (**1**, R^1 = R^2 = H, R^3 = alkyl) typically show the enamine band as a medium-strong absorption at 1560–1569 cm^{-1}, assigned[2b,c,18] as indicated above. Nitroenamines with a secondary amino group (**2**, R^2 = H), show this band as a very strong absorption at 1650–1600 cm^{-1}, assigned as the asymmetric combination of the C(1)–C(2) and C(1)–N stretching modes with contributions from δ[C(1)–H] and δ(N–H).[1,3a] As compounds **5**–**7** have structural features in common with both **1** and **3**, it could be anticipated that they would have similar coupling patterns. The spectral results show that this only holds for the open-chain compounds **5** and **6** with the s-*cis*,*E* geometry, particularly for the former. Cyclic compounds **7**, with the C=O and the C=C groups in s-*trans*,*Z* disposition, have couplings, and show IR and Raman absorptions, more similar to those of a simple nitroenamine.

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