Spectral Properties and Isomerism of Nitro Enamines. Part 2.† 3-Amino-2-nitrocrotonic Esters

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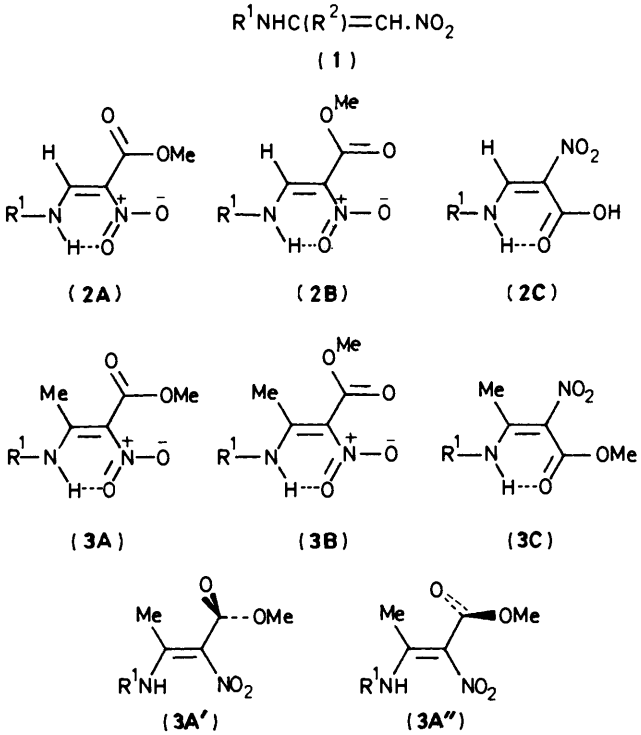
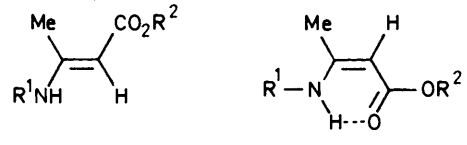
The IR, Raman, ^1H and ^{13}C NMR spectra of a series of 3-amino-2-nitrocrotonic esters (**3**), with both primary and secondary amino groups, have been studied. The spectral data show that these compounds exist in solution as equilibrium mixtures of the two enantiomeric quasi-s-*cis*-(*Z*) isomers (**3A′**) + (**3A″**) and the planar, and less polar s-*cis* (*E*)-(**3C**) isomer, the ratio [(**3A′**) + (**3A″**)]: (**3B**) being strongly dependent on the polarity of the medium. The *E*- and *Z*-forms can be easily distinguished by their vibrational and NMR spectra, and are separated by very low energy barriers ($\Delta G^{\ddagger}$ 50–70 kJ mol^{-1}), the magnitude of which decreases on increasing the electron-donor capacity of the substituent at the amino function. The spectral data and AM1 calculations indicate a strong polarization of the nitro enamine system with a large negative charge accumulation at C-2 and, to a lesser extent, at the NO_2 group. This group acts as a weak π- and a strong σ-acceptor, and the ester group acts as a weak π-acceptor group and a σ-donor.

Nitro enamines are useful intermediates in synthetic organic chemistry,[2,3] and a knowledge of the electron distribution inside these mesomeric compounds, the relative energies of their different isomeric forms and the energy barriers between them, is of paramount importance in understanding their reactivity. Spectroscopic techniques are well-suited to providing information on these matters and have proved to be useful in related push–pull ethylenes.[4] In a study of the vibrational spectra of simple nitroenamines (**1**), Ostercamp and Taylor observed[5] band doubling, indicative of isomeric coexistence, and explained the anomalies in the frequency and intensity of some bands [*e.g.* the weak IR $\nu_{as}(NO_2)$] in terms of mechanical couplings affecting the ν(C=C), $\nu_{as}(NO_2)$ and $\nu_s(NO_2)$ modes and the high polarization and low polarizability resulting from the conjugation induced by the strong electron-withdrawing NO_2 group. The spectra of 3-amino-2-nitroacrylic esters (**2**) indicate[1] that the introduction of the electron-attracting CO_2R^2 group at C-2 of the nitro enamine system partly removes the anomalies, particularly those concerning band intensities. In compounds (**2**), the NO_2 group is more strongly conjugated than CO_2R^2, although enough conjugation is retained by the latter to keep the whole conjugated system planar and to allow for the existence of the s-*cis* (**2A**) and s-*trans* (**2B**) rotamers of the *Z*-isomer.[1] These rotamers, which rapidly interconvert on the NMR time-scale, are separated from the s-*cis*, *E* form (**2C**) by energy barriers $\Delta G^{\ddagger}$ 71.1 – 83.7 kJ mol^{-1}.[6] In most cases, the (*Z*)-[(**2A**) + (**2B**)] and the (*E*)-(**2C**) forms exist in the ratio *ca.* 1 in $CHCl_3$ solution, and the three isomers (**2A–C**) can be easily distinguished by their vibrational spectra.[1] In the sterically more crowded 3-amino-2-nitrocrotonic esters (**3**), the additional C-3 methyl group would be expected to hinder planarity and to decrease conjugation with consequences for the spectral properties, the stability of the different isomers, and the energy barriers between them. Several 3-amino-2-nitrocrotonic esters have been described,[3b,7] but no detailed study of their spectra has been reported. On the other hand, the vibrational and ^1H



NMR spectra of the parent 3-aminocrotonic esters (**4**) are well documented.[8] We report here on the IR, Raman, and NMR spectra of a series of compounds (**3**) (Table 1), with both



† For part 1, see ref. 1.

Table 1. Analytical and physical data for compounds (3).

Compound (Formula)	R^1	Yield (%)	Solvent	M.p./°C		Found (%) (Required)			
				Observed	Literature	C	H	N	X
(**3a**) ($C_5H_8N_2O_4$)	H	92	$C_6H_5CH_3$	92–93	92–93[a]				
(**3b**) ($C_6H_{10}N_2O_4$)	Me	96	EtOH	102–103	102–103[a]				
(**3c**) ($C_{12}H_{14}N_2O_5$)	*p*-MeO-C_6H_4	95	EtOH	83–84	83–84[b]				
(**3d**) ($C_{12}H_{14}N_2O_4$)	*p*-Me-C_6H_4	90	EtOH	87–88	87–88[b]				
(**3e**) ($C_{11}H_{11}ClN_2O_4$)	*p*-Cl-C_6H_4	98	EtOH	90–91	90–91[b]				
(**3f**) ($C_{12}H_{12}N_2O_4$)	*o*-Me-C_6H_4	66	EtOH	78–79	—	57.4 (57.6	5.4 5.6	11.0 11.2)	
(**3g**) ($C_{11}H_{11}BrN_2O_4$)	*o*-Br-C_6H_4	53	EtOH	75–76	—	39.6 (39.9	3.2 3.0	9.2 9.3	26.6 (X = Br) 26.5)

[a] Ref. 7. [b] Ref. 3(*b*).

primary and secondary amino groups, and a dynamic ^1H NMR study of some of these. For comparison purposes, a parallel theoretical study[9] of the geometry, relative energies of the different isomers, and rotational barriers around the formal C=C double bond of compounds (**1**)–(**3**) has been performed.

Experimental

General spectroscopic techniques were as previously noted.[1] Intensities of IR bands are indicated by the usual abbreviations (see Table 2); the coexistence of isomers with partial overlapping of bands precluded the measurement of extinction coefficients. Deuterium isotope effects on ^{13}C chemical shifts, $^n\Delta^{13}C(^{2/1}H)$, were measured for compound (**3b**) 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 >1.[10] The estimated error in the $^n\Delta^{13}C(^{2/1}H)$ values is ± 15 ppb. Dynamic NMR experiments were performed at 100 MHz, using a JEOL MH-100 spectrometer fitted with a standard variable-temperature probe and a JNM (VT-3c) temperature controller. The temperature was measured by monitoring the voltage of the internal thermocouple, which was subsequently calibrated with an external thermocouple placed at the height of the receiver coil in a spinning dummy tube containing a volume of the solvent (*ca.* 0.5 cm^3) similar to that used with the sample. Temperature measurement is accurate to within ± 1 K. The spectra were recorded at slow sweep rates, and with the radio frequency field well below the saturation level, using an internal proton lock. T_2 was determined only at the low temperature limits for the exchanging signals, and was assumed to be constant with temperature. The frequency difference between the exchanging signals and the relative populations of isomers at low temperatures were estimated directly from the experimental spectrum by Lorentzian fitting until 10 K below the coalescence temperature. In the coalescence region the estimation was made by extrapolating from the data at lower temperatures. Theoretical band-shapes were calculated using the equations based on the McConnell treatment,[11] and the rate constants were evaluated by visual fitting of calculated and experimental spectra. In compound (**3b**), the isomeric equilibrium in $CHClF_2$ + $CHCl_2F$ (1:1) is strongly biased in favour of the *Z*-isomer, thus precluding band-shape analysis; in this case the method of Anet and Basus[12] was used by measuring the intensity of the Me-C(3) proton signal of the *Z*-isomer relative to the intensity of a signal from the solvent, together with its changes with temperature. Samples were prepared in precision NMR tubes, and, when $CHClF_2$ + $CHCl_2F$ (1:1) was used as solvent, degassed ($\times 3$) and sealed. Due to the small temperature range over which band-shape analysis could be performed, and owing to the uncertainty in T_2 measurement, only the $\Delta G^{\ddagger}$ values are reported, since the $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values are more prone to systematic errors. Errors in $\Delta G^{\ddagger}$ were estimated as indicated in ref. 13.

Preparation of Compounds.—Compounds (**3a–e**) were synthesized according to the literature (see Table 1). Methyl 3-*o*-toluidino-2-nitrocrotonate (**3f**) and methyl 3-*o*-bromoanilino-2-nitrocrotonate (**3g**) were prepared from methyl 3-ethoxy-2-nitrocrotonate and the appropriate amine following the procedure described.[3b] Solid samples of the *N*-deuteriated derivatives of (**3a**, **b**) and (**3f**) were prepared by repeated recrystallization of the compounds from EtOD until monitoring by IR spectroscopy indicated the absence of ν(N–H) absorption. *N*-Deuteriation of the samples in solution was performed by shaking with D_2O, separating the organic phase, filtering, and transferring it to the IR cell or NMR tube.

Results and Discussion

The main spectral features of compounds (**3**) are assembled in Tables 2–5. Consideration of these data provides a complete picture of the isomeric equilibria.

The compounds (**3**) would be expected to exist as chelates with the NH intramolecularly bonded either to the NO_2 group in the *Z*-form [(**3A**) and/or (**3B**)] or to the ester carbonyl group in the *E*-form (**3C**). The AM1 semiempirical calculations[9a] indicate that the *E*-isomer (**3C**) is more likely to achieve full planarity of the electron delocalized system. The IR and Raman spectra (Table 2) of compounds (**3a–c**) and (**3e**) exhibited in the solid state a single ν(C=O) band in the range 1 724–1 712 cm^{-1}, which was assigned to the free CO_2Me group. These compounds therefore crystallize in the *Z*-form [(**3A**) and/or (**3B**)]. The remaining compounds (**3d**) and (**3f–g**) showed a strong band at 1 673–1 661 cm^{-1}, assigned as the ν(C=O) of the intramolecularly bonded ester group, and a very weak band at 1 727–1 722 cm^{-1}. These compounds crystallize as a mixture of the two configurationally isomeric forms (*Z*)-[(**3A**) and/or (**3B**)] and the *E*-form (**3C**), with the latter overwhelmingly predominant. In solution all the compounds showed the bands due to both isomers, the relative

Table 2. IR and Raman (in italics) frequencies/cm^{-1} of compounds (**3**) and their *N*-deuteriated derivatives.

Comp.	Medium	ν(N–H)[a]	ν(N–D)[a]	ν(C=O)		ν(C=C) + ν(C–N) + δ(N–H)		ν(C=C)[b]		$\nu_a(NO_2)$	
				Z	*E*	*Z*	*E*	*Z*	*E*	*Z*	*E*
(3a)	CCl_4	3 500 s[c,d] 3 310 w		1 722 m	1 677 s	1 613 vs 1 530 s				1 510 m	*e*
	$CDCl_3$	3 485 m[d] 3 310 w		1 722 m	1 675 m	1 618 vs 1 537 m-s				1 520 sh	*e*
	b		2 615 m[d] 2 430 m	1 722 m	1 675 m			1 595 s	1 535 sh	1 515 m	*e*
	$CDCl_3$	*3 485* w[d] *3 310* w		*1 725* w	*1 680* vw	*1 620* m *1 540* m				*e*	*e*
	$[^2H_6]Me_2SO$	3 330[f] 3 140		1 725 s	1 665 m	1 630 m 1 593 s 1 570 sh				1 525 w	*e*
	b		2 510 vw[f] 2 315 w	1 725 s	1 668 w			1 592 s	1 533 w	1 508 m	*e*
	KBr	3 350 s[g] 3 215 s		1 712 vs		1 637 s 1 553 m				1 530 sh	
	b		2530 s[g] 2 375 s	1 710 vs				1 583 s		1 508 w	
	Solid	*3 355* w[g] *3 215* w		*1 712* w		*1 640* w				*1 525* sh	
	b		*2 535* w[g] *2 370* w	*1 712* w		*1 555* w		*1 583* w		*1 510* vw	
(3b)	C_2Cl_4	3 240 vw		1 722 m	1 660 s	1 608 s		1 580 s	1 545 sh	*e*	1 518 s
	$CDCl_3$	3 230 vw		1 722 s	1 647 sh	1 611 vs				1 492 m	1 514 m
	b		2 400 vw	1 722 s	1 647 w			1 590 vs	1 543 w	*e*	1 514 m
	$CDCl_3$	*e*	*e*	*1 721* vw	*1 650* sh	*1 612* m		*1 588* m	*1 540* sh	*e*	*1 514* m
	$[^2H_6]Me_2SO$	*h*		1 727 vs	1 660 sh	1 605 vs	1 590 sh			1 505 w	
	b		2 400 w	1 725 s	1 655 vw			1 589 vs	1 550 sh	1 502 w	
	KBr	3 190 vw		1 724 vs		1 625 s				1 480 w	
	b		2 400 w	1 722 vs				1 604 s		1 462 m	
	Solid	*e*		*1 722* vw		*1 603* m				*1 473* w	
	b		*e*	*1 722* vw				*1 583* m		*1 471* w	
(3c)	C_2Cl_4	3 220 vw	2 375 vw	1 724 m	1 665 s	1 599 vs		1 565 m	1 540 sh	*i*	1 500 sh
	$CDCl_3$	3 210 vw	2 370 vw	1 724 m-s	1 659 m	1 594 s	1 582s[j]	1 567 s	*e*	1 492 sh	*e*
	$[^2H_6]Me_2SO$	3 140 vw		1 727 s	1 660 w	1 593 s	1 580 s[j]			*i*	
	KBr	3 190 vw		1 723 vs		1 610 vs				1 478 m	
(3d)	C_2Cl_4	3 210 vw	2 365 vw	1 724 m	1 663 s	1 599 vs		1 567 m	1 540 sh		1 500 sh
	$CDCl_3$	3 210 vw	2 365 vw	1 723 m	1 659 m	1 595 vs		1 569 s	*e*	1 490 m	*e*
	$[^2H_6]Me_2SO$	3 150 vw		1 727 s	1 661 vw	1 592 s				1 485 m	*e*
	KBr	3 235 w		1 722 vw	1 670 vs		1 585 vs				*i*
	Solid	*e*			*1 673* m		*1 581* w				*e*
(3e)	C_2Cl_4	3 210 vw	2 360 vw	1 725 m	1 665 s	1 610 vs		1 560 sh	1 543 s	*i*	1 523 s[j]
	$CDCl_3$	3 210 vw	2 360 vw	1 723 m	1 660 m	1 603 vs		1 573 s	1 540 sh	*i*	1 513 m[j]
	$[^2H_6]Me_2SO$	*h*		1 728 s-vs	1 660 w	1 601 vs				*i*	1 510 m[j]
	KBr	3 190 vw		1 725 vs		1 603 vs				1 485 s[j]	
	Solid	*3 185* vw		*1 725* vw		*1 603* sh				*1 480* vw	
(3f)	C_2Cl_4	3 200 vw		1 723 m	1 663 s	1 593 vs	1 580 sh[j]			1 490 m[j]	1 520 vs[j]
	b		2 375 vw	1 723 m	1 663 s			1 566 s	1 522 vs[j]	*e*	*e*
	$CDCl_3$	3 200 vw		1 724 s	1 660 m	1 592 vs	1 585 sh			1 487 s[j]	1 513 s[j]
	b		2 375 vw	1 724 s	1 657 m-s			1 568 vs	1 522 s[j]	*e*	*e*
	$CHCl_3$	*e*		*1 725* vw	*1 663* vw	*1 585* m[j]				*i*	*1 510* sh
	b		*h*	*1 725* vw	*1 663* vw			*1 562* m	*1 520* sh	*i*	*i*
	$[^2H_6]Me_2SO$	*h*		1 727 s	1 660 w	1 590 s	1 580 sh			1 490 w	1 515 w
	b		2 370 vw	1 725 s	1 655 w			1 568 vs	*e*	1 490 w	1 515 w
	KBr	3 225 w		1 727 vw	1 661 vs		1 596 s				1 518 vs[j]
	b		2 390 m	1 726 vw	1 660 vs				1 550 s		1 518 vs[j]
	Solid	*3 230* vw			*1 663* w		*i*				*1 513* w
	b		*2 395* vw		*1 664* w				*1 530* m		*1 513* sh
(3g)	C_2Cl_4	3 215 vw	2 350 vw	1 724 m	1 671 s	1 604 vs		1 563 sh	1 550 s	1 500 sh	1 523 vs[j]
	$CHCl_3$	*h*	2 360 vw	1 724 m	1 665 m	1 600 vs		1 568 s	1 523 s	1 500 sh	1 515 s[j]
		h	*h*	*1 725* vw	*1 665* vw	*1 600* sh		*1 570* sh	*1 530* sh	*1 490* sh	*1 513* m
	$[^2H_6]Me_2SO$	3 150 vw		1 729 s-vs	1 664 w	1 600 vs				1 495 sh	1 515 m[j]
	KBr	3 210 vw		1 727 vw	1 677 m 1 665 m		1 605 vs				1 505 m
	Solid	*e*			*1 677* vw *1 666* vw		*1 605* sh				*i*

[a] Assigned to the intramolecularly bonded NH (or ND) group unless otherwise indicated. [b] Measured in the *N*-deuteriated derivative. [c] s, strong; m, medium; w, weak; sh, shoulder; v, very. [d] Assigned to the free NH (or ND) group. [e] Not detected. [f] Assigned to the NH (or ND) group associated with the solvent. [g] Assigned to the intermolecularly bonded NH (or ND) group. [h] Not measured. [i] Overlapped by the ν(C=C) ring band. [j] Contribution of ring ν(C=C).

Table 3. ^{1}H NMR spectral data (δ and *J*/Hz) for compounds (3).

Compound	Solvent	*T*/K	*Z*-isomer (%)	NH		CO_2CH_3		CH_3–C=		R^1
				Z	*E*	*Z*	*E*	*Z*	*E*	
(3a)	$CDCl_3$	293	67	9.51 b 6.55 b	8.89 b 5.72 b	3.85 bs		2.26 b		
		215	72	9.69 b 7.24 b	9.05 b 6.15 b	3.89 s	3.82 s	2.28 s	2.35 s	
	CD_2Cl_2	243	68	9.50 b 6.72 b	8.90 b 5.94 b	3.77 s	3.71 s	2.14 s	2.215	
	$(CD_3)_2SO$	293	—	9.29 b 9.10 b		3.70 b		2.08 s		
(3b)	$CDCl_3$	293	—	10.45 b		3.84 s		2.17 s		3.12 d (4.80)
	$CHCl_2F$ +	293	—	—		3.80 s		2.12 s		3.07 d (5.21)
	+ $CHClF_2$ (1:1)	156	98	—		3.89 s	3.78 s	2.14 s	2.28 s	3.16 d (5.27)
	$(CD_3)_2SO$	293	—	10.40 b		3.74 s		2.08 s		3.05 d (2.46)
(3c)	$CDCl_3$	293	55	10.88 b	10.98 b	3.88 bs		2.09 b		2.85 s (MeO–Ar)
	CD_2Cl_2	230	77	—	—	3.87 s	3.80s	2.06 s	2.12 s	3.84 s (MeO–Ar)
	$(CD_3)_2SO$	293	—	11.54 b		3.77 s		2.01 s		3.79 s (MeO–Ar)
(3d)	$CDCl_3$	293	65	11.95 b	11.04 b	3.88 bs		2.10 b		2.39 s (Me–Ar)
	CD_2Cl_2	237	74			3.86 s	3.80 s	2.08 s	2.15 s	2.39 s (Me–Ar)
	$(CD_3)_2SO$	293	—	11.55 b		3.77 s		2.03 s		2.34 s (Me–Ar)
(3e)	$CDCl_3$	293	58	11.86 b	10.98 b	3.89 s	3.84 s	2.10 s	2.14 s	
	CD_2Cl_2	293	—	11.68 b	10.82 b	3.78 s		2.05 s		
		232	69			3.83 s	3.76 s	2.05 s	2.11 s	
	$(CD_3)_2SO$	293	—	11.45 b		3.77 s		2.04 s		
(3f)	$CDCl_3$	293	56	11.86 b	10.97 b	3.90 bs		2.03 b	2.07 b	2.29 s (Me–Ar)
	CD_2Cl_2	236	72	—	—	3.87 s	3.81 s	2.02 s	2.09 s	2.30 s (Me–Ar, *Z*), 2.28 s (Me–Ar, *E*)
	$(CD_3)_2SO$	293	—	11.44 b		3.76 s		1.94 s		2.22 s (Me–Ar)
(3g)	$CDCl_3$	293	55	11.75 b	10.93 b	3.90 s	3.86 s	2.06 s	2.11 s	
	CD_2Cl_2	235	60	—	—	3.89 s	3.83 s	2.06 s	2.12 s	
	$(CD_3)_2SO$	293	—	11.38 b		3.78 s		1.95 s		

Table 4. Rotational barriers around the C=C bond ($\Delta G^{\ddagger}$/kJ mol^{-1}) and thermodynamic parameters ($\Delta G°$, $\Delta H°$/kJ mol^{-1}; $\Delta S°$/J mol^{-1} K^{-1}) for the $Z \rightleftharpoons$ Equilibria of compounds (2)[a] and (3).

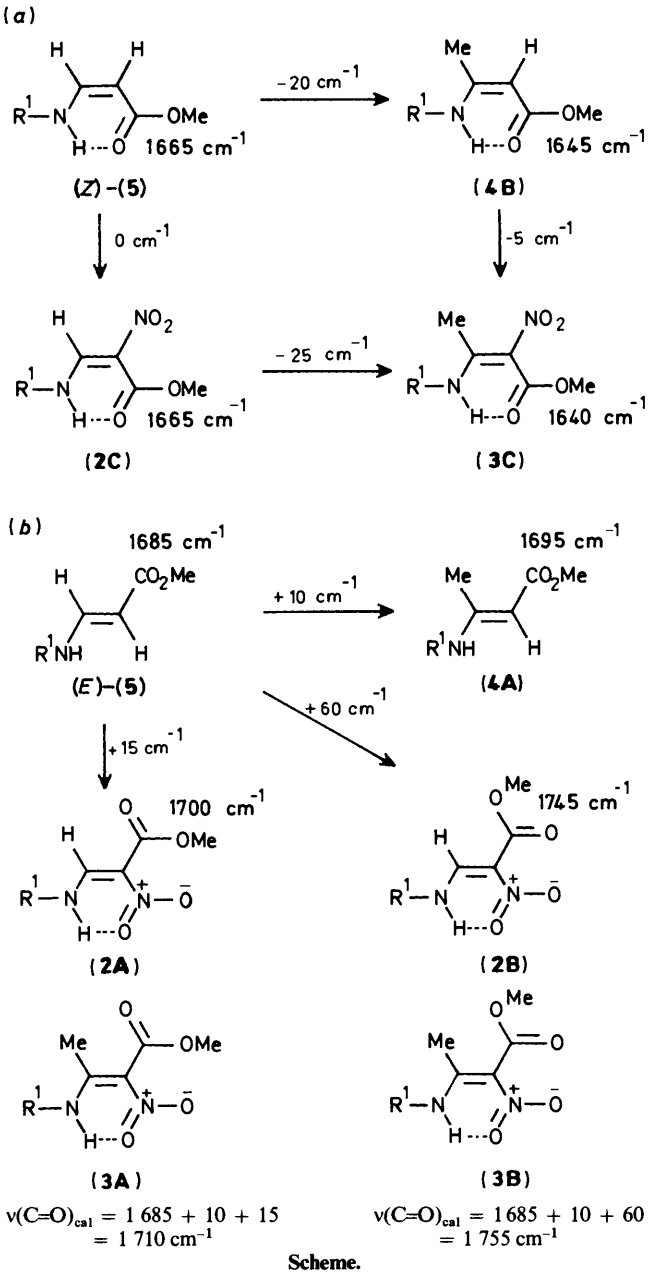
Compound	R^1	Solvent	$\Delta G°(T)$	$\Delta G°_{corr}$[b]	$\Delta H°$	$\Delta S°$	$\Delta G^{\ddagger}(T)$
(3b)	Me	$CHClF_2$ + $CHCl_2F$ (1:1)	5.43 (156)	3.71	—	—	49.2 ± 2.1 (206 ± 3)
(2)	Me	$PhNO_2$	0.69 (293)	—	—	—	85.4 ± 1.7 (347)
(3c)	*p*-MeO–C_6H_4	CD_2Cl_2	1.69 (298.2)	−0.03	3.94	7.53	59.1 ± 0.5 (262)
(2)	*p*-MeO–C_6H_4	$PhNO_2$	0.49 (293)	—	—	—	100.0 ± 1.7 (298.2)
(3d)	*p*-Me–C_6H_4	CD_2Cl_2	1.99 (298.2)	0.27	2.62	2.11	61.7 ± 0.5 (266)
(2)	*p*-Me–C_6H_4	$PhNO_2$	0.69 (293)	—	—	—	105.5 ± 1.7 (298.2)
(3e)	*p*-Cl–C_6H_4	CD_2Cl_2	1.17 (298.2)	−0.55	2.74	5.27	63.2 ± 0.5 (275)
(2)	*p*-Cl–C_6H_4	$PhNO_2$	0.49 (293)	—	—	—	113.0 ± 1.7 (298.2)
(3f)	*o*-Me–C_6H_4	CD_2Cl_2	1.51 (298.2)	−0.21	2.86	4.53	61.4 ± 0.5 (265)
(2)	*o*-Me–C_6H_4	$CDCl_3$	−0.29 (293)	—	—	—	—
(3g)	*o*-Br–C_6H_4	CD_2Cl_2	0.61 (298.2)	−1.11	1.64	3.46	72.8 ± 0.5 (312)

[a] $\Delta G°$ from ref. 1 (in $CDCl_3$), $\Delta G^{\ddagger}$ from ref. 6. [b] $\Delta G°_{corr} = \Delta G° - RT \ln 2$.

Table 5. ^{13}C NMR spectral data (δ) and two-bond deuterium isotope effects on C-3 chemical shifts ($^2\Delta$, in ppb) for compounds (3).

Compound	C(2)	C(3)	Δδ*	C=O	CH_3–C(3)	CH_3O	R^1	$^2\Delta$
(3a)	118.5	160.6	42.1	163.9	21.0	52.4	—	—
(3b)	118.4	160.6	42.2	164.1	15.9	52.3	30.7	199

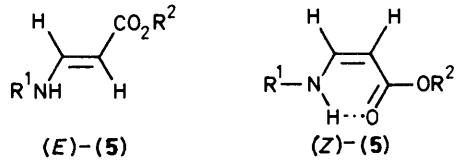
* $\Delta\delta = \delta_{C-3} - \delta_{C-2}$.



Scheme.

intensities of which depended on the polarity of the solvent. In CCl_4 and tetracloroethylene solutions the band at the lower frequency, due to the *E*-isomer, was the stronger, while in DMSO the reverse relationship was observed, thus indicating that the *Z*-isomer is the more polar. The very weak, broad ν(N–H) band observed at 3 230–3 200 cm^{-1} in the spectra for dilute solutions of (**3b–g**) in $CDCl_3$, and the ν(N–H) band at 3 310 cm^{-1} exhibited under the same conditions by compound (**3a**) with a primary amino group, confirmed the chelated structure of both isomeric forms. This band has approximately the same frequency values for both isomers. An additional weak band, exhibited by compounds (**3b–g**) at 3 165–3 140 cm^{-1}, is considered to be an overtone of the strong band at *ca.* 1 600 cm^{-1} (see below) reinforced by Fermi resonance with the ν(N–H) absorption. This band also appears in the spectra of 3-aminocrotonic esters (**4**).[8]

Contrasting with the *Z*-form of 3-amino-2-nitroacrylic esters, which show well-separated ν(C=O) values for rotamers (**2A**) and (**2B**), the single carbonyl band observed for the *Z*-isomer of compounds (**3**) suggests that they adopt only one conformation. The geometry of this conformer was deduced by considering the effects (see the Scheme) that the introduction of the NO_2 and Me groups on C-2 and C-3, respectively, of the 3-aminoacrylic esters (**5**) produces on the ν(C=O) values of the *Z*-and *E*-isomeric forms of these compounds. The frequencies



quoted in the Scheme refer to averaged values for compounds with different R^1 substituents in $CHCl_3$ solutions. The data for compounds (**4**) are taken from ref. 8(*a*), and those for compounds (**5**) from refs. 1 and 16. From the data in section (*a*) of the Scheme, which includes compounds with a chelated ester group, it can be seen that while the introduction of the 2-NO_2 group has an almost negligible effect (Δν 0 to −5 cm^{-1}), the 3-Me group causes a frequency drop of *ca.* 20 cm^{-1}. Both effects are additive as deduced by comparing the ν(C=O) of compounds (*Z*)-(**5**) and (**3C**). Assuming that the additivity is maintained in the isomers with a free ester group, the ν(C=O) values calculated for the fully planar conformational s-*cis*,(*Z*)-(**3A**) and s-*trans*,(*Z*)-form (**3B**) are 1 710 and 1 755 cm^{-1}, respectively, as indicated in section (*b*) of the Scheme. The experimental value (1 722–1 724 cm^{-1} in $CDCl_3$) suggests an intermediate disposition between (**3A**) and (**3B**), but closer to the former, *i.e.* a 1:1 mixture of the two enantiomeric quasi-s-*cis* conformations represented by (**3A′**) and (**3A″**). The small solvent effect observed for this band (Δν −3 to −5 cm^{-1} on passing from $CDCl_3$ to DMSO) as compared with those found[1] for the conformational isomers (**2A**) and (**2B**) of 3-amino-2-nitroacrylic esters (Δν −9 and −24 cm^{-1}, respectively) is also in agreement with this view. The theoretical studies[9a] also indicated that the energy of the s-*trans*, *Z* isomer (**3B**) relative to that of the more stable s-*cis*, *Z*-form (**3A**) is much larger than the value found for (**2B**) relative to (**2A**), and, furthermore, that the *Z*-isomer of (**3**) has a broad energy minimum when the planes of the CO_2Me group and the nitro enamine moiety form an angle of ±30°.

The coexistence of both the *Z*- and *E*-forms in solution was also evidenced by the ^1H NMR spectra which showed that the equilibrium between them is fairly fast on the NMR time scale. The majority of compounds (**3**) exhibited broad signals which were resolved into pairs of signals by lowering the temperature. Table 3 includes the data for different solvents and at different temperatures. For solutions in CD_2Cl_2 the highest temperature—similar for all the compounds—at which complete splitting of all the signals was observed was chosen for measurement in order to compare the *Z*:*E* ratio of the different compounds. Only the *p*-chloroanilino- (**3c**) and *o*-bromoanilino-derivative (**3g**) showed separated signals for each isomer in $CDCl_3$ and CD_2Cl_2 solutions at room temperature. For the other compounds, with the exception of (**3b**), only the NH signal appeared split under these conditions. For DMSO solutions, sharp, averaged signals were obtained for all the compounds, thus indicating that the isomerization process is much faster in this more polar solvent. The assignment of the signals of each isomeric form was made by considering the larger deshielding effect of the NO_2 group relative to that of the CO_2Me group,[1] in such a way that the 3-Me signal at highest field and the NH signal at lowest field were assigned to the *Z*-isomer. The remaining signals were assigned on the basis of their relative intensities. The ^1H NMR data confirmed that, in $CDCl_3$ and CD_2Cl_2 solutions, the *Z*-

isomer predominates and its concentration increases with the electron-donating capacity of the R^1NH group. Assuming that, as observed in 3-amino-2-nitroacrylic esters (**2**),[1] the δ_{NH} value of compounds (**3**) is mainly determined by the strength of the hydrogen bond, the data of Table 3 indicate that the *Z*-isomer is a stronger chelate than the *E*-isomer, and that the strength of the hydrogen bond increases in the order NH_2 < NHalkyl < NHaryl.

The activation barriers, $\Delta G^{\ddagger}$, to rotation around the C=C double bond of compounds (**3b–g**), determined by standard band-shape analysis of their temperature-dependent ^1H NMR spectra, are collected in Table 4, together with data, taken from the literature, corresponding to the homologous compounds (**2**). Band-shape analysis was also used to determine the relative populations at temperatures below coalescence, which gave the thermodynamic parameters ($\Delta G°$, $\Delta H°$, and $\Delta S°$) for the $Z \rightleftharpoons E$ equilibrium included in Table 4, together with $\Delta G°$ values statistically corrected for the fact that the *Z*-isomers are 1:1 mixtures of two enantiomeric forms. The $Z \rightleftharpoons E$ isomeric equilibrium in compounds (**3**) is characterized by positive values of $\Delta G°$, $\Delta H°$, and $\Delta S°$, showing that the *Z*-isomer, which is the strongest chelate, is also the most stable. The entropy contribution is small, 2–7.5 J mol^{-1} K^{-1} in favour of the *Z*-isomer, in agreement with what is generally observed for conformational equilibria. Comparison of the $\Delta G°$ values of compounds (**3**) with those determined for (**2**), also collected in Table 4, indicates that the methyl group on C-3 causes a stabilization of the *Z*-isomer relative to the *E*-isomer. This effect is attributed to the increase of the in-plane compression of the substituents around the C=C bond of compounds (**3**) which is somewhat relieved in the *Z*-isomer by the twisting of the CO_2Me group out of the plane of the nitro enamine moiety. As expected for push–pull ethylenes, the barriers to rotation around the C=C double bond are much lower than that of ethylene itself (274 kJ mol^{-1}).[14] The solvent effect mentioned above, and the structural effects observed on the $\Delta G^{\ddagger}$ values are those typical for push–pull ethylenes with a planar ground state, which isomerize *via* a thermal mechanism with a dipolar transition state.[14] Assuming this type of mechanism, recent theoretical calculations[9b] (including solvent effects) of the energy barriers of these compounds are in agreement with the experimental values. Comparing the barriers of compounds (**3**) with those of compounds (**2**), it can be observed that the introduction of the methyl group at C-3 causes a drop of 40–50 kJ mol^{-1} in the $\Delta G^{\ddagger}$ values. The same effect has been observed[15] for other push–pull ethylenes and it is attributed to the hyperconjugative interaction of the methyl group, which promotes the delocalization of the partial positive charge developed on C-3 in the transition state. The destabilization of the ground state of (**3**) due to steric interactions could also contribute to this effect.

The ^{13}C NMR spectra of compounds (**3a, b**) (Table 5) showed averaged signals for the mixture of geometrical isomers at room temperature, in parallel with their ^1H NMR spectra at the same temperature. The electron delocalization is reflected in the large chemical shift, $\Delta\delta = \delta_{C-3} - \delta_{C-2}$, between C-3 and C-2, which is larger than in the corresponding compounds (**2**).[1] This increase in $\Delta\delta$ is most likely due to the greater polarization of the carbon double bond in (**3**).

The presence of strong intramolecular hydrogen bonds in (**3**), deduced from the low values of ν(N–H) and the high values of δ_{NH}, was also evidenced by the large two-bond isotope effect, $^2\Delta^{13}C(^{2/1}H)$, observed on the C-3 chemical-shift in the partially *N*-deuteriated sample of compound (**3b**). 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.[10] The value found for (**3b**), 199 ppb, which is an average of the two geometrical isomers, is larger than that of the corresponding ester (**2**; $R^1 = R^2 = Me$) (179 and 170 ppb, for the *Z*- and *E*-isomer, respectively),[1] thus indicating a stronger hydrogen bond for the compound with a methyl group on C-3. This difference can be explained on the basis of the buttressing effect, referred to above, produced by the C-3 methyl group, which tends to approach the groups involved in the hydrogen bond, shortening the H ··· O distance.

The positions and intensities of the IR and Raman C=C bands in amino enones have attracted considerable attention,[4] and have been related to the conformation of the delocalized system, and to the polarization and polarizability of the C=C bond.[4a] In this context, the characteristics of the same vibration in the related nitro enamines are of interest. Compounds (**3b–g**), with a secondary amino group, showed a broad absorption, strong in the IR and weak or medium in the Raman, at 1 625–1 581 cm^{-1}, sensitive to *N*-deuteriation, which is assigned as a mixed vibration with main ν(C=C), ν(C–NH), and δ(N–H) components, *i.e.* the enamine band (Table 2). In the solutions of some of the aromatic derivatives this band appeared split into two very close bands. By analogy with compounds (**2**),[1] the band at the higher frequency (1 594–1 592 cm^{-1} in $CDCl_3$) is assigned to the *Z*-isomer, and the other, at 1 585–1 582 cm^{-1}, to the *E*-isomer. This assignment was confirmed by comparing the spectra of compounds such as the *p*-anisidino- (**3c**) and *o*-toluidino-derivative (**3f**), which crystallize in different isomeric forms. The former, which in the solid state adopts the *Z*-configuration, showed the enamine band at 1 610 cm^{-1} in KBr, while the latter, which in the solid state exists almost exclusively in the *E*-configuration, exhibited this band at 1 596 cm^{-1}. In order to establish the effect of *N*-deuteriation on the frequency and intensity of the enamine band of each isomeric form, solid samples of the *N*-deuteriated derivative of (**3b**)—also with the *Z*-configuration in the solid state—and (**3f**) were examined. In compound (**3f**), with chelated C=O, the isotopic effect was much larger ($\Delta\nu$ −46 cm^{-1}) than in (**3b**) ($\Delta\nu$ −21 cm^{-1}) with chelated NO_2. The solutions of the *N*-deuteriated derivatives of (**3b**) showed a band at *ca.* 1 590 cm^{-1}, strong in the IR, medium in the Raman, attributed to a vibration with a main C=C stretching component [referred to hereinafter in this and in the other compounds as ν(C=C)] of the *Z*-isomer, and a weaker one, or a shoulder, at *ca.* 1 550 cm^{-1}, due to the same vibration of the *E*-form. The *N*-dideuteriated derivative of (**3a**), also a *Z*-isomer in the solid state, had a strong IR (weak in Raman) ν(C=C) band at 1 583 cm^{-1} in KBr or as a solid, while in solution the IR bands of the *Z*- and *E*-isomer appeared at *ca.* 1 590 (strong) and 1 530 cm^{-1} (weak), respectively. The isotopic effect in compounds (**3**) is, therefore, as in the case of 3-amino-2-nitroacrylic esters (**2**), strongly dependent on the configuration, and can be, as in the latter compounds, of diagnostic value. It should also be noted that the isotopic effect found in the *Z*-form of (**3**) is quite near to that observed[5,9c] ($\Delta\nu$ −28 to −36 cm^{-1}) in the chelated *Z*-form of 2-amino-1-nitropropenes (**1**; $R^2 = Me$), and that found for the *E*-form of (**3**) resembles that ($\Delta\nu$ −50 to −60 cm^{-1}, in CCl_4)[8a] of the chelated *Z*-isomers (**4B**) of 3-aminocrotonic esters.

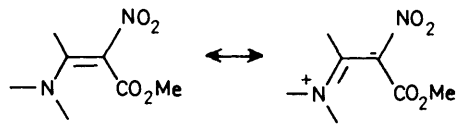
Comparing the frequencies (1 651–1 624 cm^{-1} in $CDCl_3$) of the enamine band of compounds (**2**) with a secondary amino group[1] with those of (**3b–g**), it can be seen that the C-3 methyl group causes a frequency drop of *ca.* 30 cm^{-1}, and the same effect is observed when comparing the 2-amino-1-nitroethenes (**1**; $R^2 = H$) (1 646–1 639 cm^{-1} in $CDCl_3$ or CH_2Cl_2) with their homologous compounds (**1**; $R^2 = Me$) (1 613–1 604 cm^{-1}).[5,9c] A similar frequency shift is observed when comparing the 3-aminoacrylic esters (**5**)[1,16] with their homologous compounds (**4**).[8a] Two factors may be responsible for this effect: (i) the electron-donating capacity of the Me group, which would

Table 6. Mulliken population analysis from AM1 calculations: total charges on the main groups of compounds (**2**)–(**5**) (R^1 = H). (The excess (−) or default (+) of π-electron population is given in parentheses).

Compound	C-2	C-3	NH_2	NO_2	CO_2Me
(**2A**)	−0.37	0.17	0.20	−0.16	−0.03
	(−0.41)	(0.23)	(0.33)	(−0.08)	(−0.07)
(**2B**)	−0.36	0.17	0.19	−0.15	−0.03
	(−0.41)	(0.22)	(0.32)	(−0.07)	(−0.08)
(**2C**)	−0.37	0.17	0.20	−0.14	−0.05
	(−0.41)	(0.23)	(0.33)	(−0.07)	(−0.08)
(**3A′**)	−0.37	0.24	0.18	−0.16	−0.03
	(−0.43)	(0.23)	(0.31)	(−0.08)	(−0.07)
(**3C**)	−0.38	0.24	0.18	−0.14	−0.05
	(−0.43)	(0.23)	(0.31)	(−0.08)	(−0.08)
(**4A**)	−0.36	0.15	0.07	—	−0.13
	(−0.28)	(0.14)	(0.25)	—	(−0.08)
(**4B**)	−0.37	0.16	0.10	—	−0.14
	(−0.30)	(0.14)	(0.23)	—	(−0.09)
(*E*)-(**5**)	−0.36	0.09	0.07	—	−0.12
	(−0.27)	(0.14)	(0.21)	—	(−0.08)
(*Z*)-(**5**)	−0.37	0.10	0.10	—	−0.13
	(−0.29)	(0.14)	(0.24)	—	(−0.09)

reduce the bond order of the formal C=C bond, and/or (ii) a different composition of the enamine band that in compounds such as (**1**; R^2 = H), (**2**), and (**5**), with a HC=C group, may have a significant contribution of the δ(C–H) mode. Theoretical studies[9c] indicate that, in addition to ν(C=C) and δ(N–H), the stretching ν(C–NH) and the in-plane deformation δ(C–H), contribute to the enamine mode of nitro enamines such as (**1**; R^2 = H) and (**2**).

It should also be pointed out that the enamine band of compounds (**3**) has almost the same frequency value as that of 2-amino-1-nitropropenes (**1**; R^2 = Me),[5,9c] and is higher than that[8a] of 3-aminocrotonic esters (**4**). Similar observations were made[1] when comparing the enamine band of (**2**) with their similarly related compounds (**1**; R^2 = H) and (**5**). These results suggest that the electron distribution in compounds (**3**) is, as in the 3-amino-2-nitroacrylic esters (**2**), mainly governed by the strong electron-attracting NO_2 group, and that the electron-withdrawing power of the ester group is greatly inhibited. The twisting of the CO_2Me group out of the plane of the enamine system in the *Z*-form of (**3**) while in the *E*-form the NO_2 group remains coplanar with the rest of the delocalized system, can also be explained by considering the poorer electron-accepting ability of the ester group relative to that of the NO_2 in these compounds. The high frequency and IR intensity of the enamine band of (**2**) and (**3**) are indicative of the strong polarization of the C(2)–C(3) bond with a high accumulation of negative charge at C-2, and suggest that the resonance canonical form (**6b**) is the main ionic contributor to the ground state of these, and related, nitro enamines. The great stability of



(**6a**) (**6b**)

this canonical form is determined by the +*R* effect of the amino group reinforced by the large −*I* effect of the NO_2 group and, to a much lesser extent, by its −*R* effect. In amino enones such as (**4**) and (**5**) the carbonyl group participates more effectively in the resonance. The enamine band of nitro enamines could then be viewed as a skeletal vibration of the strongly polarized $H^+N–C–C^-$ grouping, and should therefore have properties different from those of the similar band in amino enones, as observed in this and other[1,5] work. The results (Table 6) of the AM1 semiempirical calculations[9c] of the charge distribution in compounds (**2**) and (**3**), and in their counterparts, compounds (**5**) and (**4**), lacking the nitro function, are in agreement with the interpretation of spectral data. In both (**2**) and (**3**) most of the negative charge goes to C-2, almost all by π-electron delocalization, and to a lesser extent to the NO_2, by π-electron delocalization and mainly by σ-induction. The charge at the ester group is almost nil, the result of this group being a weak π-acceptor and, in the presence of the NO_2 group, a σ-donor. In the reference compounds (**5**) and (**4**), the ester group acts both as π- and σ-acceptor, and while the negative charge at C-2 remains high, there is a much lesser electron withdrawing effect from the amino group and C-3.

The assignment of the $\nu(NO_2)$ bands of most of the compounds (**3**) studied was complicated by the absorptions due to the aromatic ring and the ester group. The $\nu_a(NO_2)$ value of the derivatives with a secondary amino group appeared in solution as two bands at 1 520–1 500 and 1 505–1 470 cm^{-1}, of variable intensity in the IR and much weaker in the Raman, assigned to the *E*- and *Z*-forms, respectively, by comparing their intensity changes with those of the ν(C=O) bands on changing the polarity of the medium. In the anilino-derivatives these bands are usually stronger, probably because of contributions due to the ring ν(C=C). The frequencies of these bands were almost the same (but their intensities were weaker) than those of 3-amino-2-nitroacrylic esters (**2**). The $\nu_s(NO_2)$ band appeared as one or two strong IR and Raman bands in the range 1 290–1 240 cm^{-1}; the assignments were complicated by the other absorptions anticipated in this region.

In conclusion, the spectra of 3-amino-2-nitrocrotonic esters (**3**) show that these compounds exist in solution as an equilibrium mixture of the planar s,*cis*-*E*-isomer (**3C**) and the more polar *Z*-isomer, which is a mixture of the two enantiomeric forms (**3A′**) and (**A″**) with the ester group twisted out of the plane of the nitro enamine moiety. The *E*- and *Z*-isomers are separated by very low energy barriers, and can be easily recognized by their IR, Raman and low temperature ^1H NMR spectra. Most of the compounds adopt the *Z*-form in the solid state, while the *ortho*-substituted anilino-derivatives have a greater tendency to crystallize in the *E*-form. The spectra of (**3**) show significant differences from those of the 3-amino-crotonic esters (**4**), which can be understood in terms of (**3**) and (**4**) having different electron distributions as a result of the stronger electron-withdrawing ability of the NO_2 group (mainly by σ-induction) by comparison with that of the CO_2Me group. Compounds (**3**), and the homologous 3-amino-2-nitroacrylic esters (**2**), are strongly polarized with a great accumulation of negative charge at C-2 and, to a lesser extent, at the nitro group.

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