Spectral Properties and Isomerism of Nitroenamines. Part 1. 3-Amino-2-nitroacrylic Esters†

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3-Amino-2-nitroacrylic esters (**1**) with primary and secondary amino group crystallize either in the *s-cis,Z* (**1A**), the *s-trans,Z* (**1B**), or the *s-cis,E* (**1C**) isomeric forms, and in solution they exist as equilibrium mixtures of the three forms, in ratios strongly dependent on the polarity of the solvent. Each isomeric form has easily distinguishable i.r. absorptions. On the other hand, their ^1H and ^{13}C n.m.r. spectra show signals due to the *s-cis,E* form (**1C**), and a second set of signals attributed to the two rapidly interconverting conformations (**1A** and **B**) of the *Z* isomer.

The spectral properties of enamines having one or two electron-acceptor (usually acyl) groups at C-2 have been extensively investigated[1] because of the information they provide on the isomerism and electron distribution inside these mesomeric systems. As part of a continuing study[2,3] on the spectral and chemical properties of nitroenamines, we have prepared a series of 3-amino-2-nitroacrylic esters (**1**), some typical examples of which appear in Table 1, and found that they can crystallize either in the *s-cis,Z* (**1A**), *s-trans,Z* (**1B**), or *s-cis,E* (**1C**) isomeric forms, or as mixtures of them. We report here on the vibrational and ^1H and ^{13}C n.m.r. spectra of the different configurational and conformational isomeric forms. Bakhmutov *et al.*[7] have previously investigated the ^1H n.m.r. spectra of (**1**), and established that the compounds exist as solvent-dependent equilibrium mixtures of the intramolecularly bonded *Z*- and *E*-forms; they also observed low energy barriers (ΔG^+ 17—20 kcal mol^{-1}) to rotation around the carbon double bond. An *X*-ray crystallographic investigation[8] of methyl 3-methylamino-2-nitroacrylate (**1b**) has shown that this compound adopts the *s-cis,Z* disposition (**1A**; $R^1 = R^2 =$ Me) in the solid state, and that the whole conjugated system is planar although the CO_2Me group is very weakly conjugated with the enamine moiety. The vibrational spectra of compounds (**1**) have been little investigated. From a study of solid samples, Wolfbeis[6] concluded that they usually crystallize in the *Z*-form with the ν(C=O) band in the range 1 730—1 700 cm^{-1}; the less frequently encountered *E*-form showed a band at *ca.* 1 650 cm^{-1} assigned to the stretching of the chelated C=O group. The observation, in many cases, of two bands, at 1 720 and 1 650 cm^{-1}, in solution indicated mixtures of isomers. Little attention has been given to the i.r. spectra of the parent 3-aminoacrylic esters (**2**); although Huisgen *et al.*[9] observed that these compounds exhibited two ν(C=O) bands attributed to the equilibrium mixture of the chelated *Z*-isomer and the *E*-isomer, they did not go any further in their analysis of the spectra. Along with this, Ostercamp and Taylor[10] have studied the vibrational spectra of simple nitroenamines [*i.e.*, (**3a**, **b**)]; they assigned frequencies to the bonds characteristic of the nitroenamine system, and explained some unusual features of the spectra, such as the weak ν(C=C) Raman band and the absence of a strong band attributable to $\nu_{as}(NO_2)$, in terms of the high degree of electronic polarization and the coupling between the NO_2, C=C, and C–N bonded units. Gate *et al.*[11] have reported on the i.r. spectra of (**3c**) and its *N*-deuteriated derivative.

Experimental

I.r. spectra were recorded on a Perkin-Elmer 599B spectrophotometer; the measurements were performed in the solid state (KBr discs and Nujol mulls) and in solution at 0.004—0.3M, depending on the solvent, in 1—0.03 mm cells. The i.r. spectra of very dilute (saturated) solutions of methyl 3-methylamino-2-nitroacrylate (**1b**) in CCl_4 were registered on a Nicolet 50XE spectrophotometer. Intensities of bands are indicated by the usual abbreviations (see Table 2); the coexistence of several isomeric forms with partial overlap of bands precluded measurements of extinction coefficients. Raman spectra were obtained for solid samples and $CDCl_3$ solutions on a Ramanor U-1000 (5 145 Å) spectrometer. ^1H and ^{13}C N.m.r. spectra were registered at 200 and 50.3 MHz, respectively, on a Varian XL-200 instrument, with Me_4Si as internal standard. Deuterium isotope effects on carbon-13 chemical shifts were measured on partially deuteriated samples prepared by the addition of a calculated amount of EtOD to a 0.2M solution of the compound in $CDCl_3$, so that the H:D ratio would be slightly greater than unity.[12] $CHCl_3$, $CDCl_3$, and CCl_4 (all Merck) were purified before use by shaking with saturated $NaHCO_3$, drying over $MgSO_4$ or BaO, and distilling.

Preparation of Compounds.—Compounds (**1**) (see Table 1) were synthesized according to the literature. Methyl 3-(n-butylamino)acrylate (**2a**) and methyl 3-anilinoacrylate (**2b**) were prepared as described;[9] their physical properties agreed with those reported.[9] Solid samples of the *N*-deuteriated derivatives of (**1a**—**d**) and of (**2b**) were prepared by repeated recrystallization of the compounds from D_2O or EtOD. *N*-Deuteriation of samples in solution was performed by shaking with D_2O, separating the organic phase, filtering it, and transferring it to the i.r. cell or the n.m.r. tube.

Results and Discussion

Key i.r. and Raman bands for compounds (**1**) appear in Table 2. Table 3 lists the most significant ^1H and ^{13}C n.m.r. spectral data. For purposes of comparison, data for compounds (**2a** and **b**) are also included in the Tables.

In order to assign the i.r. absorptions due to each of the three

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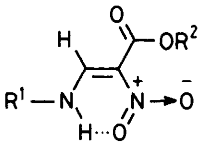
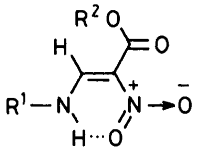
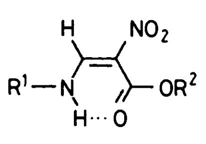
Table 1. Analytical and physical data for compounds (**1**)

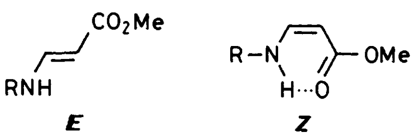
Compound (Formula)	R^1	R^2	Yield (%)	Solvent	M.p. (°C) Observed	M.p. (°C) Literature	Found (%) (Required) C	H	N	X
(**1a**) ($C_4H_6N_2O_4$)	H	Me	97	H_2O	165—166	163.2—163.6[a]				
(**1b**) ($C_5H_8N_2O_4$)	Me	Me	78	EtOH	122—123	126.0—126.5[b]	37.4 (37.5	5.1 5.0	17.7 17.5)	
(**1c**) ($C_{10}H_{10}N_2O_4$)	Ph	Me	76	EtOH	111—112	114.0—114.5[b]				
(**1d**) ($C_{11}H_{12}N_2O_4$)	Ph	Et	73	EtOH	79—80	79—81[c]				
(**1e**) ($C_{11}H_{12}N_2O_4$)	p-MeC_6H_4	Me	48	EtOH	93—94	96.0—96.5[b]				
(**1f**) ($C_{11}H_{12}N_2O_5$)	p-$MeOC_6H_4$	Me	40	EtOH	108—109		52.5 (52.4	4.9 4.8	10.8 11.1)	
(**1g**) ($C_{10}H_9ClN_2O_4$)	p-ClC_6H_4	Me	42	EtOH	134—135	137—138[b]				
(**1h**) ($C_{10}H_8Cl_2N_2O_4$)	o,p-$Cl_2C_6H_3$	Me	30	EtOH	169—170		40.9 (41.2	2.9 2.8	9.4 9.6	24.4 (X = Cl) 24.4)
(**1i**) ($C_{11}H_{12}N_2O_4$)	o-MeC_6H_4	Me	45	EtOH	104—105		55.9 (55.9	5.2 5.1	11.8 11.9)	

[a] Ref. 4. [b] Ref. 5. [c] Ref. 6.

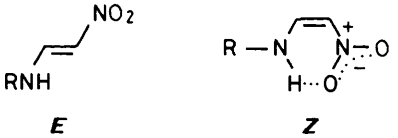

(**1A**)


(**1B**)

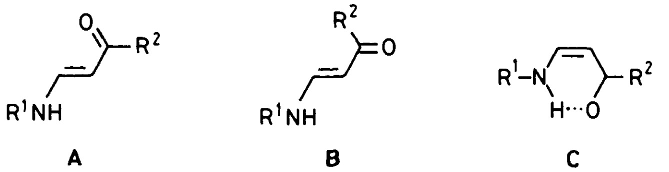

(**1C**)



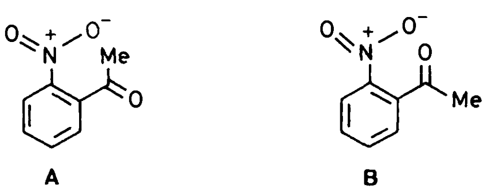
(**2**) a R = Bu^n
b R = Ph



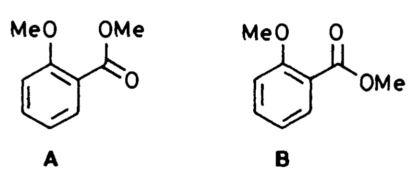
(**3**) a R = Me
b R = Bu^t
c R = Ph



(**4**)



(**5**)



(**6**)

isomeric forms *s-cis,Z* (**1A**), *s-trans,Z* (**1B**), and *s-cis,E* (**1C**), it is convenient to consider first the spectra of the anilino derivatives. Methyl 3-(2,4-dichlorophenylamino)-2-nitroacrylate (**1h**) showed in the solid state, and in cool, freshly prepared solutions in CCl_4 and $CHCl_3$, two strong bands in the double bond region, at *ca.* 1 670 and 1 625 cm^{-1}, the latter being sensitive to *N*-deuteriation (see below); these two bands are assigned to the stretching of C=O intramolecularly bonded to the NH group, and to the mixed enamine [ν(C=C) + ν(C–N) + δ(N–H)] band,[1] respectively, of the *s-cis,E* form (**1C**). Similarly, the ^1H n.m.r. spectrum of (**1h**) in a freshly prepared solution of $CDCl_3$ exhibited the signals expected for a single isomer which is therefore considered to be (**1C**). On standing at room temperature, two new i.r. bands appeared at *ca.* 1 738 and

1 700 cm^{-1}, which are assigned as the ν(C=O) of the two forms (**1B** and **A**), respectively.* These two bands grew gradually at the expense of the band at *ca.* 1 670 cm^{-1} until equilibrium was reached in 2—3 h. Concomitantly, a second set of signals appeared in the ^1H n.m.r. spectrum which is assigned to the two conformations (**1A** and **B**) of the *Z*-isomer which rapidly interconvert in the n.m.r. time-scale. In $CDCl_3$ solution the equilibrium between the *Z*-form (**1A** + **B**) and the *s-cis,E*-form (**1C**) was reached when they were in the approximate ratio 28:72. Compound (**1h**) crystallizes, therefore, in the form (**1C**), and in solution partly isomerizes into a mixture of (**1A** and **B**). Compound (**1i**), as well as other *ortho*-substituted anilino derivatives examined, behaved similarly, although the isomerization process was faster. On the other hand, methyl 3-(*p*-toluidino)-2-nitroacrylate (**1e**) showed, in the solid state, a C=O band at 1 693 cm^{-1} attributed to form (**1A**), while the i.r. and ^1H n.m.r. spectra of its freshly prepared solutions already exhibited absorptions due to (**1A**—**C**), thus indicating that the equilibrium between the three forms had been attained very rapidly. The conversion (**1A**) $\longrightarrow$ (**1B**) is particularly easy and could be observed even in the solid state. Thus, when KBr pellets of (**1e**) were allowed to stand, the band at 1 728 cm^{-1} appeared and grew at the expense of the band at 1 693 cm^{-1}; furthermore, the number of ν(C=O) peaks observed for this, and for other compounds, often depended on the way the pellets or the mulls were prepared. The pure *s-trans,Z* form (**1B**) was observed in ethyl 3-anilino-2-nitroacrylate (**1d**): this compound showed, in KBr pellets, a band at 1 730 cm^{-1} attributed to (**1B**). On the other hand, in a freshly prepared $CDCl_3$ solution two bands at 1 727 and 1 690 cm^{-1} due to rotamers (**1B** and **A**), respectively, were first observed; on standing the solution the band at 1 656 cm^{-1}, due to the *s-cis,E* form (**1C**), also appeared and grew till it became strongest. The equilibrium was reached in *ca.* 2 h, and the ^1H n.m.r. spectra then indicated that the ratio (**1A** + **B**):(**1C**) was *ca.* 46:54. The other anilino derivatives (**1d**, **f**, and **g**) were already mixtures of form (**1C**) and one, or both, conformational isomers of the *Z*-form in the solid state; in solution the equilibrium mixture of the three forms was always observed.

As there are data for the *X*-ray crystallographic structure of methyl 3-(methylamino)-2-nitroacrylate (**1b**),[8] their spectra were examined in detail. This compound showed in solution the i.r. carbonyl bands due to (**1A**—**C**), and from its ^1H n.m.r. spectrum in $CDCl_3$ it could be deduced that in the equilibrium the *Z* (**1A** + **B**) and the *s-cis,E* (**1C**) isomers were in the approximate ratio 57:43. The i.r. spectra in the solid state were simpler: two bands were observed, at 1 700 (strong) and 1 680 cm^{-1} (very strong) in KBr pellets, while in Nujol a third weak absorption at 1 650 cm^{-1} appeared, and the relative intensities of the other two C=O bands depended on the way the mull was prepared. On the other hand, the Raman spectrum of a solid sample of the compound showed only the band at 1 681 cm^{-1} attributable to the *s-cis,Z* isomer (**1A**). It seems, therefore, that compound (**1b**) crystallizes in the *s-cis,Z* form, and that a partial conversion into the other forms takes place readily during the handling of the solid samples.

Both the positions and intensities of the bands at *ca.* 1 730 and 1 690 cm^{-1} depended on the polarity of the solvent. The strongest effect was observed for the higher frequency band, which was displaced to lower frequency [$\Delta\nu$ −24 cm^{-1} for compound (**1b**)], and its intensity markedly increased on increasing the polarity. The other band showed a similar, although smaller [$\Delta\nu$ −9 cm^{-1} for compound (**1b**)], solvent effect on the frequency, but its intensity decreased on increasing the polarity of the solvent. Assuming that the changes in the relative intensities of the two bands reflect approximately the concentration changes of the isomers, it follows that the high frequency band is due to the more polar conformational isomer; this is considered to be (**1B**) which has a more extended conjugated system than (**1A**). The latter gives then rise to the band at *ca.* 1 690 cm^{-1}. The position of the chelated carboxy band changed very little with the polarity of the solvent and with concentration, and its intensity was usually the strongest of the three ν(C=O) bands.

The doubling of the carbonyl absorption due to the presence of the *s-cis* and *s-trans* rotamers in the *E*-form of enones and β-aminoenones [for example, (**4**)] is well documented.[13,14] In these cases, the high frequency band has been assigned to the *s-cis* conformation (**4A**) and the other to *s-trans* (**4B**), the latter band being the one whose relative intensity increased on increasing the polarity of the medium.[13a] The difference in the carbonyl frequencies has been considered[14,15] to be due to differences in conjugation and mechanical coupling between the ν(C=O) and ν(C=C) vibrations in the two conformations. This assignment of the carbonyl bands is the opposite to that made above for compounds (**1**). On the other hand, the doubling of the bands is too small to be observed in acrylic esters[16] and in their 3-amino derivatives (**2**).[9] Consequently, we suggest that in compounds (**1**) the large band separation is due to the presence of the NO_2 group α to the carbonyl. In conformation (**1B**) the two groups can interact through space by a dipolar field effect and by interaction of their occupied orbitals; this would result in an enhancement of the double bond character of C=O and a rise in its stretching frequency. A similar effect has been considered to be responsible for the difference in ν(C=O) of conformations **A** and **B** of 2-nitroacetophenone (**5**)[17] and of several *o*-substituted methyl benzoates, such as (**6**);[18] in the latter compounds the band at the highest frequency, due to form (**4B**), is the one whose intensity increases with the polarity of the solvent.

The effect of isomerism was less apparent in the i.r. absorptions due to the other functional groups. Splitting of bands was, however, observed in several instances, and their assignments were made by considering the carbonyl band(s) observed under the same conditions, and their changes of intensity with the polarity of the medium. In some cases, as for instance (**1d**), where the compounds crystallized in a single isomeric form, the mere heating of the KBr pellets for a period of time and the recording of the spectrum at different intervals, made it possible to observe the appearance, and growth, of new ν(C=O), enamine, and $\nu_{as}(NO_2)$ bands, thus facilitating their assignments.

Compounds (**1b**—**i**) with secondary amino group showed a broad absorption, very strong in the i.r., at 1 651—1 622 cm^{-1} (in $CDCl_3$), which is assigned as the mixed ν(C=C) + ν(C–N) + δ(N–H) vibration (the enamine band) of the three forms (**1A**—**C**). Its shape was complex: it usually had a shoulder(s) or was even split (see Table 2). In these cases, the high frequency component of the band, or of the doublet, could be associated with the *Z*-form(s), and the low frequency component, usually a shoulder, with the *E*-isomer. Better resolution could be achieved in the Raman spectra: for example, the very strong i.r. band at 1 651 cm^{-1} with a shoulder at 1 640 cm^{-1} (in $CDCl_3$) of (**1b**) became two Raman bands at these frequencies, both of medium intensity and partially polarized. In the *N*-deuteriated compounds, the δ-NH component of the mixing is lost, and the corresponding new band [referred to hereinafter as ν(C=C)] is nearer the C=C stretching.[1,10,14] Interestingly, the effect of the exchange was much larger in the *E*-form [$\Delta\nu$ −47 cm^{-1}, for (**1b**) in $CDCl_3$] than for the *Z*-form ($\Delta\nu$ −13 cm^{-1}) in such a way that the two ν(C=C) bands were quite well separated, the band corresponding to the *Z*-form being much stronger than that of the *E*-isomer. In the Raman spectrum, both bands were of medium intensity. These assignments were confirmed by studying pure samples of the *N*-

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* The assignment previously made[2a] is now revised.

Table 2. I.r. and Raman (in italics) frequencies (cm^{-1}) of compounds (**1**), (**2**) and their *N*-deuteriated derivatives

		ν(C=O)			ν(C=C) + ν(C–N) + δ(N–H)		ν(C=C)[a]		$\nu_a(NO_2)$	
		Z		*E*	*Z*	*E*	*Z*	*E*	*E*	*Z*
Compound	Medium	*s-trans*	*s-cis*							
(**1a**)	$CDCl_3$	1 733m[b]	1 692w	1 673s	1 642vs	1 635 (sh) 1 528m	1 623s	1 585m	*c*	*c*
	CH_2Cl_2	1 735s	1 694w	1 675s	1 644vs 1 547 (sh)	1 637 (sh) 1 530m	1 624s	1 585m	1 495w	1 470m
	$[^2H_6]Me_2SO$	1 724s		1 677m	1 626s	1 590 (sh)			1 495m	1 462s
	a	1 723s		1 675m			1 621vs	1 584w	1 500m	1 470m
	KBr		1 685 (sh)	1 665vs		(1 665)[d] 1 537m			1 493s	
	Nujol[a]			1 655vs				1 600m-s	1 495vs	
	Solid		*1 685*w	*1 660*vw		(*1 660*)vw[d] *1 540*w			*1 492*m	
(**1b**)	CCl_4	1 745vw	1 699m	1 665vs	1 650m 1 640m	1 630m			*e*	*e*
	$CDCl_3$	1 730m	1 692m	1 668vs	1 651vs	1 640 (sh)			1 513s	1 492 (sh)
	a	1 729m	1 690m	1 666vs			1 638vs	1 593w	1 510s	1 490 (sh)
	$CHCl_3$	*1 729*m, pp	*1 694*w, pp	*1 664*w, pp	*1 651*m, pp	*1 640*m, pp	*1 638*m	*1 596*m	*1 512*s, pp	~*1 500* (sh),[e] pp
	CH_2Cl_2	1 731s	1 696m	1 668vs	1 651vs	1 635 (sh)	1 640vs	1 595w	1 513s	1 492 (sh)
	$[^2H_6]Me_2SO$	1 721s	1 690m	1 671m	1 648vs	~1 630 (sh)			1 498m	1 490 (sh)
	a	1 721s	1 687m	1 671m-s			1 636vs	1 603 (sh)	1 498m	1 476m
	Nujol	1 699s	1 685 (sh)	1 650w	1 616s				*e*	*e*
	a		1 688vs				1 612vs	1 560m	*e*	*e*
	KBr	1 700s	1 680vs	1 650 (sh)	1 618vs					1 496vs 1 472vs
	a	1 691vs	1 671vs	1 652m			1 614vs	1 558w		1 484vs 1 469vs
	Solid		*1 681*w		*1 622*m					*1 505*m *1 471*w
	a		*1 674*w				*1 621*s			*1 494*m *1 470*w
(**1c**)	CCl_4	1 747w	1 702s	1 668vs	1 640 (sh)	1 630vs			1 522vs	1 490 (sh)
	$CDCl_3$	1 735m	1 697m	1 665vs	1 638 (sh)	1 631vs	1 620s	1 572s	1 518s	1 490m
	$C_6H_5NO_2$	1 735s	1 700m	1 666s	1 638vs	1 631vs			*c*	1 491s
	MeCN	1 732s	1 702w	1 666m	1 637vs				1 517s	1 493s
	$[^2H_6]Me_2SO$	1 725s	1 693 (sh)	1 660 (sh)	1 632vs				1 505 (sh)	1 482s
	KBr		1 702vs	1 672m	1 629vs				1 513m	1 495vs

(1d)	CDCl$_3$[f]	1 727m	1 690m	1 656w	1 638vs		1 630 (sh)			1 514w-m	1 490 (sh)
	a,f	1 723s	1 686s					1 619vs			1 480vs
								1 594vs			
	a	1 723m	1 686m	1 658vs				1 620vs	1 571s	1 514s	1 485 (sh)
								1 595vs			
	[^{2}H$_6$]Me$_2$SO	1 721s	1 690m	1 655 (sh)	1 632vs						1 493s
	a	1 720s	1 688m	1 655 (sh)				1 628s	1 590[g]	1 508 (sh)	1 493s
	KBr	1 730vs			1 643vs						1 493vs
	a	1 724vs						1 618s			1 454m[g]
(1e)	CDCl$_3$	1 732m	1 696m	1 663s	1 635 (sh)		1 630vs			1 510vs	
	a,f	1 733s	1 693s	1 664m				1 621vs	1 575m	1 509w	1 485s
	a	1 733m	1 693m	1 664vs				1 621s	1 575s	1 509vs	1 485m
	[^{2}H$_6$]Me$_2$SO	1 727vs	1 693m	1 662 (sh)	1 631vs						1 502vs
	a	1 727vs	1 692m	1 662 (sh)				1 630vs			1 505vs
	KBr		1 693vs		1 637vs						1 486vs
	a	1 725w	1 690vs					1 625s			1 472vs
(1f)	CDCl$_3$	1 730m	1 695m	1 660vs		1 628vs				1 508vs	1 490 (sh)
	[^{2}H$_6$]Me$_2$SO	1 728vs	1 693m	1 665 (sh)	1 630vs						1 508vs
	KBr		1 693vs	1 655m	1 630vs						1 496vs
(1g)	CDCl$_3$	1 736m	1 698m	1 667vs	1 640 (sh)		1 629vs			1 518s	1 493vs[g]
	[^{2}H$_6$]Me$_2$SO	1 728s	1 697m	1 678m		1 630vs				1 510 (sh)	1 496vs[g]
	KBr	1 735w	1 698vs	1 662m		1 623vs					1 495vs
(1h)	CHCl$_3$[f]	1 736vw		1 667vs			1 624vs			1 521s	
		1 736m	*1 701m*	*1 668s*	*1 631 (sh)*		*1 622vs*			*1 521m*	
	a,f	1 736vw		1 667vs					1 579vs	1 520s	
	a	1 736m	1 700w	1 676vs				1 620vs	1 579s	1 520s	
	[^{2}H$_6$]Me$_2$SO	1 730m	1 702w	1 668m		1 627vs				1 519m	*g*
	KBr			1 678vs			1 632vs			1 513s	
	a			1 676vs					1 584s	1 505s	
(1i)	CHCl$_3$	1 730m	1 695m	1 660vs		1 630vs		1 620vs	1 574s	1 514s	*g*
	[^{2}H$_6$]Me$_2$SO	1 727s	1 695m	1 660s		1 630vs				1 512s	*g*
	KBr			1 657vs			1 630vs			1 511s	
(2a)	CHCl$_3$		1 663vs[h]	1 685 (sh)		1 613vs		1 579vs	~1 612vs		
			1 669w[h]	~*1 685vw*		*1 614vs*		*1 579vs*	*1 613vs*		
	Liquid		~1 673vs[h]	1 685 (sh)		1 615vs					
(2b)	CHCl$_3$[f]			1 690vs			1 632vs				
			1 669vs[h]		*1 627vs*						
	a,f			1 688vs					1 624vs		
	a		1 669vs[h]					1 585vs			
	KBr			1 699s			1 615s				
	a			1 692s					1 612vs		

[a] Measured in the *N*-deuteriated derivative. [b] Abbreviations: s, strong; m, medium; w, weak; sh, shoulder; v, very; pp, partially polarized. [c] Not measured. [d] ν(C=O) and enamine bands cannot be differentiated in the present case. [e] Partially overlapped by the medium. [f] Freshly prepared solution. [g] Possible contribution of ring ν(C=C). [h] Intramolecularly bonded CO group.

Table 3. Key n.m.r. spectral data (δ; J Hz) for compounds (**1**) and (**2**)

			NH		3-H ($^3J_{3\text{-H,NH}}$)		C-1 ($^3J_{\text{C.1-H}}$)		C-2		C-3		Δδ*	
Compound	Solvent	(Z:E) ratio	Z	E	Z	E	Z	E	Z	E	Z	E	Z	E
(**1a**)	$CDCl_3$	48:52	8.7br, s		8.15d (9.2)	8.23d (9.2)								
	[$^2H_6$]Me_2SO	—	8.6br, s		8.3br, s		161.7	162.9	115.2	116.8	152.1	155.5	36.9	38.7
(**1b**)	$CDCl_3$	57:43	9.6br, s	9.2br, s	8.12d (15.0)	8.66d (14.6)	161.3 (2.0)	164.5 (7.4)	115.2	115.9	154.1	157.9	38.9	42.0
	[$^2H_6$]Me_2SO	67:33	10.05br, s	9.3br, s	8.21br, d (14.4)	8.78br, s								
(**1c**)	$CDCl_3$	50:50	11.2br, d	10.95br, d	8.59d (14.6)	9.11d (14.4)	161.2 (2.6)	164.7 (7.7)	117.5	118.6	145.2	149.1	27.7	30.5
	[$^2H_6$]Me_2SO	61:39	11.4br, s	10.7br, s	8.49br, s	8.98br, s								
(**1d**)	$CDCl_3$	46:54	11.1br, d	10.95br, d	8.57d (14.9)	9.10d (14.2)	160.9	164.5	118.0	119.0	145.2	149.0	27.2	30.0
	[$^2H_6$]Me_2SO	60:40	11.3br, s	10.7br, s	8.47br, s	8.98br, s								
(**1e**)	$CDCl_3$	57:43	11.0br, s		8.50d (14.0)	9.01d (14.0)	161.5	165.5	117.3	118.3	145.4	149.3	28.1	31.0
	[$^2H_6$]Me_2SO	60:40	11.41d	10.72d	8.42d (14.8)	8.99d (14.6)								
(**1f**)	$CDCl_3$	55:45	11.1br, s		8.47d (14.5)	9.00d (14.5)	161.4	164.9	116.9	117.9	145.6	149.5	28.7	31.6
	[$^2H_6$]Me_2SO	63:37	11.4br, d	10.8br, s	8.38d (12.7)	8.9br, s								
(**1g**)	$CDCl_3$	55:45	11.0br, s		8.48d (14.0)	9.00d (14.0)	161.2	164.7	117.8	119.2	145.1	149.0	27.3	29.8
	[$^2H_6$]Me_2SO	63:37	11.40d	10.70d	8.42d (14.7)	8.96d (14.0)								
(**1h**)	$CDCl_3$	28:72	11.39d	11.26d	8.50d (14.5)	9.02d (13.8)	161.4	164.6	119.5	120.8	143.6	147.7	24.1	26.9
	[$^2H_6$]Me_2SO	45:55	11.35d	11.02d	8.59d (14.4)	9.15d (14.0)								
(**1i**)	$CDCl_3$	47:53	11.34d	11.12d	8.58d (14.4)	9.11d (14.1)	161.2	165.1	117.6	118.7	145.8	149.5	28.2	30.8
	[$^2H_6$]Me_2SO	56:44	11.42d	10.92d	8.52d (14.5)	9.14d (14.1)								
(**2a**)	$CDCl_3$	82:18	7.7br, s	4.9br, s	6.55dd (13.2)	7.45dd (8.4)	171.2	170.2	80.8	84.7	152.5	152.3	71.7	67.6
(**2b**)	$CDCl_3$	100:0	9.8br, s	7.0m	7.0m	7.90t (13.0)	170.5 (10.4)	169.5 (3.7)	86.8	91.8	143.2	143.2	56.4	51.8

* $\Delta\delta = \delta_{\text{C-3}} - \delta_{\text{C-2}}$.

deuteriated derivatives of (**1d**, **e**, and **h**). Thus, a freshly prepared $CDCl_3$ solution of the *N*-deuterio analogue of (**1h**) (that is, containing almost exclusively the *s-cis-E* isomer) showed ν(C=C) at 1 579 cm^{-1}, overlapping the phenyl absorption, and as the isomerization progressed, a band at 1 620 cm^{-1} appeared and grew. At equilibrium, when the *Z*- and *E*-forms were in the ratio *ca.* 3:7 (^{1}H n.m.r.), the new band was strong, and the band at 1 579 cm^{-1} was of weaker intensity, thus indicating that the *Z*-isomer has much stronger absorption than the *E*-form. In a similar experiment, the *N*-deuteriated derivative of (**1d**) showed first the strong band at 1 619 cm^{-1} corresponding to the *Z*-form, and, after the equilibration (when the *Z*:*E* ratio was 46:54), the weaker band at 1 571 cm^{-1} was also present.

The dependence of the isotopic effect on the configuration has been previously observed[13b,c] for the aminoenones (**4**), being larger for the chelated *Z*-form (from -45 to -55 cm^{-1}) than for the *E*-form (from -10 to -15 cm^{-1}). Our measurements (see Table 2) on the *N*-deuteriated aminoacrylic esters (**2**) also indicated an isotopic shift of -34 to -42 cm^{-1} (in $CHCl_3$) for the *Z*-form and of -1 to -8 cm^{-1} for the *E*-form, the ν(C=C) band of the former being the strongest of the two. Likewise, the *Z*-forms of nitroenamines (**3b** and **c**) showed[10] an isotopic effect of -16 cm^{-1} (in CH_2Cl_2) while it was nil in the *E*-form of (**3a**) in the solid state.[11] Therefore, regarding the isotopic effect, the *Z*-forms of compounds (**1**) behave similarly to the *Z*-form of nitroenamines (**3**), and the *E*-form of (**1**) with a chelated C=O is similar to the chelated *Z*-form of 3-aminoacrylic esters (**2**). These results suggest that the degree of coupling of δ(N–H) with the remainder of the enamine system is, to a large extent, a consequence of the intramolecular hydrogen bond between the NH and the C=O or NO_2 groups, an effect which could be rationalized by considering that this bond raises the frequency of δ(N–H), bringing it closer to the frequencies of the other [ν(C=C) and ν(C–N)] coupled modes. However, other factors may also operate since the hydrogen bond between the NH and NO_2 groups in the *Z*-forms of (**1**) is stronger than the hydrogen bond between the NH and C=O groups of the isomer (**1C**).

Compound (**1a**), with a primary amino group, showed in the solid state a band at 1 665 cm^{-1}, extremely strong in the i.r. and much weaker in the Raman, which is considered to include the ν(C=O) band of form (**1C**) and the absorption due to the C=C–NH_2 group also expected[19] in this region; this band had a shoulder at 1 685 cm^{-1}, resolved into a weak band in the Raman, which is assigned as ν(C=O) of minor amounts of form (**1A**). In accord with that, the spectrum of the *N*-dideuteriated derivative in Nujol had ν(C=O) and ν(C=C) bands at 1 655 and 1 600 cm^{-1}, respectively. Therefore this compound crystallizes preferentially in the form (**1C**). The i.r. spectra in solution exhibited the usual pattern of three C=O bands, and the additional bands due to the C=C–NH_2 group. In the *N*-dideuteriated derivative the two usual ν(C=C) bands at 1 623 (strong) and 1 585 cm^{-1} (medium) attributable to the *Z*-forms and to the *E*-form (**1C**), respectively, were observed. The ^{1}H n.m.r. spectrum indicated that, in $CDCl_3$ solution, the *Z* (**1A** + **B**) and the *s-cis,E* (**1C**) forms were in the ratio 48:52.

The frequency of the enamine band of compounds (**1**) with secondary amino group is approximately the same as those of nitroenamines (**3a**, **b**) (1 646—1 639 cm^{-1} in CH_2Cl_2),[10] and, on the other hand, it is higher than that of the analogous 3-aminoacrylic esters (**2**) (1 630—1 615 cm^{-1} in $CDCl_3$). It seems therefore that the introduction of the strong electron-attracting NO_2 group at C-2 of (**2**) inhibits conjugation between the C=O and the C=C–NH groups, as anticipated, and creates an electron distribution similar to that existing in simple nitroenamines (**3**). However, the loss of conjugation of the carbonyl group is not so much reflected in the ν(C=O) frequencies: the values corresponding to the *s-cis,Z* (**1A**) and to the *s-cis,E* (**1C**) forms are fairly close to those of the similar *E*- and *Z*-forms, respectively, of (**2**). The higher ν(C=O) value found for the *s-trans,Z* form (**1B**) may be due to the through-space interaction with NO_2 (see above). Furthermore, enough conjugation must be retained to maintain the whole unsaturated system planar and to allow for the existence of rotamers (**1A** and **B**).

In accord with this picture, the $\nu(NO_2)$ bands of compounds (**1**) were strongly displaced to low frequencies. Thus the i.r. spectra of (**1a**) and its *N*-dideuterio analogue showed in the solid state [that is, in form (**1C**)] a strong band at 1 493 cm^{-1} assigned as the $\nu_{as}(NO_2)$ vibration of the isomer *s-cis,E* (**1C**); this band was of medium intensity in the Raman spectrum of (**1a**). In solution a second strong band appeared at 1 470—1 462 cm^{-1} arising from the *Z*-forms (**1A** and **B**). In the *N*-methyl derivative (**1b**), the separation between the two bands was smaller, the lower frequency one appearing as a shoulder of the other; in the Raman, their intensities were medium or even strong. The compounds containing a phenyl group showed these bands partly overlapping the phenyl ring absorption, but in most cases their assignments could be made. Compared with those of nitroenamines (**3a**, **b**),[10] the $\nu_{as}(NO_2)$ of (**1**) appeared at almost the same frequencies, but it differed in its stronger intensity, both in the i.r. and in the Raman, thus indicating that the perturbation produced in the electronic distribution and mechanical couplings of (**3**) by introducing the CO_2R^2 group is better reflected in the intensity of the band than in its frequency. The $\nu_s(NO_2)$ band appeared as several strong bands in the range 1 315—1 280 cm^{-1}; the assignments were complicated by the absorptions due to the CO_2R^2 group in this region.

The proton resonances for the *Z* and *E* forms of (**1**), assigned by correlation with the i.r. spectra observed under the same conditions, were fully consistent with those previously reported,[6,20,21] assigned on different grounds. Two points still merit comment. First, in most compounds the *Z*:*E* ratio was *ca.* 1 in $CDCl_3$ solution, with a slight preference for the *Z*-configuration; the exceptions are compound (**1**) with a primary amino group, and the *ortho*-substituted anilino derivatives (**1h** and **i**) (as well as some other *o*-anilino derivatives examined) which are precisely the compounds which crystallize in form (**1C**). On the other hand, in [$^2H_6$]Me_2SO solution the equilibria were shifted towards the *Z*-form(s), a fact that can be explained by considering that in this very polar solvent the proportion of the *s-trans,Z* form (**1B**), considered to be the most polar, must increase at the expense of the others, as indicated by the i.r. spectra. Secondly, the magnetic anisotropy of the NO_2 group is the factor allowing a distinction between the geometrical isomers: in the *E*-form the olefinic proton (1-H) is strongly deshielded by the *cis*-NO_2 group, and in the *Z*-forms the NH proton appears at lower field than in the *E*-form because of the stronger hydrogen bond between the NH and NO_2 groups (see below) and the deshielding effect provided by the former.

The assignment of the ^{13}C n.m.r. spectra of the *Z* and *E* forms of (**1**) was made by correlating them with the i.r. bands observed, as well as with the ^{1}H n.m.r. signals and their intensity ratios. For compounds (**1b** and **c**), confirmation of the assignment was obtained by measuring the coupling constant ($^3J_{C\text{-}1,3\text{-}H}$) between C=O and 3-H. As established,[22] these coupling constants in a trisubstituted ethylene such as (**1**) should be larger for the *trans* than for the *cis* nuclei: the values found for the *Z* (2.0—2.6 Hz; C-1 and 3-H *cis*) and *E* (7.4—7.7 Hz) forms of (**1b** and **c**) obey this rule. These couplings are smaller than those observed for the 3-aminoacrylic ester (**2b**) (10.4 Hz for the *Z* form, C-1 and 3-H *trans*; 3.7 Hz for the *E* isomer) and for simpler model compounds (*cis* nuclei, 4.3—10 Hz; *trans* nuclei 9.5—16.9 Hz),[22] as expected considering the electronegativity of the NO_2 and NHR^1 substituents around the carbon double bond, and the strong electron delocalization which considerably reduces the order of the double bond. A similar effect is most

Table 4. Two-bond deuterium isotope effects on C-3 chemical shifts ($^2\Delta$, in p.p.b.) and, in parentheses, hydrogen bond energies (E_H/kcal mol^{-1}) for compounds (**1**) and (**2**)[a,b]

Compound	$^2\Delta$ (E_H)	
	Z-isomer	E-isomer
(**1b**)	179 (6.8)	170 (6.6)
(**1c**)	259 (7.8)	236 (7.6)
(**1e**)	248 (7.7)	233 (7.5)
(**1f**)	240 (7.6)	235 (7.6)
(**1g**)	256 (7.8)	244 (7.7)
(**1h**)	247 (7.7)	235 (7.6)
(**1i**)	263 (7.9)	236 (7.6)
(**2a**)	161 (6.5)	—
(**2b**)	214 (7.3)	97 (5.1)[c]

[a] In $CDCl_3$ solution at 0.2M concentration. [b] $^2\Delta = 10^3[\delta_{C-3}(NH) - \delta_{C-3}(ND)]$; $\ln(^2\Delta) = 2.783 + 0.354E_H$ (ref. 12*b*). [c] Intermolecularly bonded.

likely responsible for the low values of the vicinal proton couplings observed[10] in nitroenamines (**3**). The electron delocalization is also reflected in the large chemical shift, $\Delta\delta = \delta_{C-3} - \delta_{C-2}$, between C-3 and C-2. The larger values found for the *E* form indicate that delocalization is larger when the NO_2 and the NHR^1 groups are *trans*; furthermore, $\Delta\delta$ increases when increasing the electron-donating power of the substituent R^1.

The presence of strong hydrogen bonds in (**1**) was indicated by the low values of the ν(N–H) and δ_{NH}. However, it was not possible to deduce from these parameters which of the two geometric isomers is the strongest chelate: the stretching of the NH group appears in solution as a weak, rather broad and complex absorption including the bands of both isomeric forms; on the other hand, the downfield shift of the NH signal of the *Z*-isomer relative to that of the *E*-isomer is probably due, to some extent, to the magnetic anisotropy of *cis*-NO_2 (see above). A decision could be made by considering the two-bond isotope effect ($^2\Delta$) observed in the partially deuteriated NH group on the resonance of C-3. Deuteriation of an amino group involved in 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.[12b] The $^2\Delta$ values, measured for compounds (**1**) and (**2a**, **b**), and the corresponding hydrogen bond energies appear in Table 4. It is clear from these results that the hydrogen bond of the *Z* form is the strongest with an energy difference of 0—0.3 kcal mol^{-1}. Comparison of these energy differences with the *Z*:*E* ratios indicates that, with the exception of (**1h** and **i**), the main factor determining the stability of the configurational isomers is the strength of the hydrogen bond. The tendency observed in (**1h** and **i**), and other related *o*-anilino derivatives, to adopt the *E* configuration must be attributed to factors other than chelation.

In conclusion, the vibrational spectra of 3-amino-2-nitroacrylic esters (**1**) allow the recognition at first sight of the configuration and conformation adopted by these compounds in the solid state. Each of the conformational and configurational isomers (**1A**—**C**) has characteristic and easily distinguishable ν(C=O), enamine, ν(C=C), and $\nu_{as}(NO_2)$ bands. The spectra show significant differences from those of the related 3-aminoacrylic esters (**2**) and nitroenamines (**3**), which can be understood in terms of (**1**) having a strong conjugation of the NH group with the NO_2 group and a weaker, but still significant, one with the CO_2R^2 group. The most salient of these differences are: (i) the observation of conformational isomers in the *Z*-form of (**1**), attributed to the through-space interaction between the C=O and NO_2 groups in (**1B**) and (ii) the presence of a strong $\nu_{as}(NO_2)$ band [which is absent in (**3**)], and the variable intensities observed for the enamine and $\nu(NO_2)$ Raman bands [which are extremely weak in (**3**)]. These difference features can be related to differences in the electron distribution and mechanical couplings in (**1**) and (**3**). The n.m.r. spectra allow the distinction of the geometrical isomers, and indicate a stronger intramolecular hydrogen bond in the *Z* than in the *E* isomer.

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