Vinylogous Systems. Part 5.[1] Vibrational Spectroscopy of the Nitroenamine System

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Vibrational frequencies have been assigned to those bonds which comprise the conjugated core (**IIa**) of a nitroenamine. The results are compared and contrasted with recent infrared studies of the aminoenone system (**Ia**). The analysis for (**IIa**) rests upon the postulate that vibrational coupling of the multiply bonded units is reinforced by the accompanying electronic flux, leading to an unprecedentedly low value (1 280—1 250 cm^{-1}) for the symmetric nitro vibration of the NC=CNO$_2$ unit. No dramatic differences between the i.r. spectra of *cis*- and *trans*-isomers were apparent. The high degree of electronic polarisation that exists in nitroenamines is reflected in extremely weak Raman bands for all major functional groups.

The nature and extent of the vibrational interactions between electron donor, carbon double bond, and electron acceptor within the aminoenone structure (I) has been the subject of active investigation,[2–6] beginning with the seminal report of Cromwell *et al.* in 1949.[7] One of us has shown[4] that, compared with a simple enone, the change in intensity and fall in frequency observed for each double bond vibration in (I) is reasonably understood in terms of (*i*) the contribution of dipolar canonical form (**Ib**), and (*ii*) coupling of ν(C=O) with ν(C=C) to give symmetric and antisymmetric modes.

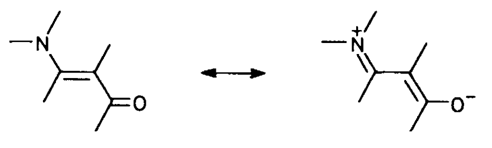
No such systematic attention has apparently been given to nitroenamines (II),[8,†] even though nitro is a stronger electron acceptor[9,10] than the carbonyl group. All reported spectra[11–18] show a strong band at 1 630 ± 30 cm^{-1}, attributed variously to ν(C=C) (**IIa**) or ν(C=N) (**IIb**). There is also disagreement with respect to the nitro-group vibrations, which some investigators[12,14,15] have assigned to bands near 1 530 and 1 350 cm^{-1}, but which others,[13,16–18] sensitive to the obvious connections between (I) and (II), have associated with two, or even three, strong bands in the region between 1 400 and 1 150 cm^{-1}. In selecting mainly or exclusively nitroenamines with phenyl groups or aromatic rings as model compounds, several workers[12,14,15] have needlessly complicated, and perhaps even compromised, their conclusions.

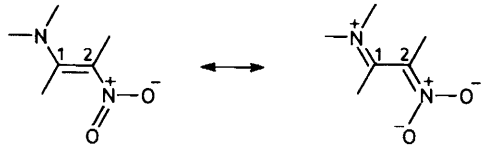
Compounds prepared for this project are assembled in Table 1. We have focused upon simple, fundamental structures and, with the exception of the anilino-compound (7), have avoided aromatic substituents. Our basic vibrational assignments are necessarily preceded by the u.v. and ^{1}H n.m.r. evidence as to the configurations in which these compounds exist. Spectroscopic data are assembled in Tables 2—5; an expanded version of Tables 4 and 5 is available as a Supplementary Publication.

Table 1. Analytical data for the nitroenamines (**1**)—(**10**)[a]

Compound	Yield (%)	M.p. (°C) Observed	M.p. (°C) Literature	Recrystallisation solvent
(**1**)	82	103—104	104[b]	EtOH
(**2**)	35	79—80	78[c]	EtOH
(**3**)	68	82—83	83[d]	Pr^{i}OH
(**4**)	88	76—77	77—78[e]	C_6H_{12}–EtOAc
(**5**)	75	90—91	93—94[f]	C_6H_{12}–EtOAc
(**6**)	86	111—112		EtOAc
(**7**)	15	93—94	94—95[g]	95% EtOH
(**8**)	44	78—79	81—82[h]	Et_2O
(**9**)	83	111.5—112	113—113.5[h]	C_6H_{14}–Et_2O
(**10**)	93	68.5—69.5		Et_2O

[a] Analytical data for new compounds as follows. (**6**), Found: C, 53.8; H, 7.7; N, 18.3. $C_7H_{12}N_2O_2$ requires C, 53.8; H, 7.7; N, 17.9%. (**10**), Found: C, 53.1; H, 9.1; N, 17.8. $C_7H_{14}N_2O_2$ requires C, 53.1; H, 8.9; N, 17.7%. [b] H. Meerwein, W. Florian, N. Schoen, and G. Stopp, *Justus Liebigs Ann. Chem.*, 1961, **641**, 1. [c] T. Severin and B. Bruck, *Chem. Ber.*, 1965, **98**, 3847. [d] T. Severin, D. Scheel, and B. Adhikary, *Chem. Ber.*, 1969, **102**, 2966. [e] Ref. 19. [f] Ref. 20. [g] W. Meister, *Chem. Ber.*, 1907, **40**, 3435. [h] Ref. 17.


(Ia) (Ib)


(IIa) (IIb)

Experimental

Raman spectra were obtained for solid samples on a Nicolet MX-3600 Raman spectrometer; no spectrum could be obtained for nitroenamine (**2**) due to excessive fluorescence. Infrared spectra were recorded on a Perkin-Elmer 580B spectrophotometer equipped with a Model 3600 Data Station, which was used to subtract the solvent background from the solution spectra. Nuclear magnetic resonance (^{1}H n.m.r.) spectra were obtained on a Bruker HFX-90 instrument, and peak positions are given in parts per million downfield from tetramethylsilane as internal lock. Ultraviolet spectra were obtained on a Unicam SP 8100 spectrophotometer. Melting points were determined using open capillaries and are uncorrected. All reactions were performed under a nitrogen atmosphere. Commercial samples were employed as reactants, with amines

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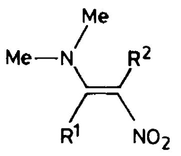
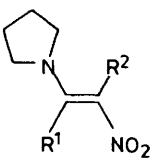
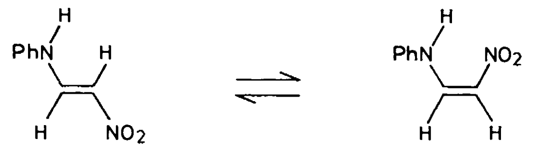
† The two carbon atoms and their substituents are labelled as in (II).



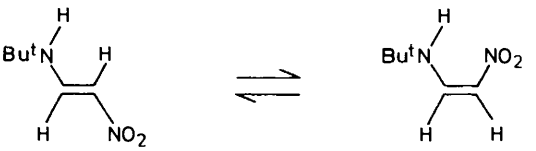
(1) $R^1 = H$, $R^2 = H$
(2) $R^1 = H$, $R^2 = Me$
(3) $R^1 = Me$, $R^2 = H$



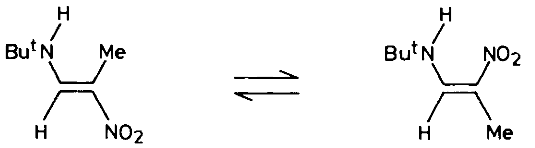
(4) $R^1 = H$, $R^2 = H$
(5) $R^1 = H$, $R^2 = Me$
(6) $R^1 = Me$, $R^2 = H$



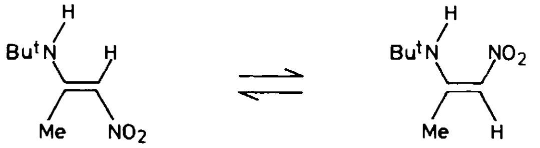
(7a) (7b)



(8a) (8b)



(9a) (9b)



(10a) (10b)

being distilled from BaO prior to use. Reaction progress and product purity were monitored by thin-layer chromatography. The value of pK_a 8.60 for (**7**) was obtained at 25 °C by potentiometric titration on a Metrohm Potentiograph E 436.

Preparation of Compounds.—Compounds (**1**)—(**3**), and (**7**) were synthesized according to the literature (see Table 1). Transamination of (**1**)—(**3**) (as per the method of Marchetti and Passalacqua[19]) with pyrrolidine (absolute MeOH solvent) or t-butylamine (neat, in large excess) gave nitroenamines (**4**)—(**6**) and (**8**)—(**10**), respectively. Formation of 2-t-butylamino-1-nitropropene (**10**) required three weeks at 40 °C.

Results and Discussion

Configuration and Planarity.—The tertiary nitroenamines (**1**)—(**6**) are expected to exist in the *trans*-form since this maximises conjugation and minimises steric hindrance. The proton n.m.r. spectra of (**1**) and (**4**) in DMSO (Table 2) show the presence of a single isomer whose two CH signals are doublets with *J ca.* 10.6 Hz. This value is very low for *trans*-vinylic coupling (expected range 13—18 Hz[21]) so further evidence is needed. It is provided by (**8**) in the same solvent, which exists as a mixture of isomers with *J* 10.1 and 5.9 Hz, respectively. Hence (**1**) and (**4**) can be firmly identified as *trans*-isomers and assignments for their H-1 and H-2 proton signals follow by comparison with (**2**) and (**3**). Similar considerations permit the separate assignment of all four CH signals for (**8**) by comparison with (**9**) and (**10**). These n.m.r. data are compatible with those reported in the literature for these and similar compounds.[20,22] An approximate estimate of the isomer balance for the four secondary nitroenamines (**7**)—(**10**) appears in Table 2; it is presumed that (**1**)—(**6**) will exist as 100% *trans*-isomer under all conditions. Qualitatively similar differences between the isomer balance of secondary and tertiary nitroenamines have been reported by Fetell and Feuer.[20]

Table 2. Key ^{1}H n.m.r. spectral data of nitroenamines

		Solvent	
Compound	Parameter	[$^2H_6$]Me$_2$SO	CDCl$_3$
(**1**)	δ(H-1)	8.16 (d)	
	δ(H-2)	6.70 (d)	
	$J_{1,2}$	10.56 Hz	
(**2**)	δ(H-1)	8.30 (s)	
(**3**)	δ(H-2)	6.54 (s)	
(**4**)	δ(H-1)	8.34 (d)	
	δ(H-2)	6.62 (d)	
	$J_{1,2}$	10.60 Hz	
(**7b**)	δ(H-1)		7.3 (d)
	δ(H-2)		6.6 (d)
	$J_{1,2}$		6.3 Hz
	δ(NH)		8.4 (br)
	(**7a**:**7b**) ratio		0:100
(**8a**)	δ(H-1)	8.16 (d)	
	δ(H-2)	6.76 (d)	
	$J_{1,2}$	10.1 Hz	
	δ(NH)	8.75 (br)	
(**8b**)	δ(H-1)	7.38 (q)	6.84 (q)
	δ(H-2)	6.45 (d)	6.42 (d)
	$J_{1,2}$	5.9 Hz	5.9 Hz
	δ(NH)	9.4 (d)	9.35 (d, br)
	$J_{1,NH}$	*ca.* 18 Hz	*ca.* 19 Hz
	(**8a**:**8b**) ratio	55:45	0:100
(**9a**)	δ(H-1)	8.32 (d)	8.38 (d)
	δ(NH)	7.3 (br)	*a*
	$J_{1,NH}$	*ca.* 15 Hz	*ca.* 15 Hz
(**9b**)	δ(H-1)	7.64 (d)	7.02 (d)
	δ(NH)	9.75 (d)	9.7 (br)
	$J_{1,NH}$	*ca.* 16 Hz	*ca.* 14 Hz
	(**9a**:**9b**) ratio	30:70	15:85
(**10a**)	δ(H-2)	6.80 (s)	
	δ(NH)	7.4 (br)	
(**10b**)	δ(H-2)	6.60 (s)	6.47 (s)
	δ(NH)	10.7 (br)	10.7 (br)
	(**10a**:**10b** ratio)	5:95	0:100

[a] Not identified.

Inspection of CPK space-filling models suggests that, while there should be no bar to planarity for (**1**) and (**4**), the 2-methyl substituent of (**2**) must cause considerable twisting of NMe$_2$, perhaps by as much as 30°, while the effect of 1-methylation in (**3**) on the planarity of both NMe$_2$ and NO$_2$ will be less but not negligible. The pyrrolidinyl-derivatives (**5**) and (**6**) should suffer less hindrance. Their u.v. spectra in water (Table 3) qualitatively bear this out: (**2**) shows a drop of *ca.* 20% in intensity whereas the effect on (**5**) is much less and (**3**) and (**6**) are barely affected. The generally higher u.v. intensities of (**4**)—(**6**) are consistent with the exceptional electron-donor ability of the pyrrolidine nitrogen atom.[4,23] The shifts in $\lambda_{max.}$ brought about by *C*-methylation are similar in a comparative sense, but not

Table 3. Ultraviolet spectral data of nitroenamines

Compound	Water $\lambda_{max.}$/nm	Water ε/l mol^{-1} cm^{-1}	Cyclohexane $\lambda_{max.}$/nm	Cyclohexane ε/l mol^{-1} cm^{-1}
(1)	361	24 900	336	17 300
(2)	380	19 000		
(3)	359	25 800		
(4)	366	29 000		
(5)	384	24 500		
(6)	357	27 200		
(7)	388	25 000	361	8 100
(8)	355	25 200	336	8 800
(9)	368	21 600	354	10 200
(10)	350	20 400	346	15 700

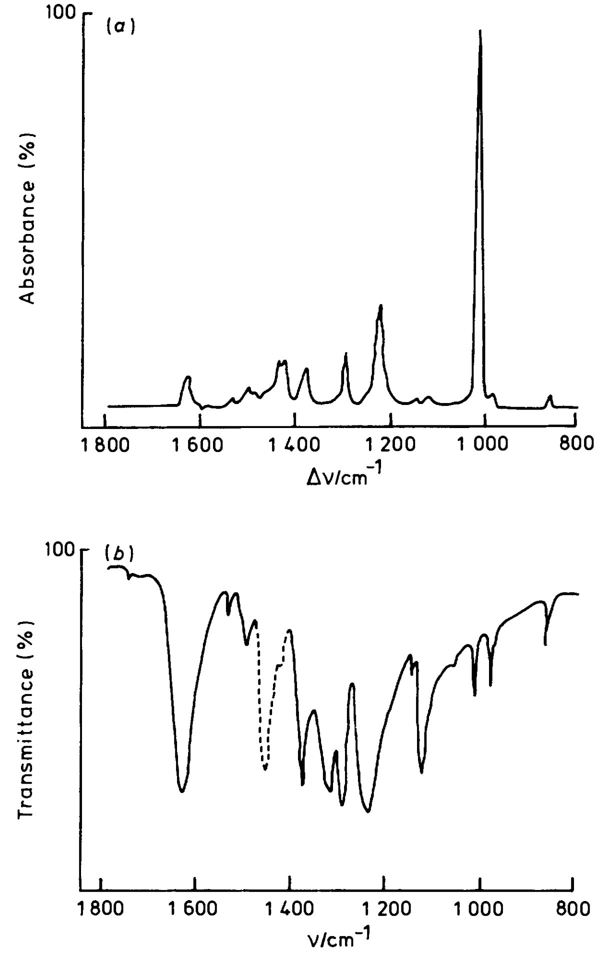


Figure 1. The solid-state Raman spectrum (*a*) and Nujol mull infrared spectrum (*b*) of compound **(1)** in the range 1 800—800 cm^{-1}

absolutely, to the 1—10 nm and 14—20 nm found by Dabrowski and Kamienska-Trela[24] for the alkylation of aminoenones at positions corresponding here to C-1 and C-2, respectively.

In interpreting the u.v. spectra of **(7)**—**(10)** it is first of all necessary to note the very large solvent effect on **(1)**: in cyclohexane, $\lambda_{max.}$ falls by 25 nm and the intensity by a third. All these compounds show a broad u.v. band at 330—380 nm and the above evidence identifies it as a $\pi \longrightarrow \pi^*$ transition, as for the aminoenones[25] (a weaker band near 230 nm,[11,20,26] possibly due to the nitroethylene moiety,[11] is not considered here). The change in isomer population brought about on **(8)** by solvent (Table 2) leads to the prediction that the *trans*-isomer should preponderate in water but the *cis*-form in cyclohexane, and we interpret its u.v. spectrum in these terms. If this interpretation is correct, $\lambda_{max.}$ is barely affected by isomerisation but intensity is roughly halved in the *cis*-form, again as found for the related aminoenones.[24,25]

Compound **(7)** appears to behave in the same simple way. The bathochromic shift in **(7)** relative to **(8)** is presumably caused by additional conjugation with the phenyl moiety. The claim by Freeman and Emmons[11] that *cis*-secondary ('chelated') nitroenamines can be distinguished from the *trans*-forms by a bathochromic shift is probably vitiated by the fact that all the cases they quote contain the PhNH group; however, evidence is presented below that sterically forced hydrogen bonding does indeed give rise to a bathochromic shift.

The cases of **(9)** and **(10)** are more complex. Compound **(9)** shows a lower wavelength and intensity in water and higher values for both in cyclohexane than would have been anticipated from the obvious cross-correspondences. Models show that both isomers face steric constraints which must make both conjugation in the *trans*-form and hydrogen bonding in the *cis*-form less than usually advantageous. This may account for the surprisingly small solvent effect on isomer balance revealed by Table 3, and consequently we interpret its u.v. spectrum as due mostly to the *trans*-isomer in water but with some of this still remaining in cyclohexane. The case of **(10)** is quite different. Here models show that the very severe steric hindrance present in the *cis*-isomer is not readily offset by loss of planarity and is much more likely to be relieved by in-plane bond deformations in such way as to induce forced intramolecular hydrogen bonding. The *cis*-isomers of aminoenones quite often isomerise to the *trans*-form in polar solvents[24,27] and the nitro-group is a poorer proton acceptor than carbonyl[28] so *a priori* isomerisation might be expected here, but such bonds reinforced by buttressing can be very strong and resistant to intermolecular attack. This will explain why the *cis*-form of **(10)** predominates even in DMSO and is consistent with the NH proton shifts (Table 2), which indicate an order of intramolecular hydrogen-bond strength **(10)** $\gg$ **(9)** > **(8)** > **(7)**. Consequently we believe **(10)** to exist as the *cis*-isomer even in water, the strength and relative solvent insensitivity of its u.v. spectrum being due to the extra electronic polarisation resulting from this buttressing. Consistently, **(10)** is the only compound of these four which does not exist as a mixture of isomers in the solid state (see below). Some degree of forcing in **(9)** could account for the surprisingly high value of $\lambda_{max.}$ in cyclohexane for this compound also.

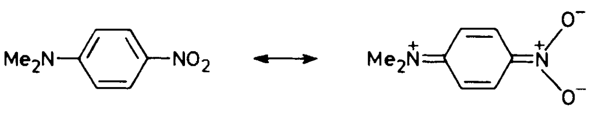
Some further comments are pertinent in the light of the unusual i.r. features to be discussed below. A typical *trans*-aminoenone will possess[24,25] $\lambda_{max.}$ *ca.* 300 nm with $\varepsilon > 30\,000$ l mol^{-1} cm^{-1}; the longer wavelengths but lower intensities of compounds **(1)**—**(6)** are consistent with the greater overall electronegativity of the nitro-group than carbonyl but its lesser resonance component.[9,10] There is indeed, as will appear, evidence for an extreme electronic polarisation in these compounds. Similarly, the CH chemical shifts are downfield of their nearest aminoenone analogues and *J* is even lower,[29] reminiscent indeed of the values typical for aromatic rings.[30] One distinct difference is a lesser tendency to give the *cis*-isomer, which would be formed exclusively in $CDCl_3$ by almost any NH-containing aminoenone.[4,24,27] This presumably results from the lesser proton-acceptor ability of the nitro-group as noted above, even though probably this is greater than normal; consistently, the NH proton signal of aminoenones is typically at lower field than found here.[27,29]

Table 4. Key bands in the infrared and Raman spectra of tertiary nitroenamines[a,b,c]

(1)			(2)		(3)			
Raman	CHCl$_3$		CHCl$_3$		Raman	CHCl$_3$		Notes
1 628 (mw)	1 637	*1 330*	1 640	*880*	1 548 (mw)	1 567	*660*	ν(C=C) or mode C
1 503 (w)	1 499	*180*	1 498	*70*	1 490 (w)	1 505	*80*	$\nu_{as}(NO_2)$ or mode D
1 315 (vw)	1 326	*970*	1 267	*1 250*[d]	1 320 (vw)	1 351	*480*	ν(C-NR$_2$)
1 293 (mw)	1 309	*820*	1 246	. . .	1 194 (w)	. . .[e]		ν(C-NO$_2$)
1 240 (vw)	1 264	*620*	1 267	*1 250*[d]	1 240 (w)	1 282	*1 040*	$\nu_s(NO_2)$ or mode E
1 012 (vs)	1 016	*50*			1 038 (vs)	1 025	*230*	See text

(4)			(5)			(6)			
Raman	CHCl$_3$		Raman	CHCl$_3$		Raman	CHCl$_3$		Notes
1 610 (w)	1 624	*1 090*	1 614 (vw)	1 632	*1 040*	1 548 (w)	1 560	*690*	ν(C=C) or mode C
1 525 (vw)	1 477	*260*	1 501 (mw)	1 478	*90*	1 520 (vw)	1 478	*200*	$\nu_{as}(NO_2)$ or mode D
	1 353	*260*	1 255 (vw)	1 249	. . .	1 305 (vw)	1 337	*450*	ν(C-NR$_2$)
1 292 (mw)	1 311	*1 710*	1 237 (w)	. . .[f]		1 242 (w)	1 233	*150*	ν(C-NO$_2$)
1 245 (sh)	1 255	*720*	1 205 (sh)	1 259	*1 200*	1 260 (vw)	1 277	*1 250*	$\nu_s(NO_2)$ or mode E
1 015 (vs)	1 013	*30*	1 153 (vs)	1 169	*160*	1 044 (vs)	1 072	*140*	See text

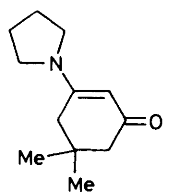
[a] Frequencies in ν or Δν cm^{-1}. [b] Intensities (ε_A) in solution are *italicised*; in the solid state are comparative. [c] A dotted line means a particular frequency is obscured by solvent or other bands. [d] Bands combined. [e] At 1 235 cm^{-1} in CH$_2$Cl$_2$. [f] At 1 229 cm^{-1} (ε_A *890*) in CH$_2$Cl$_2$.



(11a) (11b)

Vibrational Spectroscopy.—It is convenient to consider the tertiary nitroenamines first, since the spectroscopy of the remainder is complicated by isomerism. Key i.r. and Raman data are given for (1)—(6) In Table 4 and for (7)—(10) in Table 5; expanded versions of these giving full band assignments are available as a Supplementary Publication * along with solution spectra. Figure 1 shows the solid-state i.r. and Raman spectra for nitroenamine (1).

Tertiary Nitroenamines (1)—(6).—The ν_{as} and ν_s nitro-group vibrations are found as a strong band at 1 570—1 550 cm^{-1} and a somewhat weaker one at 1 390—1 330 cm^{-1}, respectively, in the i.r. spectra of nitroalkanes.[31,32] The position of ν_{as} correlates with inductive effects[32] and is lowered by conjugation; ν_{as} and ν_s appear at 1 550—1 500 cm^{-1} and 1 360—1 320 cm^{-1} in nitroalkenes,[33] while most aromatic nitro-compounds show similar ranges.[34] In both series of compounds, ν_{as} in general is more affected by conjugation and remains the stronger band. The exception is the 4-nitroanilines, studied by Flett,[35] where (11) for example shows ν_{as} as a weak band at 1 492 cm^{-1} but $\nu_s NO_2$ as a very strong one at 1 324 cm^{-1}; one presumes a major contribution from the dipolar canonical form (**11b**). In the nitroenamines (1)—(6), $\nu_{as}NO_2$ appears as a very weak band in the i.r. and Raman spectra at 1 525—1 497 cm^{-1} while no strong band consistently appears in the range which, on the above evidence, would be expected for ν_s. Fetell and Feuer[22] assign the NO$_2$ vibrations of (5) to bands at 1 375 and 1 250 cm^{-1}, but without giving evidence, whereas Freeman and co-workers[11,26] note the lowering in ν_{as} but do not assign ν_s, and the assignments by Belon and Perrot[14] of some 1-phenyl-1-amino-2-nitroethylenes are complicated and possibly vitiated by an alleged enamine–ketimine tautomerism for which the evidence cited appears inadequate.



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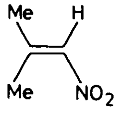
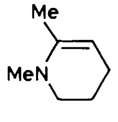


(13)



(14)

The carbon double bond of simple ethylenes gives rise to a weak i.r. and strong Raman band at 1 680—1 620 cm^{-1} [36] which is lowered on conjugation with carbonyl[37] and still more when also β-substituted with an amino-group; the aminoenone (12) shows ν(C=C) as a very strong i.r. (and weaker Raman) band at 1 566—1 550 cm^{-1} according to solvent.[4] However, neither nitro-substitution nor amino-substitution separately has much effect on ν(C=C); compounds (13)[33,38] and (14)[39] each show ν(C=C) near 1 650 cm^{-1}. This insensitivity of ν(C=C) to nitro-substitution has previously been noted as anomalous by Rao.[40] It persists in the nitroenamines where, except for (3) and (6), ν(C=C) is at 1 650—1 600 cm^{-1}. The high i.r. intensity of this band and its relative weakness in nitroethylenes such as (13)[38] constitute an obvious point of resemblance to the equivalent carbonyl compounds,[4,36] but there is no resemblance in the frequencies, so the aminoenone analogy[11,26] is not exact.

One of us[4] has analysed the double-bond frequencies of aminoenones in terms of a resonance-reinforced vibrational coupling which lends ν_{as} and ν_s character to ν(C=O) and ν(C=C), respectively. We believe that a rather similar form of coupling takes place in the nitroenamines; the two cases are compared in the Scheme. It is suggested that ν(C=C) and the two ν(NO$_2$) couple to give three vibrational modes which are roughly characterised as C—E. The analogy with the aminoenones is not exact since, unlike A and B, these modes cannot be simply described as ν_{as} and ν_s; instead, we suggest the approximate descriptions shown. The accompanying electronic character helps to explain the frequency and intensity changes. The low intensity of $\nu_{as}(NO_2)$ is postulated to result from the opposed dipoles of mode D, and while both C and E are high-intensity vibrations, this follows for different reasons. The latter is an all-symmetric mode which results, as for B, in low

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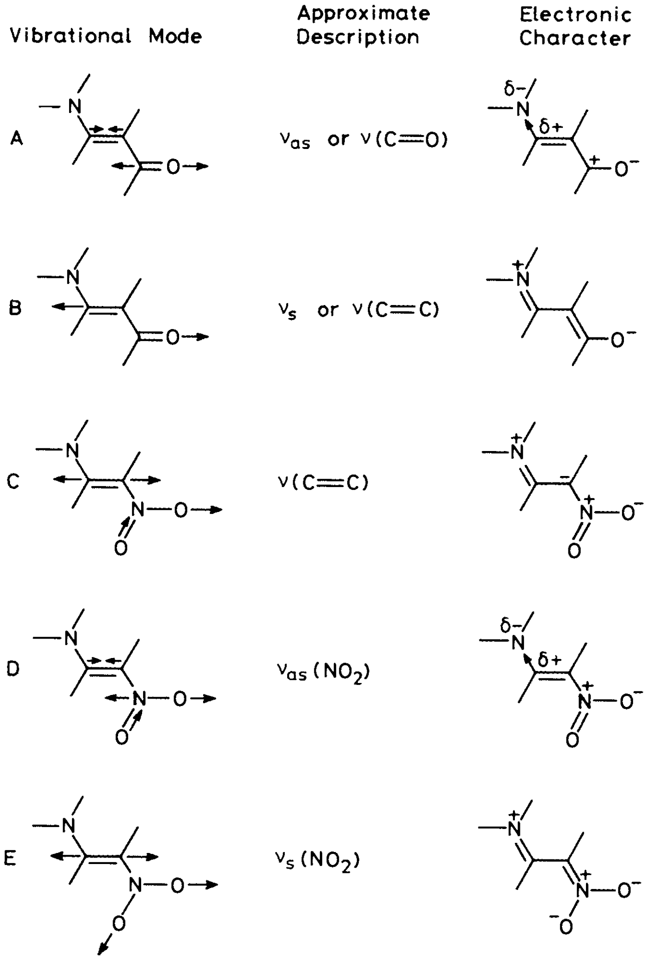
* Supplementary data available (No. SUP 56228, 10 pp.). See Instructions for Authors, section 4.0 (January issue).

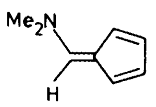


Scheme.

frequency as well as high intensity. However, the electronic character of C is better described in π-inductive than in resonance terms, and frequency is little affected although intensity is high. Another way of approaching the problem is by analogy with the 4-pyridones, for which the mostly ν(C=O) vibration is at lower frequency than ν(C=C); the latter is relatively insensitive to solvent and substitution since the effects of conjugation and coupling are then opposed.[4]

Mode E is therefore expected as a strong band at a frequency exceptionally low for $\nu_s(NO_2)$. By analogy with the aminoenones,[4] two other strong bands expected in much the same region are those for $\nu(C\text{-}NR_2)$ and $\nu(C\text{-}NO_2)$. The former occurs[4] at 1 257 cm^{-1} in (**12**) while the latter in (**13**) may be the prominent band near 1 190 cm^{-1}. In fact, the i.r. spectra of all these nitroenamines are dominated, in addition to ν(C=C), by three strong bands in the region 1 350—1 200 cm^{-1}. The most constant in position of these, and generally the strongest especially in the solid state, we assign to $\nu_s(NO_2)$; this (in $CHCl_3$) lies in the relatively narrow range 1 282—1 255 cm^{-1}, *i.e.*, 70—80 cm^{-1} below that for nitroalkenes.[33] This fall in frequency is even greater than that expected (*ca.* 65 cm^{-1})[4,6] for carbonyl on β-amino-substitution into a simple enone, though it has to be remembered that $\nu_{as}(NO_2)$ falls much less and that, as in the aminoenones, the *mean* frequency shift is probably the true index of conjugation[6] (see later).

The position of $\nu(C\text{-}NR_2)$ and $\nu(C\text{-}NO_2)$ depends on the substitution pattern in a manner subtly related to planarity and hence to conjugation. The effect of conjugation on these frequencies is not equivalent. Since the amino-group is the electron donor, its own conjugation is lost only to the extent that it itself is twisted, whereas that of the nitro-group is lost to the extent that *either* group is twisted. This leads to an asymmetry in the frequency pattern which helps to confirm both assignments. In (**1**), $\nu(C\text{-}NR_2)$ and $\nu(C\text{-}NO_2)$ are the strong bands (in $CHCl_3$) at 1 326 and 1 309 cm^{-1}, respectively. As seen above, the nitro-group of (**3**) is probably somewhat twisted, so $\nu(C\text{-}NO_2)$ falls to 1 235 cm^{-1} while $\nu(C\text{-}NR_2)$ remains at 1 351 cm^{-1}. In (**2**) the amino-group is twisted so both frequencies fall, to 1 267 and 1 246 cm^{-1}, respectively. This pattern is repeated for (**4**)—(**6**). The $\nu_s(NO_2)$ vibration preserves a relative constancy since it is not so wholly dependent on conjugation for its double-bond character. Obviously this analysis over-simplifies; the wide variations in relative intensity shown in Table 4 are testimony to the high degree of vibrational mixing among all these polar modes.



(**15**)

All five polar modes are extremely weak in the Raman spectrum, the result of the extreme polarisation and minimal latent polarisibility of these molecules. We have encountered a parallel situation for 2-substituted-1,1-diacylethylenes,[41] whose two carbonyl functions are perhaps roughly equivalent in electronegativity to one nitro-group.[9,10] In fact the highest frequency for a strong Raman vibration in any compound except (**7**) is at *ca.* 1 150 cm^{-1}. Provisionally we assign this to a CH bending mode since these might be able to generate some degree of electronic flux at right angles to the molecular dipole. This assignment is of course in conflict with the usual one[42] which assigns *trans*-δ(CH), *cis*-δ(CH), and isolated δ(CH) to Raman bands near 1 305, 1 265, and 1 360—1 322 cm^{-1}. It is of course possible that *trans*-δ(CH) in (**1**) and (**4**) is coincident with $\nu(C\text{-}NR_2)$ near 1 310 cm^{-1} (the i.r. band is expected[42] near 1 295 cm^{-1}) but there is no appreciable Raman band near any of these positions. Whatever their origin, a cluster of strong Raman bands is observed which is diagnostic of the substitution pattern (see Table 4) and consistent with the assignments proposed (see Supplementary Tables).

Among the important polar vibrations the only apparent anomaly is the lowered frequency of ν(C=C) in (**3**) and (**6**), to *ca.* 1 560 cm^{-1}. However, bearing in mind that ν(C=C) and both $\nu(NO_2)$ are coupled, and that the $\nu(NO_2)$ modes rise somewhat, the nett fall in mean frequency is only *ca.* 15 cm^{-1}. Similar self-compensating changes in double-bond frequency have been noted for the aminoenones.[6] The slight nett fall for (**3**) and (**6**) may be genuine, the result of induced resonance donation from the 1-methyl group (a 2-substituent of course cannot do this). A similar effect may be present in aminoenones,[6,41] though there the electron demand is not so extreme. Another small but detectable effect is the double-bond-lowering propensity of the pyrrolidine group, especially on $\nu_{as}(NO_2)$; other consequences of its very strong electron donation have been noted above.

One apparently surprising feature is the solvent insensitivity of the nitroenamine double-bond vibrations; almost the only effect visible is the (unexplained) tendency of $\nu_s(NO_2)$ to *rise* slightly from CH_2Cl_2 to $CHCl_3$, especially in (**1**) and (**4**). By contrast, ν(C=O) and ν(C=C) in (**12**) fall by 10 and 6 cm^{-1}, respectively, between these solvents, and this effect is typical for aminoenones.[4,6] We have previously drawn attention to the solvent insensitivity of the enamine (**15**), and postulated that the key factor in aminoenones is the presence of highly polarisable

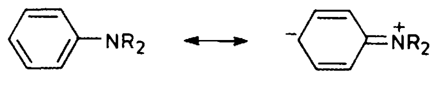
Table 5. Key bands in the infrared and Raman spectra of secondary nitroenamines[a]

(7)				(8)				
	CH_2Cl_2				CH_2Cl_2			
Raman	NH		ND	Raman	NH		ND	Notes
. . .	1 646[b]	*650*	1 628[c]	1 628 (mw)	1 639	*870*	1 623[d]	ν(C=C) or mode C
1 485 (vw)	1 485 (sh)		1 478[c]	1 535 (w)	1 478	*230*	1 467[d]	$\nu_{as}(NO_2)$ or mode D
. . .	1 408	*130*	1 052[c]	. . .	1 374	*200*	1 155[d]	δ(NH)
1 351 (vs)	1 373	*370*	1 399[c]	1 332 (vw)	1 324	*160*	1 323	ν(CN)
1 315 (vw)	1 330	*90*	*1 294*[c]		1 356	*470*	1 305[d]	$\nu(C\text{–}NR_2)$
1 297 (vw)				1 350 (vw)				
1 241 (mw)	1 270			1 229 (vw)	1 240[e]	*440*	1 228[d]	$\nu_s(NO_2)$ or mode E
. . .	1 195	*500*	1 193	1 183 (mw)	1 185	*550*	1 185	$\nu(C\text{–}NO_2)$
				1 147 (vw)	1 137		1 137	
1 013 (ms)	964	*130*	951	993 (vs)	989	*100*	988	See text

(9)			(10)				
	CH_2Cl_2			CH_2Cl_2			
Raman	NH		Raman	NH		ND	Notes
. . .	1 647	*750*	1 586 (vw)	1 603	*840*	1 567[f]	ν(C=C) or mode C
1 503 (vw)	1 483	*130*	1 480 (w)	1 485	*340*	1 465[f]	$\nu_{as}(NO_2)$ or mode D
. . .	1 394	*190*	. . .	1 445		1 252[f]	δ(NH)
. . .	. . .		. . .	1 216		1 225	ν(CN)
1 350 (vw)	1 370	*540*	1 347 (vw)	1 357	*500*	1 306[f]	$\nu(C\text{–}NR_2)$
1 326 (mw)	1 323	*430*					
1 270 (vw)	1 233[g]	*310*	1 267 (mw)	. . .[h]		. . .	$\nu_s(NO_2)$ or mode E
. . .	1 184	*480*	1 171 (vw)	1 183	*750*	1 184	$\nu(C\text{–}NO_2)$
. . .	1 155	*460*					
1 149 (ms)	. . .		981 (vs)	982	*80*	982	See text

[a] See footnotes *a*, *b*, and *c* in Table 4. Note that many of the present intensities are exaggerated by band overlap where both *cis*- and *trans*-isomers exist (see text). [b] At 1 648 and 1 632 cm^{-1} in Nujol. [c] Coupled vibrations; Σδ(NH):δ(ND) = 1.34. [d] Σδ(NH):δ(ND) = 1.27. [e] At 1 268 and 1 242 cm^{-1} in $CHCl_3$. [f] Σδ(NH):δ(ND) = 1.27. [g] At 1 251 and 1 235 cm^{-1} in $CHCl_3$. [h] At 1 272 cm^{-1} (ε_A *510*) in $CHCl_3$.

lone-pair electrons, rather than of polarity as such.[43] While the nitro-group is more polar than carbonyl it has been noted above that its lone-pair electrons are less available for hydrogen bonding. The above hypothesis appears therefore to be confirmed.



(16a) (16b)

Secondary Nitroenamines (**7**)—(**10**).—The coexistence of isomers complicates most of these spectra. The exception is (**10**) (*cf.* Table 2) whose relative simplicity has been invaluable in interpreting the remainder. This exists throughout as the *cis*-isomer, with key bands (in $CHCl_3$) at 3 140 cm^{-1} [ν(NH)], 1 603, 1 485, 1 445 cm^{-1} [δ(NH), removed on deuteriation], 1 358, 1 272, and 1 181 cm^{-1}, all readily assigned by analogy with the tertiary nitroenamines described above. Solid-state frequencies are very similar and, once again, there is no strong Raman band at above 1 000 cm^{-1}. Comparison of these frequencies with those for its nearest tertiary analogues (**3**) and (**6**) reveals few significant differences except that ν(C=C) for (**10**) is *ca.* 40 cm^{-1} higher and $\nu(C\text{–}NO_2)$ is *ca.* 40 cm^{-1} lower. These differences are plausibly attributed to poorer conjugation in the *cis*-isomer but the effect is very much smaller than in the ostensibly parallel aminoenone case.[4,6] A probable reason for this rests, once again, on the much lower resonance component in the electronegativity of the nitro-group relative to carbonyl,[9,10] as already noted in other contexts.

The presence of coexistent isomers shows itself in band doubling. In (**7**), for example, ν(C=C) at 1 646 cm^{-1} in $CHCl_3$ becomes a doublet at 1 648 and 1 632 cm^{-1} in the solid state, and a similar doubling is shown by $\nu_s(NO_2)$, $\nu(C\text{–}NR_2)$, and $\nu(C\text{–}NO_2)$, but not by $\nu_{as}(NO_2)$, unless this is masked by a benzene ring mode. In this way it is possible to show that (**8**) and (**9**) exist as isomeric mixtures under all conditions, (**7**) only in the solid state, and (**10**) never. (The greater tendency for the *trans*-form to be present in the solid state probably results from the nature of this as a relatively polar medium; *cf.* Table 2.) The apparent existence of (**8**) as a mixture in solution is rather difficult to understand in the light of Table 2, unless this is explained as due to the presence of ethanol in the i.r. but not the n.m.r. solvent. In general there is little difference in either frequency or intensity between the components of each doublet, which though it makes identification easy, also makes it difficult to assign either of the pair to a particular isomer, and no such assignment has been attempted. This again helps to emphasise the relative insensitivity of these spectra to isomerisation that is noted above. It is particularly curious that only in (**7**) does ν(C=C) show doubling; the expected effect in the aminoenones can be calculated[6] as a rise of *ca.* 25 cm^{-1} in the *cis*-isomer.

The anilino-derivative (**7**) is unique in possessing a strong Raman band at 1 351 cm^{-1} where in no other compound does one exist at above 1 000 cm^{-1}. Tentatively, we assign this band to the ν[N–C(phenyl)] mode [listed in Table 5 as ν(CN)] unique to this compound. This may owe its strength to some contribution from the dipolar canonical form (**16b**). While this will not be an important contributor to the ground state of the molecule, so should not be strong in the i.r. spectrum, it does represent a large potential source of polarisibility in the course of the vibration. The equivalent alkyl ν(CN) modes are assigned to lower-frequency bands weak in both the i.r. and the Raman spectrum.

Deuteriation has proved of enormous value in disentangling the complex coupling pattern of the aminoenones[4–6,27,43] but results here have proved equivocal. It is clear that, in (**8**), δ(NH) couples with ν(C=C), ν(C–NR$_2$), and both ν(NO$_2$) vibrations, but the isotope ratio is low and some band movements must have gone undetected. Furthermore these band movements except for δ(NH) itself are mostly less than those observed for aminoenones, indicative of lesser vibrational mixing. The pattern is probably similar for (**10**); decomposition of (**9**) precluded analysis. Compound (**7**) shows additional involvement of at least one other mode. In view of the general principle[5] that *N*-methylation and *N*-deuteriation have rather similar consequences for the associated vibrational modes, the close resemblance between ν(C=C) for (**10**) after deuteriation, and the equivalent frequency for (**3**) and (**6**) which possess the same ring-substitution pattern, is of some interest. There is a similar resemblance between (**8**) and (**4**). Both again help to emphasise the relative insensitivity of the key vibrations for these compounds to isomerisation.

Conclusions

The vibrational spectroscopy of nitroenamines possesses the following salient features.

(*a*) The 6 μ region is characterised by a very strong band assigned to ν(C=C), generally at 1 650—1 600 cm^{-1} but sometimes below this, and the *absence* of any strong band attributable to ν_{as}(NO$_2$). The latter is at 1 530—1 480 cm^{-1} and weak, easily confused with aromatic ring or CH$_2$ deformation modes when present.

(*b*) There are three strong bands in the 1 350—1 150 cm^{-1} region. The most constant of these, and generally the strongest in the solid state, is ν_s(NO$_2$) at 1 280—1 250 cm^{-1}. The others, attributed to ν(CNR$_2$) and ν(CNO$_2$), are much more variable in position and intensity in a way that seems chiefly to depend on distortions from planarity.

(*c*) All these modes, including the carbon double-bond vibration which is normally intense, give extremely weak bands in the Raman spectrum.

(*d*) Isomerism has little effect. Typically the co-presence of *cis*- and *trans*-isomers, which is quite common for secondary nitroenamines in the solid state as well as in solution, results in band doubling. Tertiary nitroenamines probably exist exclusively as the *trans*-isomer.

It will be seen that intensity is, if anything, a more important spectroscopic criterion than frequency, a trait shared in part with the aminoenones.[4,6] No other class of nitro-compound combines such a weak ν_{as}(NO$_2$) i.r. vibration with such a strong and low-frequency ν_s(NO$_2$) mode, and in few other classes of compound containing carbon double bonds is their Raman intensity so low.

Finally we comment on the scope and limitations of the analogy between the aminoenones (**I**) and the nitroenamines (**II**) that helped give rise to this investigation. Despite the extreme degree of electronic polarisation found in the nitroenamines and their unprecedentedly low value for ν_s(NO$_2$), the infrared consequences are not here so spectacular. This is most objectively seen by comparing the effect of amino-substitution on *mean* double-bond frequency ν_m, which we have previously shown[43] to be the most relevant index of conjugation when coupling occurs. The effect of β-amino-substitution into an enone is calculated[6] to lower the mean of modes A and B by 75 cm^{-1}. A parallel estimate applied to modes C—E gives results here which vary from 56 to 67 cm^{-1}. This is in accord with the lesser *resonance*-acceptor ability of the nitro-group than carbonyl[9,10] despite a greater overall electronegativity which is demonstrated *inter alia* by pK_a 8.60 for (**7**) as against values of *ca.* 15 for the nearest equivalent aminoenones.[44] It may even be that the insensitivity of these i.r. spectra to isomerism, in such puzzling contrast to the aminoenones,[2,4,6] is some further consequence of this major distinction between these two substituent groups.

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