Conformational and Tautomeric Studies of Acylguanidines. Part 2.[1] Vibrational and Carbon-13 Nuclear Magnetic Resonance Spectroscopy

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The i.r. and Raman spectra are described and discussed for molecules which embody in fixed form six of the possible conformers of an acylguanidine. Four of these correspond to structural units common in heterocyclic chemistry, and it is shown that all are readily distinguished by a variety of criteria which depend on the frequencies and intensities of the ν(C=O) and ν(C=N) modes. It is shown that the above are strongly coupled in all cases but two, the nature of the coupling depending on the conformation and being responsible in large part for the characteristic differences between the structural types.

Where C=O and C=N are conjugated an analogy is drawn with the aminoenones, and the analysis is carried out on similar lines. An important difference is that, here, the *s-cis* (**E**) is preferred to the *s-trans* (**A**) conformer because of lone-pair repulsion in the latter; the former is better conjugated and has much lower double-bond frequencies. Evidence is presented that neither form is as electron-rich as the aminoenones.

The sp^2-carbon signals show a clear distinction between through-conjugated and cross-conjugated types, which is sharper for carbonyl since uncomplicated by hybridisation changes. These affect the imine ^{13}C signals considerably and, as a result, some subsidiary criteria emerge. An unexpected bonus exists in the distinction between the *N*-methyl signals of 5- and 6-membered rings, a distinction which appears to be of general applicability.

The i.r. and ^{13}C n.m.r. results are critically compared in several respects, one being an instructive contrast between the effects of through (i.r.) and localised (^{13}C) electrical forces.

Despite the central position of the oxoheterocycles in heterocyclic chemistry, their vibrational spectroscopy has been almost entirely neglected. The leading exception is the pyridones, to which Bellamy and Rogasch,[2] Katritzky and Jones,[3] and Spinner and co-workers,[4] in particular, have made notable contributions; in these compounds, vibrational coupling between ν(C=O) and ν(C=C) has been recognised and is tolerably well understood.[4,5] Elsewhere, attention has been virtually confined to noting the existence of ν(C=O), as in a ^{13}C n.m.r. study[6] which considers such interesting contrasts as across the set (**16**)—(**19**). This study is typical in that structures were known in advance and were used to rationalise the spectroscopy rather than *vice-versa*. It is also typical in two other respects. Firstly, these compounds contain a multitude of conjugated double bonds whose differing arrangement might reasonably be expected to give rise to characteristic differences in their vibrational spectroscopy. Secondly, their paucity of protons makes proton n.m.r. spectroscopy, so valuable elsewhere, virtually useless as a guide to compound structure.

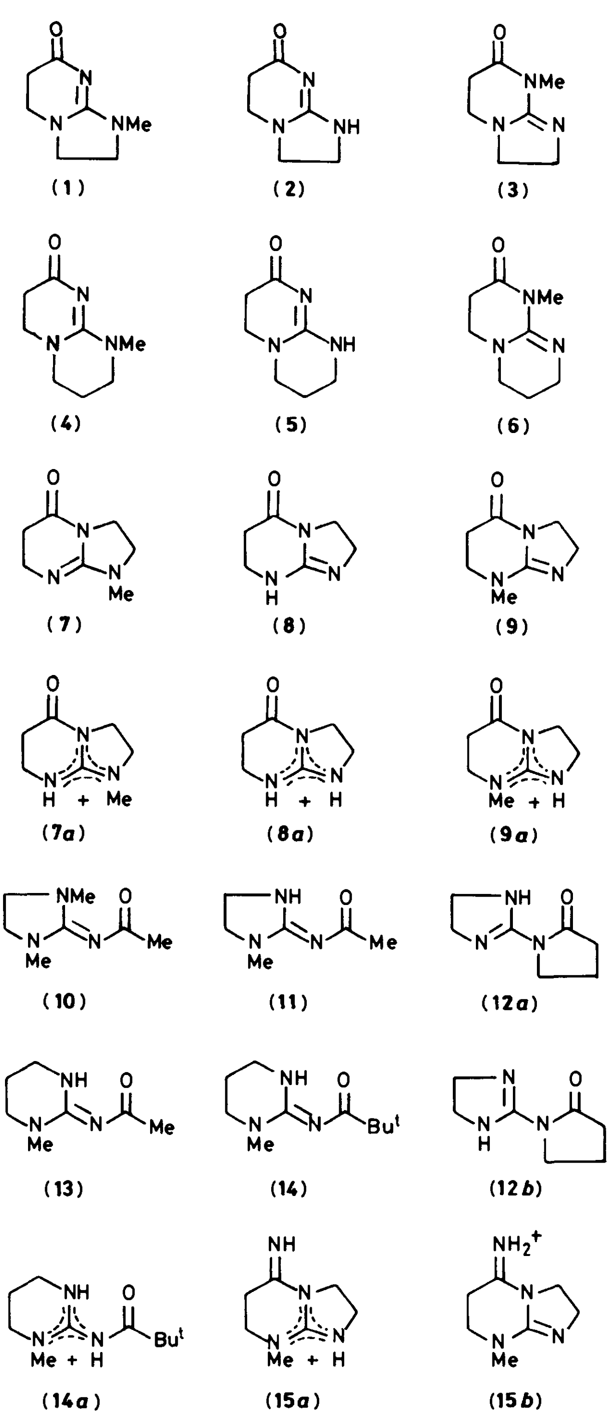
One purpose of this paper is to act as the first in a series that will attempt to show that the i.r. and Raman spectroscopy of the oxoheterocycles, properly interpreted, not only forms the method of choice for their structural elucidation, but can also provide important insights into their electronic nature. These methods have been used by one of us (P. J. T.) for some years in the *de novo* elucidation of isomeric and tautomeric problems, and some of these studies have been published.[7] We are also concerned to explore the potential of ^{13}C n.m.r. spectroscopy in a similar context, and this is here pursued in parallel.

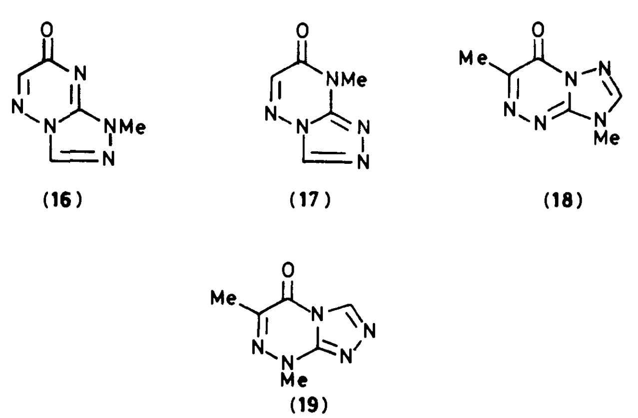
The synthesis of a series of isomeric and tautomeric acylguanidines as model compounds in another context[1] provides an opportunity to start by reducing this problem to its simplest form. The compounds to be considered are set out in grid form in Scheme 1; their general resemblance to fused oxoheterocycles such as (**16**)—(**19**) will be apparent. Formally, the latter class may be regarded as acylguanidines possessing extra double bonds. While this additional conjugation may be expected to distort any simple picture derived from compounds (**1**)—(**14**), and does, we have found that enough of the key spectroscopic distinctions survive to be useful in structural analysis.[7,8]

The five basic structural arrangements to be found in these compounds are shown as (**A**)—(**E**). Of these, (**A**)—(**D**) precisely parallel compounds (**16**)—(**19**), respectively. Structure (**E**) is the *s-cis* variant of (**A**) and is preferred, as we shall show, where freedom exists for the acyl group to rotate. It may be noted that (**A**) and (**E**) parallel the *s-trans* (**F**) and *s-cis* (**G**) forms of the aminoenones[5] and related compounds[9] which we have previously investigated. This parallelism is important, both were it leads to similar conclusions and where it does not, and will be much stressed in this analysis.

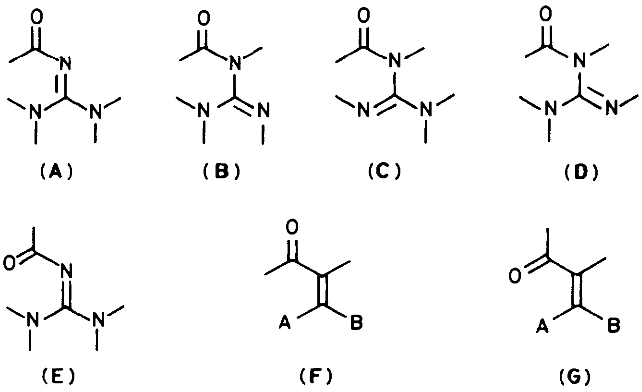
Results and Discussion

The structural unit $N_2C=X$ possesses four characteristic vibrational modes which for guanidine ($X = NH$) are displayed in Figure 1, with their frequencies and approximate descriptions.[10] Of these, the bending mode at 773 cm^{-1} may be the strong Raman band found near 700 cm^{-1} in many of these compounds (and at 718 cm^{-1} in cyanoguanidine[10]), while ν_s(NCN) does not appear to give rise to a characteristic vibration. The other two modes are expected above 1 450 cm^{-1}; with carbonyl, one therefore anticipates three bands in the 'double bond' region. This is found throughout, though ν_{as}(NCN) is often merely a shoulder on ν(C=N) where the frequency of the latter is low; however, in (**4**) and (**5**) all three are strong and well resolved (Figure 2). In (**2**) and (**5**), but not elsewhere, δ(NH) has been identified as a strong band in the same region. A further characteristic band at 1 415—1 370





Scheme 1.



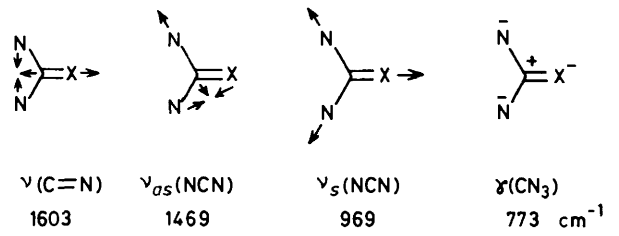


Figure 1. Four characteristic vibrational modes for guanidine, X = NH

cm^{-1}, described as ν(CN) in Tables 1–3, is tentatively assigned to a mode associated with the C–N link between carbonyl and the guanidine unit. Discussion will be confined to these five modes, plus ν(NH) where appropriate.

It will be convenient to discuss in sequence the 'through-conjugated' structures (A) and (E) and the 'cross-conjugated' structures (B)—(D).* Guanidinium cations (Table 2), of whatever type, are considered separately. Discussion of the ^{13}C n.m.r. data follows that of the vibrational spectroscopy.

Types (A) *and* (E).—We have previously shown[5,9,11] that the $\nu(C{=}O)$ and $\nu(C{=}C)$ bands of aminoenones and related compounds are partially coupled vibrations that possess some of the character of ν_{as} and ν_s, respectively. Since the dipoles oppose in ν_{as} but reinforce in ν_s (Scheme 2), the result is a great increase in intensity for the nominal $\nu(C{=}C)$ vibration somewhat offset by a fall in intensity for $\nu(C{=}O)$; at the same time, both frequencies are greatly reduced by conjugation. For the four possible aminoenone alignments $\varepsilon_A(C{=}C)$ is, indeed, almost linearly related to the N $\cdots$ O separation,[5] as is consistent with the above analysis. Another consequence is that ν_m, the mean of $\nu(C{=}O)$ and $\nu(C{=}C)$, is a better index of conjugation than either frequency alone, since it is less sensitive to variations in degree of coupling or other perturbations that should equally affect both frequencies.[9a,11] It is of interest to discover how far this analysis will fit the acylguanidines.

Replacement of C=C in the aminoenones by C=N in the acylguanidines might be expected to increase the molecular dipole still further and, with it, the disparity between $\varepsilon_A(C{=}O)$

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* In this context, 'conjugated' is intended as a convenient shorthand; 'cross-conjugated' has no implication regarding the degree of conjugation.

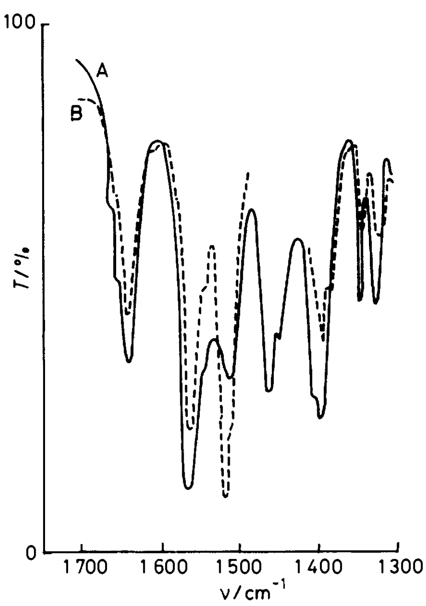
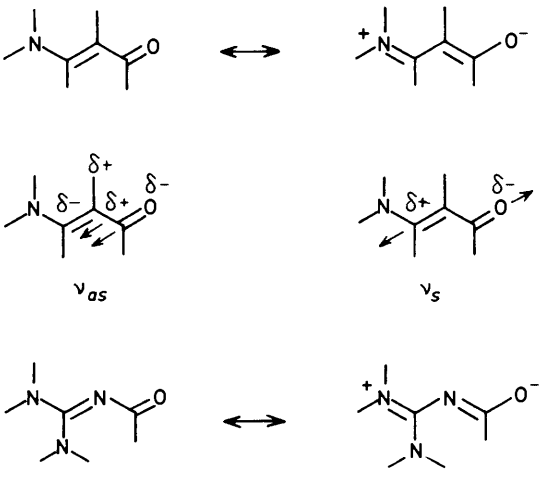
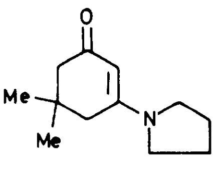


Figure 2. Solution i.r. spectra of (**4**) in chloroform (**A**) and methylene dichloride (**B**)

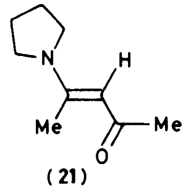


Scheme 2.

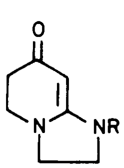
and ε_A(C=X), X = C or N, noted above. This is in fact found to be so. In chloroform solution, ε_A(C=C) for (**20**) is five times greater than ε_A(C=O); in (**1**), the corresponding ratio is over 12 times. Nevertheless, ε_A(C=X) is not much different *per se* and ν_m, at 1 614 cm^{-1} for (**1**), is appreciably higher than 1 572 cm^{-1} for (**20**) despite the presence in the former of two donor atoms. Replacement of CH by the much more electronegative nitrogen atom will at least in part explain both phenomena, since there are now two electronegative centres competing for electrons, not one, and it is arguable that two donor atoms in place of one are required to restore the balance. Using our additive rules[9a] it is possible to calculate ν(C=O) and ν(C=C) frequencies of 1 550 and 1 510 cm^{-1}, *i.e.*, ν_m 1 530 cm^{-1}, for the hypothetical molecule (**22**) in chloroform solution.* It is also arguable that ν(C=N) should be intrinsically a higher frequency than ν(C=C), though it is difficult to find cases that strictly compare,



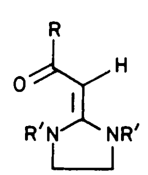
(**20**)



(**21**)



(**22**)



(**23**)

especially when their different bond angle requirements are considered,[1] and we prefer not to invoke this argument.

However, this is not the whole story. Despite presumptive evidence[1] for its non-planarity, ν_m for (**10**) at 1 570 cm^{-1} is much below that for (**1**), and this marks a radical departure from the aminoenones, for which ν_m is virtually independent of conformation.[5,9] We believe the explanation to lie in lone-pair repulsion between N and O, which will be much enhanced in the dipolar canonical forms of *s-trans* conformers (Scheme 2) but can be relieved when rotation to the *s-cis* form is permitted. The close i.r. frequency resemblance between (**10**) and (**11**), for the latter of which the *s-cis* conformer is virtually obligatory in solution, confirms a conformational shift as the source of the difference. Further evidence comes from the low solution ν(NH) values of (**13**) and (**14**), allied to similar double-bond frequencies.† We believe that the *s-cis* conformer (**E**) will *always* be preferred over (**A**) for acylguanidines (for aminoenones the balance is even[5]) where the choice is open, and that the difference in ν_m, indicating a sharp improvement in conjugation, is a simple consequence of this. (U.v. evidence has been adduced[12] for a similar conformational preference in an acylamidine.) The origin of this improvement, as relief of a lone-pair repulsion which inhibits the full development of negative charge on oxygen, is consistent with most of the effect on ν_m being shown in ν(C=O). The failure of this improvement to be reflected in ε_A(C=N), which is much lower for (**10**) than for (**1**), probably results from the non-planarity of the former; ε_A(C=N) for (**11**), which should be planar, is similar to ε_A(C=C) for (**21**) just as the corresponding values for (**1**) and (**20**) are comparable (1 270 and 1 280 for the former pair, 1 770 and 1 670 for the latter). Again, it is as if two donors and two acceptors in the acylguanidines give results very similar to one of each in the aminoenones.

A further point of difference between aminoenones and acylguanidines emerges from this analysis. In the former $\Delta\nu$, the frequency difference between ν(C=O) and ν(C=C), is greater for *s-cis* conformers than *s-trans* because of greater vibrational coupling even though ν_m remains substantially unaffected. Here the disproportionate drop in ν(C=O) reduces $\Delta\nu$ along with ν_m and any change in coupling there may be is obscured by electronic effects; the $\Delta\nu$ values of 103 and 50 cm^{-1} found for (**1**) and (**10**) compare with 40 and 80 cm^{-1}, respectively, predicted for (**22**) and (**23**). This is another features that can be useful in structural diagnosis.

An increase in ring size from 5- to 6-membered decreases the

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* Here and subsequently we quote frequencies for chloroform solution in these cross-comparisons unless clearly stated otherwise, since the aforesaid additive rules[9a] are for this solvent.

† The difference in ν(NH) between (**11**) and (**13**) relates simply to the effect of ring size on the length and directionality of the intramolecular hydrogen bond.

Table 1. Solid-state i.r. and Raman spectra of neutral species (cm^{-1})[a,b]

Species	ν(NH)	ν(C=O)	δ(NH)	ν(C=N)	ν_{as}(NCN)	ν(CN)	Others		
(1) I.r., ν	—	1 659ms	—	1 549vs,br	1 520sh	1 410m		1 296ms	
Raman, $\Delta\nu$	—	1 657vs	—	1 540mw,br	...	...		...	680s
(2) I.r., ν	3 090ms,vbr	1 656m	1 598vs	1 538s	...	1 402m		1 282m	
Raman, $\Delta\nu$	...	1 666vs	...	1 555mw	...	...		...	665m
(3) I.r., ν	—	1 683s	—	1 632ms	1 500ms	1 403m	1 328ms	1 290ms	
Raman, $\Delta\nu$	—	1 690s	—	1 628ms	1 500w	1 404w	1 322w	...	635ms
(4) I.r., ν	—	1 633ms	—	1 568 1 554 ms	1 511s	1 405m	1 325w	1 285m	
Raman, $\Delta\nu$	—	1 636s	—	1 556vw	1 525vw	...	...	1 275w	680ms
(5) I.r., ν	3 070w,br	1 630m	1 575vs,br		1 540sh	1 422s	1 340ms	1 291m	
Raman, $\Delta\nu$	...	1 630s	...	1 560m	...	1 428mw	1 340m	1 292m	720s
(6) I.r., ν	—	1 682s	—	1 636vs,br	1 491ms	1 406m	1 365m	1 310ms	
Raman, $\Delta\nu$	—	1 674s	—	1 622mw	1 499vw	1 406vw	1 368w	1 302vw	
(7) I.r., ν	—	1 690vs,br	—	1 592vw	(1 492)	1 398s			
Raman, $\Delta\nu$	—	1 679ms	—	...	1 495w	1 405vw			
(8) I.r., ν	3 155w 3 085mw	1 704s,br	1 572ms	1 666s,br	(1 482)	1 398s			
Raman, $\Delta\nu$	...	1 674s	...	1 652mw	1 480ms	...			
(9) I.r., ν	—	1 660vs,br	—	1 660vs,br	1 501s	1 400br			
Raman, $\Delta\nu$	—	1 661s	—	1 640sh	1 494mw	1 404m			
(10) I.r., ν	—	1 600sh	—	1 550vs	1 481mw	1 404ms			
Raman, $\Delta\nu$	—	1 605m	—	...	1 492m	1 400vw			710s
(11) I.r., ν	3 320s	1 590vs,br	...	1 530s,br	1 487mw	1 378s			
Raman, $\Delta\nu$	3 350w	1 607s	...	1 515mw	1 485mw	1 372vw			1 060m
(12) I.r., ν	3 400vs	1 702s,br	...	1 613s	1 498m	1 393ms	1 331m	1 271ms,br	
Raman, $\Delta\nu$	...	1 696ms	...	1 612s	...	1 390vw	1 336vw	...	
(13) I.r., ν	3 190s	1 595vs	...	1 575vs	...	1 380s	1 324ms	1 278ms	
Raman, $\Delta\nu$	...	1 588s	...	1 567ms	1 525m	1 380ms	...	1 280mw	880s
(14) I.r., ν	3 160 3 080 mw	1 590vs,br	...	1 555s,sh	1 522m,sh	1 391ms	1 326ms	1 276ms	
Raman, $\Delta\nu$	...	1 584mw	...	1 553m	1 525vw	1 391mw	...	1 276vw	

[a] See text for definition of the vibrational modes. As oil for (**7**), as Nujol mulls for the remainder. [b] Intensities: s, strong; m, medium; w, weak; v, very; also sh, shoulder; br, broad. Dots indicate hidden or missing bands, dashes indicate bands not expected to be present.

Table 2. Solid-state i.r. and Raman spectra of cations (cm^{-1})[a,b]

Cation	ν(NH$^+$)	ν(C=O)	ν_{as}(CN$_3$)	ν_s(CN$_3$)	ν(CN)
(7a) I.r., ν	3 100—2 800br	1 730s	1 701s	1 537ms	1 386ms
Raman, $\Delta\nu$	...	1 718s	1 691vw	1 544vw	...
(8a) I.r., ν	3 300—3 000m,br	1 724s	1 695s,sh	1 542s	1 378s
Raman, $\Delta\nu$	3 300—3 000w,br	1 715s	1 698w,sh	1 540vw	1 375vw
(9a) I.r., ν	3 100m,br	1 731ms	1 703s	1 532ms	1 383ms
Raman, $\Delta\nu$	3 090w	1 716s	...	1 530mw,br	1 372w
(14a) I.r., ν	3 180m	1 706s	1 671s	1 583ms	—[c]
Raman, $\Delta\nu$	...	1 704m	1 678vw	1 588mw	—
(15a) I.r., ν	3 200—3 050ms,br	1 655s[d]	1 684s	1 548s	1 220ms
Raman, $\Delta\nu$	...	1 653s	...	1 555vw	1 220vw

[a] For key see Table 1. [b] (**7a**) as bromide; (**8a**), (**9a**), and (**15a**) as iodide; (**14a**) as chloride of monohydrate [ν(H$_2$O) at 3 070m,br]. [c] Replaced by amide II at 1 509ms (i.r.), 1 515vw,br (Raman); also amide ν(NH) at 3 335s (i.r.), 3 330ms (Raman). [d] ν(C=NH); corresponding ν(NH) at 3 210ms (i.r.), 3 210m (Raman).

Table 3. Solution i.r. spectra (cm^{-1})[a]

	Solvent									
Compound	$CHCl_3$		CH_2Cl_2			Dioxane		CCl_4		Assignment
(1)	1 665	*140*	1 664	*190*		1 679	*190*	1 685		ν(C=O)
	1 562	*1 770*	1 565	*1 730*		1 571	*1 750*	1 560		ν(C=N)
	1 520sh		1 525sh			1 525sh		1 520		ν_{as}(NCN)
	1 410	*150*	...			...		1 408		ν(CN)
(2)	3 450		3 440			...				ν(NH)
	1 659	*90*	1 661	*120*	1 660[b]	1 658	*300*			ν(C=O)
	1 593	*870*	1 602	*1 130*	—	1 605	*1 230*			δ(NH)
	1 574	*970*	1 573	*1 240*	1 563	1 578	*550*			ν(C=N)
	(1 530)		1 528	*340*	1 535	(1 528)				ν_{as}(NCN)
	1 402	*150*	...		...	...				ν(CN)
(3)	1 692	*400*	1 694	*480*		1 695	*240*	1 703	*560*	ν(C=O)
	1 621	*1 160*	1 625	*1 270*		1 627	*1 100*	1 630	*1 220*	ν(C=N)
	1 494	*150*	1 495	*250*		...		1 492		ν_{as}(NCN)
	1 408	...	...			...		1 409		ν(CN)
(4)	1 638	*380*	1 639	*430*		1 660	*530*	1 665		ν(C=O)
	1 563	*800*	1 562	*1 080*				1 565		ν(C=N)
						1 545	*440*	1 545		
	1 510	*320*	1 516	*1 130*		1 518	*750*	1 515		ν_{as}(NCN)
	1 392	*450*	(1 392)			...		1 401		ν(CN)
(5)	...		3 430			...				ν(NH)
	1 635	*170*	1 639	*190*		1 651	*50*			ν(C=O)
	1 595	*910*	1 598	*950*		1 605	*940*			δ(NH)
	1 570sh		1 568	*610*		(1 605)				ν(C=N)
	1 548	*610*	1 547	*760*		1 557	*290*			ν_{as}(NCN)
	1 412	*200*	(1 402)			...				ν(CN)
(6)	1 679	*270*								ν(C=O)
	1 632	*780*								ν(C=N)
	1 490	*170*								ν_{as}(NCN)
	1 413	*140*								ν(CN)
(7)	1 688	*520*	1 691	*600*		1 692	*440*	1 696	*490*	ν(C=O)
	...		...			...		...		ν(C=N)[c]
	1 480	*70*	1 478			...		1 481	*50*	ν_{as}(NCN)
	1 396	*150*	1 391	*120*		...		1 388	*120*	ν(CN)
(8)	3 420		3 420		...	...		...		ν(NH)
	1 694	*660*	1 695	*700*	1 692	1 692	*610*	1 701		ν(C=O)
	1 666	*700*	1 666	*700*	1 661	1 670	*730*	1 674		ν(C=N)
	1 480	*70*	1 482	*50*	(1 482)	...		...		ν_{as}(NCN)
	1 395	*250*	1 391	*200*	(1 395)	...		1 390		ν(CN)
(9)	1 682	*710*	1 686	*820*		1 688	*850*	1 695	*890*	ν(C=O)
	1 655	*940*	1 658	*1 040*		1 656	*940*	1 660	*1 060*	ν(C=N)
	1 488	*200*	1 487	*300*		...		1 487	*250*	ν_{as}(NCN)
	1 402	*300*	1 400	*250*		...		1 400	*500*	ν(CN)
(10)	1 595	*480*	1 603	*480*		1 606	*390*	1 612		ν(C=O)
	1 545	*800*	1 555	*840*		1 555	*650*	1 558		ν(C=N)
	1 478	*80*	1 481	*80*		...		1 479		ν_{as}(NCN)
	1 398	*400*	1 396	*200*		...		1 402		ν(CN)
(11)	3 340	*150*	3 340		...	...		...		ν(NH)
	1 601	*590*	1 606	*710*	1 608	1 613	*520*	1 618	*620*	ν(C=O)
	1 569	*1 270*	1 573	*1 520*	1 554	1 570	*1 200*	1 567	*650*	ν(C=N)
	1 520	*240*	1 520	*250*	1 508	1 515	*100*	1 515		ν_{as}(NCN)
	1 372	*450*	1 370	*550*	1 372	...		1 368	*500*	ν(CN)
(12)	3 405	*140*	3 400					3 400	*140*	ν(NH)
	1 709	*840*	1 709	*690*				1 718	*550*	ν(C=O)
	1 622	*660*	1 624	*550*				1 627	*470*	ν(C=N)
	1 496	*440*	1 493					1 496	*200*	ν_{as}(NCN)
	1 393	*400*	...					1 391	*190*	ν(CN)

Table 3 (*continued*)

Compound	Solvent CHCl$_3$		CH$_2$Cl$_2$		Dioxane		CCl$_4$		Assignment
(13)	3 160br		3 160br		...		3 160br		ν(NH)
	1 588 1 575	*1 280*	1 591 1 580	*1 660*	1 592 1 577	*1 380*	1 585	*1 290*	ν(C=O) ν(C=N)
	1 535		1 540		1 540		1 540	*900*	ν_{as}(NCN)
	1 379	*500*	1 379	*800*	...		1 380	*1 000*	ν(CN)
(14)	3 150br		3 150br		3 150br		3 150br		ν(NH)
	1 580	*1 760*	1 583	*1 480*	1 586	*1 820*	1 580		ν(C=O) ν(C=N)
	(1 515)		(1 540)		(1 540)		(1 540)		ν_{as}(NCN)
	1 391		1 391		...		1 391		ν(CN)

[a] ε_A in italics. Frequencies in parentheses are estimated against background and approximate. Dashes indicate absent frequencies, dots those lost against background. [b] Frequencies in this column for CH$_2$Cl$_2$ after deuteriation. [c] A very weak band at *ca.* 1 600 cm^{-1} is at least in part due to the trace amount of water almost irremovable from these compounds.

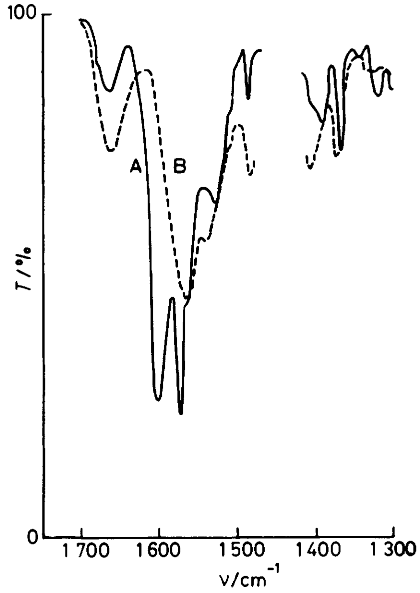
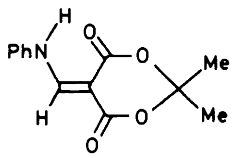


Figure 3. Methylene dichloride i.r. spectra of (2) (A) before and (B) after deuteriation



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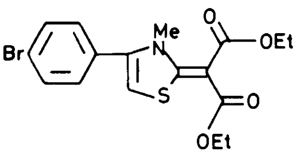


(25)

frequency of exocyclic double bonds typically[13] by *ca.* 20 cm^{-1}, and the same factor is found in the additive rules for aminoenones.[9a] The fall in *carbonyl* frequency by about this amount between (**1**) and (**4**) and between (**2**) and (**5**) is therefore unexpected, and may be some obscure consequence of a change in the coupling pattern. The likelihood of this is enhanced by the remarkable changes in relative intensity shown as a function of solvent by (**4**) and (**5**) and illustrated on Figure 2. A further complication for (**2**) and (**5**) lies in the presence of δ(NH) as a strong vibration near 1 600 cm^{-1}, identified as such by its removal on deuteriation (Figure 3) and by its near-zero Raman intensity. This is exceptionally elevated for δ(NH) but precedents exist among the pyridones[4] and aminoenones.[5] On the latter analogy, δ(NH) is more commonly expected in the range 1 400—1 250 cm^{-1}, but we have failed to locate it elsewhere. The movement of ν(C=N) and ν_{as}(NCN) on deuteriation is evidence for yet further coupling involving δ(NH), at least in these compounds. There is ample precedent for this among the aminoenones.[5] Between (**11**) and (**13**) ν_m falls by <5 cm^{-1} but, in view of these coupling complications [and despite our inability to locate δ(NH) *via* deuteriation], the significance of this is uncertain.

In the Raman spectra of aminoenones $\Delta\nu$(C=C) is in general weaker than $\Delta\nu$(C=O),[14] reversing the usual[15] tendency. We interpret this as a degree of polarisation which tends to concentrate most of the mobile electron density into the carbonyl group. When two acyl groups are present this trend becomes so extreme that $\Delta\nu$(C=C) is very weak and can even disappear altogether; this happens equally for one donor atom, as in (**24**), or two as in (**25**).[14] This extreme situation is also approached for acylguanidines of types (**A**) and (**E**). We interpret it on rather similar lines to the discussion of frequency and intensity above: in brief, the effect of two electronegative heteroatoms is very similar whether these are both oxygens (two carbonyl groups) or one N and one O as in the present case. Intrinsically, of course, $\Delta\nu$(C=N) is a much weaker Raman band than $\Delta\nu$(C=C), and this is another factor, so that the distinction in this respect between the 'through-conjugated' (**A**) and (**E**) and the 'cross-conjugated' (**B**)—(**D**) types is not hard and fast, though the trend is there (see Figure 4). Nevertheless, it turns out that this distinction in Raman intensity between $\Delta\nu$(C=N) for such pairs of isomers has proved of great value diagnostically when applied to the more complex 'aromatic' molecules for which these acylguanidines are putative models.[8] One reason for its sharper distinction in that case is no doubt that, when C=N does not conjugate with carbonyl, it frequently conjugates with an electron-rich source such as C=C or a benzene ring; when that happens, $\Delta\nu$(C=N) becomes quite a strong Raman band.[8]

Types (**B**) *and* (**D**).—Comparison of (**6**) with (**4**) and of (**3**) and (**9**) with (**1**) will reveal that the large changes in frequency for ν(C=O) and ν(C=N) are accompanied by a surprisingly similar pattern of relative and even absolute intensities. Again, the reason lies in vibrational coupling. It is well established[13,16,17] that the two nominally identical carbonyl frequencies of *Z,Z*-imides such as succinimide (**26**) couple to give ν_s and ν_{as} modes

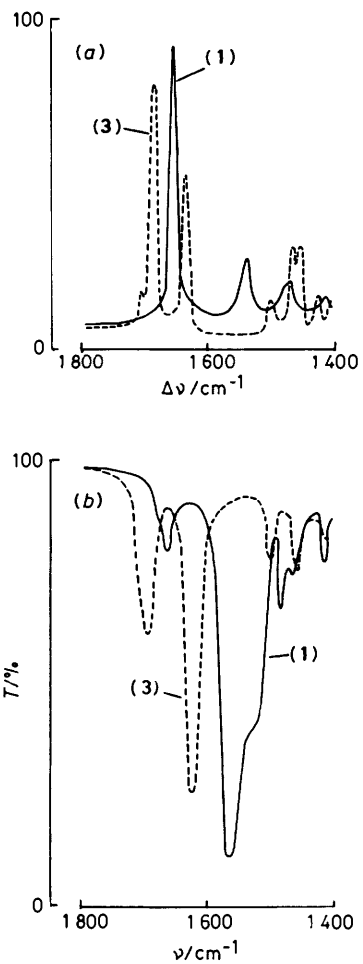
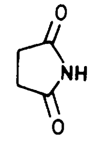


Figure 4. Solid-state Raman spectra (*a*) and chloroform solution i.r. spectra (*b*) of (**1**) and (**3**)

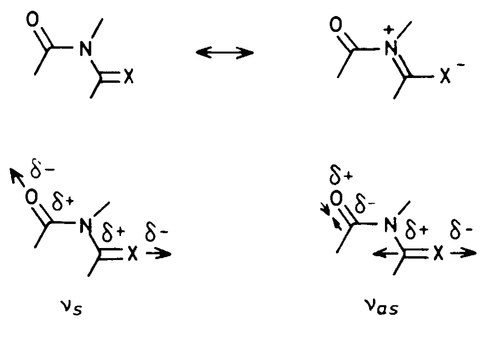
of which the latter is lower in frequency and much higher in intensity through the contribution of dipolar canonical forms; Scheme 3, X = O. This is precisely the inverse situation to Scheme 2 but its consequences are remarkably similar; the changes in partial charges written for the vibrational modes in these Schemes are intended to emphasise that point. Accordingly we regard the nominal ν(C=O) and ν(C=N) modes of these type (**B**) and (**D**) compounds as possessing a considerable degree of ν_s and ν_{as} character, respectively; the high intensity of the latter is thereby explained.

It is also well established[18] that the effect of opening out the bond angle between the two nominally identical carbonyl groups is progressively to increase both $\Delta\nu$, and the intensity ratio of ν_{as} to ν_s. This trend is reflected by (**6**) and (**3**), whose $\Delta\nu$ values of 47 and 71 cm^{-1}, respectively, parallel values of 42 and 71 cm^{-1} for glutaric and succinic anhydrides.[13] This, together with a near-identity of ν_m indicative of no change in conjugation, is powerful evidence for the manner of coupling proposed. [It is unclear whether the 13 cm^{-1} difference in ν_m between (**1**) and (**4**) really reflects a difference in conjugation or is merely a consequence of the '5-membered ring effect.'[13]]

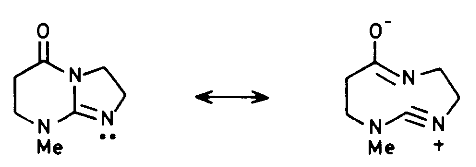
The above treatment is inadequate to explain the difference in ν_m and $\Delta\nu$ between (**3**) and (**9**), *i.e.*, between types (**D**) and (**B**), even though the trend for the latter quantity is in the direction expected for the likely changes in bond angle. We believe that this extra effect stems from back-donation of the *sp*^{2}-nitrogen lone pair into the antiperiplanar C–N bond and thence to carbonyl. (Baldwin and Norris[19] characterise this as an *n*–σ* interaction.) It is difficult to represent σ-resonance effects such as this within the framework of current chemical convention but we attempt it in Scheme 4. The chief i.r. consequence is to impart some triple-bond character to C=N, offset only in part by a fall in ν(C=O). A similar effect is found for (**8**), which as already discussed[1] is unequivocally in the tautomeric form shown. The fall in i.r. *and* Raman intensity for ν(C=N) in (**8**) and (**9**) relative to (**3**) may be some further consequence of this phenomenon. It is absent in type (**B**) because carbonyl is wrongly placed to benefit. While phenomena of this type are well established in chemistry at large,[19] we believe this to be the first detected instance in vibrational spectroscopy. Its result is that, surprisingly, types (**B**) and (**D**) are commonly distinguishable, and the considerable enhancement that is found in heteroaromatic analogues[8] makes this another powerful diagnostic tool.



(**26**)



Scheme 3.

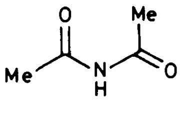


(**9**)

Scheme 4.

Type (**C**).—The only unequivocal member of this class is (**7**), which is distinguished by the apparent absence of ν(C=N) from its i.r. and Raman spectrum. It is unclear whether this mode is coincident with ν(C=O), or is represented by the very weak band present at 1 592 cm^{-1} in the solid state or near 1 600 cm^{-1} in solution. The former may be possible if ν(C=N) is elevated by the mechanism of Scheme 4 even more for (**7**) than for (**8**) or (**9**). The latter seems more likely on the expectation of similar ν_m. In either case, it is clear that ν(C=N) is exceedingly weak, and that (**C**) is the only type to which this applies.

It is established that, while the two ν(C=O) of imides, for example, are coupled in the *Z,Z*- (and *E,E*-[20]) conformations, this is not so for the *Z,E*-alignment as in (**27**).[21] If that applies here, we have a ready explanation for the weakness of ν(C=N) in (**7**) since the expected fall in ε_A(C=N) through competition for electrons with carbonyl is not compensated by coupling on the



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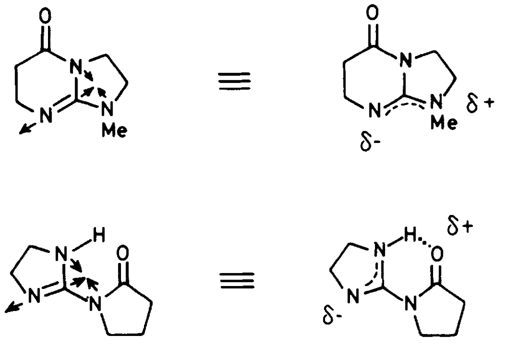


(7)

(12)

Scheme 5.

lines of Scheme 3. It is interesting that ν(C=O) for (7) at 1 688 cm^{-1} and ν(C=N), if at 1 592 cm^{-1}, compare with ν(C=O) at 1 690 cm^{-1} for piperidin-2-one[13] and ν(C=N) at 1 603 cm^{-1} for guanidine itself[10] or near 1 610 cm^{-1} in imidazolines;[22] *i.e.*, it is as if the 'amide' and 'amidine' moieties were virtually independent. This may be circumstantial evidence that the assignment of ν(C=N) to *ca.* 1 600 cm^{-1} is correct.

The apparently anomalous behaviour of (**12**) provides further evidence. While the 5*s*-acylguanidine conformation[1] (**12b**) would formally be possible, its existence in all media examined as the 4*s*-conformer (**12a**) as virtually proved by the presence of ν(NH) at high but constant frequency [3 400 cm^{-1}, Tables 1 and 3; contrast the behaviour *e.g.*, of (**2**)]. Evidently even this weak intramolecular hydrogen bond is sufficient to lock the structure. Despite the *Z,E*-alignment that it shares with (**7**), however, ν(C=N) in (**12**) is a strong vibration which is even more notable for its high solid-state Raman intensity. A more detailed consideration of these contrasting cases leads to the picture displayed in Scheme 5. In (**7**), ν(C=N) is not only uncoupled but its dipole moment change in the course of the vibration must take place almost at right angles to that of carbonyl, assuming that the principal π-donor nitrogen atom will be that not carrying an acyl group. In (**12**) with the same argument, not only is this extremely unfavourable geometry avoided, but the variation in NH $\cdots$ O distance induced in the course of the vibration will add a second form of dipole flux to reinforce the first. The induced polarisibility resulting from variable incorporation of the carbonyl lone pair might then be responsible for the high Raman intensity of ν(C=N) unique to this series [note also that ν(NH) is exceptionally intense in the solid state]. If this explanation is correct the same phenomenon is possible for the 3*s*-conformer, but no examples are available.

Compound (**7**) by contrast exemplifies a common alignment in heteroaromatic chemistry and, on the evidence of (**12**), we can reasonably propose that ν(C=N) would be found near 1 600 cm^{-1} if visible. This has been confirmed by the study of heterocycles where ν(C=N) owes its intensity to further conjugation[8] as is elaborated below.

Cation Spectra.—These have been recorded for the solid state alone (Table 2).

The separate ν(C=N) and ν_{as}(NCN) modes of guanidine (Figure 1) become degenerate in the guanidinium cation and split to give two bands near 1 650 and 1 550 cm^{-1}.[10] We designate these bands as ν_{as}(CN$_3$) and ν_s(CN$_3$) in Table 2; except in (**14a**) where they may be distorted by the 'forced' intramolecular hydrogen bond, they occur near 1 690 and 1 540 cm^{-1}. Carbonyl substitution no doubt accounts for the slight rise in ν_m. The carbonyl mode itself occurs as a band at $>$1 700 cm^{-1} which, as expected by analogy with the neutral forms, is strong in the Raman spectrum where all the rest are weak. All these features are consistent with protonation on the guanidine moiety and not on carbonyl, as already noted for aqueous solution;[1] consistent too is the generally close resemblance of all these spectra regardless of structural type.

Table 4. Carbon-13 n.m.r. data (p.p.m.)

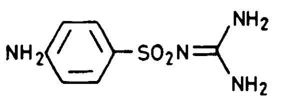
Compound	Solvent	C=O	C=N	MeN
(**1**)	(CD$_3$)$_2$SO	176.0	164.1	30.4
(**2**)	(CD$_3$)$_2$SO	175.9	165.7	
(**3**)	CDCl$_3$	167.7	158.7	28.4
(**4**)	(CD$_3$)$_2$SO	176.6	157.7	36.9
(**5**)	(CD$_3$)$_2$SO	174.2	157.4	
(**6**)	(CD$_3$)$_2$SO	167.8	146.8	27.3
(**7**)	CDCl$_3$	168.8	150.9	31.4
(**8**)	(CD$_3$)$_2$SO	166.5	152.4	
(**9**)	(CD$_3$)$_2$SO	165.0	152.8	36.6
	CDCl$_3$	164.6	152.8	36.2
(**10**)	CDCl$_3$	174.6	162.3	32.0
(**11**)	CDCl$_3$	183.1	162.4	30.5
(**12**)	CDCl$_3$	175.7	157.0	
(**13**)	CDCl$_3$	182.5	157.5	35.4
(**14**)	CDCl$_3$	190.5	158.2	36.0

Further confirmation comes from the imine (**15a**) where the strong Raman band has moved, compared with (**9a**), from 1 731 to 1 655 cm^{-1} in the i.r. spectrum, the others remaining unchanged. This is clearly exocyclic ν(C=NH) in place of ν(C=O) and its presence, proving protonation on the guanidine moiety once again, helps to confirm this for the rest. Hence structure (**15b**) can be discounted. The shift of ν(CN) from 1 383 to 1 220 cm^{-1} in this changed context helps to confirm the identity of this band throughout the remaining spectra.

*Carbon-*13 *Spectroscopy.*—Two solvents have been employed (Table 4) according to solubility, and while only (**9**) has been examined in both, its negligible solvent shift is sufficient evidence that this factor can be ignored. The exceptions would have been (**11**)—(**14**), where deuteriochloroform was employed so as to preserve the intramolecular hydrogen bond evident from the i.r. studies.

The sp^2-carbon signals fall in the ranges 165—191 and 147—166 p.p.m. Assignment of the former to carbonyl carbon is supported by its notably greater intensity, since it is closer to the nearest protons, except where NH is present, when intensities can be comparable. Except in (**11**)—(**14**) where an intramolecular hydrogen bond induces a further downfield shift, these signals appear in the narrow ranges 175—177 and 165—169 p.p.m. for the 'through-conjugated' (**A**) and (**E**) and 'cross-conjugated' (**B**)—(**D**) isomers, respectively. Except in (**12**) carbonyl always appears in open-chain structures or 6-membered rings so hybridisation effects are not expected. These are present however for imine carbon, which appears in a variety of surroundings, often *endo* to one ring and *exo* to the other, which accounts in broad terms for the much wider ranges of 157—166 and 147—159 p.p.m., respectively. The former range compares with 158.1 p.p.m. for imine carbon in 4-aminophenylsulphonylguanidine (**28**)[23a] whose assignment is unambiguous and where the type of conjugation is essentially similar.

It has been noted above that, on the evidence of ν(C=O) and



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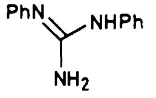

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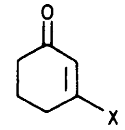

(30)

ν(C=N), the 'amide' and 'amidine' moieties of (7) behave as if essentially independent. For the same compound, the sp^2-carbon signals at 168.8 and 150.9 p.p.m. compare with 169.2 for *N*-methylpiperidone[23b,24] and 148.5 p.p.m. for 1,3-diphenylguanidine (29),[23c] respectively. An even closer comparison is with the signals of 167.8 and 146.8 p.p.m. for (6), arguably[1] the least strained compound in the 'cross-conjugated' set since its 6,6-ring fusion allows easy optimisation of the bond angles. It seems probable that the downfield shifts in imine carbon for (8), (9), and especially (3) reflect varying degrees of hybridisation strain brought about by ring fusion. It is just possible that the attenuation of this downfield shift in (8), (9), and possibly (7) derives from the same σ-resonance effect that has been detected in the i.r. spectrum for the former; this might induce an upfield shift by converting C=N part way into C≡N (Scheme 4).

Replacement of sp^3- by sp^2-carbon next to carbonyl causes an upfield shift of 10—12 p.p.m. in the signal for the latter,[25] and qualitatively the same effect is registered by a fall in ν(C=O).[13] However, the nominally equivalent replacement of amino by imino nitrogen in these compounds leads to a *downfield* shift in the carbonyl carbon signal of 8.3 ± 1.2 p.p.m. ($n = 5$) which is in the opposite direction to the sharp drop in ν(C=O) of *ca.* 30 cm^{-1} (Table 3). A similar effect was observed by Daunis *et al.*[6] This apparent paradox points to an important distinction between these two types of spectroscopic information. That supplied by infrared pertains to the whole bond dipole, whereas ^{13}C n.m.r. refers only to the positive end of it. The above downfield shift is caused by the substitution of electron-deficient for electron-rich nitrogen and is a localised effect which in no way challenges the through-resonance pattern of Scheme 2. Loosely expressed, this carbon atom is only a staging-post in the transfer of electron density from amino nitrogen onto oxygen; we have noted previously how, in the parallel case of 3-X-substituted cyclohexenones (30), the carbonyl signal is scarcely affected by the nature of the donor atom X.[26] Clearly, electron densities on oxygen as supplied by photoelectron or ^{17}O n.m.r. spectroscopy would be of the greatest interest. The detection of localised effects within the general framework of through-resonance is one of the recent achievements of ^{13}C n.m.r. spectroscopy and has been reviewed.[27]

The downfield shift of the imine carbon resonance between types (B)—(D) and types (A) and (E) can be discussed on similar lines, but is here complicated by hybridisation shifts caused by changes in ring size. Substitution of a 5- for a 6-membered ring produces a downfield shift of 4.5 ± 0.4 p.p.m. ($n = 2$) in terms of C=N as *exo*-group which rises to 7.3 ± 1.0 p.p.m. ($n = 2$) when *endo*-fusion into a 6-membered ring is also present. This difference points to its origin in strain but it cannot be quantified further. If (4) and (6) are taken as strain-free then the effect of 'through-conjugation' is a downfield shift of *ca.* 11 p.p.m. which is halved when the comparison is made between (1) and (3), as seen above because, in all probability, of strain in the latter.

Table 5. Summary of the i.r., Raman, and ^{13}C n.m.r. criteria for structural types (A)—(E)[a]

Parameter		(A)	(B)	(C)	(D)	(E)
C=O	ν/cm^{-1}	1 660	1 690	1 690	1 680	1 590
	ε_A (i.r.)	w	m	m	s	ms
	δ/p.p.m.	176	168	169	166	175—183[b]
C=N	ν/cm^{-1}	1 570	1 620	1 600	1 650	1 560
	ε_A (i.r.)	vs	vs	vw[c]	s	s
	A (Raman)	vw	m	vw[c]	w	vw
	δ/p.p.m.	165	159	151	153	162
	ν_m[c]/cm^{-1}	1 615	1 655	1 645	1 665	1 575
N-Me	δ/p.p.m.	30	28	31	36	30

[a] For 6,5-ring fusions and similar; see text for more detailed notes. [b] Higher value refers to intramolecular hydrogen bond. [c] See text.

The overall picture is that of a clear distinction between the 'through-conjugated' and 'cross-conjugated' types somewhat distorted, in the latter case, by complex and subtle hybridisation effects. In their absence it seems probable that types (B)—(D) would all appear closely similar. An analogous but differently patterned distortion takes place in the i.r. double-bond frequencies as a result of vibrational coupling, as seen above. It is interesting that these carbon-13 results fail to reflect the profound difference in conjugation between types (A) and (E) revealed by the i.r. frequencies and discussed above. Again, the explanation can be seen in the distinction between through and local electrical effects. The reason that ν(C=O) in (A) does not fall by the expected amount relative to (B)—(D) results from failure of the negative charge on oxygen to develop fully, so that the fall in C=O bond order is correspondingly reduced; the *positive* end of the dipole, however, appears to be little affected.

The third ^{13}C signal of diagnostic value turns out to be methyl on ring nitrogen. There is clear evidence in the literature,[28] which appears to have gone without comment, for a characteristic difference in the N–Me signal according as to whether the nitrogen atom is incorporated into a 6- or a 5-membered ring,[29] and these compounds illustrate it clearly. For N–Me not adjacent to carbonyl, the values are 36.2 ± 0.7 p.p.m. ($n = 4$) and 31.1 ± 0.8 p.p.m. ($n = 4$), respectively. This difference of *ca.* 5 p.p.m. is reflected by ring amines and amides[24,28] despite their considerable differences in absolute value. Its chief use here is to provide a very clear distinction between types (C) and (D), which complements and can override the i.r. criteria.[8,29] Daunis *et al.*[6] also observed this effect but do not comment on its generality.

Summary and Conclusions

We summarise in Table 5 the most important i.r. and Raman criteria for distinguishing structural types (A)—(E), as they have emerged from this study. For (A)—(D) we have based this comparison on the 6,5-ring fused types since these are the most relevant to the oxoheterocycles that are our ultimate target. It is obvious that type (A) is the most clearly distinguishable at sight. Nevertheless sufficient criteria exist to distinguish the remainder; even the pseudo-imides (**B**) and (**D**) show more points of contrast than might have been expected, and these differences are in fact greatly magnified in the fully aromatic oxoheterocycles themselves.[8]

The only one of these structures for which aromatisation produces a qualitative shift of balance is (**C**).[8] As stated above, this happens because conjugation between C=N and, for example, a benzene ring introduces a major new factor not present in the original, whose chief effect is greatly to increase i.r. and Raman intensity; some rise in frequency also sometimes results. Nevertheless, frequencies and intensities for ν(C=N) normally remain below those of types (**B**) and (**D**), so that there is little difficulty in practice in distinguishing them.

It will be noted throughout this argument that changes associated with ν(C=N) have proved of at least as much, and generally more, diagnostic value than those associated with the carbonyl band. Nothing could more graphically illustrate the information that is currently going to waste through the neglect of i.r. and Raman spectroscopy in the structural diagnosis of complex organic molecules. We have made the same point in the past concerning the ν(C=C) vibration in aminoenones and related compounds.[9]

Information on type (**E**) compounds may also be relevant to the many contexts in which the grouping =NCOR finishes exocyclic to a heteroaromatic ring. Here we have shown that the *s-cis* conformation is strongly preferred. The resulting very low, and at times virtually coincident, ν(C=O) and ν(C=N) modes may often have confused diagnosis in such cases, as in similar examples involving ν(C=O) and ν(C=C) that we have previously encountered.[9]

By contrast with the i.r. and Raman criteria those for ^{13}C n.m.r. spectroscopy are, at this stage, relatively sparse. Nevertheless, that involving ring N-methyl is the clearest criterion in any category and has proved most valuable. Elsewhere the prime distinction is between the carbonyl shifts for the 'conjugated' and 'unconjugated' types; the very large effect of an intramolecular hydrogen bond may also be useful on occasion. Shifts for the imine signal are complicated by hybridisation changes, but in addition to showing the same distinctions as carbonyl, it is possible that the difference between types (**B**) and (**D**) will turn out to be significant.

In conclusion we would make the point that the extremely high intensity of ν(C=N) (or ν_s) in types (**A**) and (**E**), and their low frequencies, is equivocal evidence for exceptional conjugation. As in the case of nitro-enamines[30] and the diacyl derivatives that we have previously examined,[14] it results from an extreme of polarisation which, by concentrating electron density onto the most electronegative atoms, might even be seen as having reduced conjugation somewhat. Here solvent shifts are relevant. We have previously demonstrated[31] that the solvent sensitivity of ν(C=O) is related to the overall 'electron richness' of the molecule as measured roughly by its frequency, and that for aminoenones such as (**20**) and (**21**) these shifts are exceptionally large. When we started this investigation we envisaged that the solvent shifts for acylguanidines would also be exceptional. In fact the effect is considerably attenuated: the *combined* solvent shifts for ν(C=O) and ν(C=N) in (**1**), (**4**), and (**10**) of 22, 29, and 30 cm^{-1} between chloroform and carbon tetrachloride compare with 51 and 45 cm^{-1} for (**20**) and (**21**), respectively, and elsewhere the effect is generally much less. As in our analysis of the frequency and intensity parallelism to the aminoenones, we return to the point that two donor atoms and two acceptors in the one conjugated unit perhaps even fail to balance one of each.

Experimental

The preparation of these compounds has been described.[1] I.r. spectra were obtained on a Perkin-Elmer 580B infrared spectrophotometer, Raman spectra for solid samples on a Nicolet MX-3600 Raman spectrometer, and ^{13}C n.m.r. spectra on a JOEL FX 90Q spectrometer.

Acknowledgements

We thank Mr. B. W. Cook for the Raman spectra.

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