Vibrational Spectroscopy and Conformations of 2,2-Diacylethenamines†

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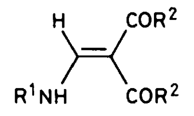
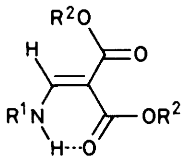
The i.r., Raman, and ^1H n.m.r. spectra of 2,2-diacetylethenamines (**3**) and 2-aminomethylene-5,5-dimethylcyclohexane-1,3-diones (**4**) show that these substances exist exclusively in the chelated enamino-diketone form, and that the conjugated system contained in them is essentially planar. The open-chain enamino-diketones (**3**) exist either in the solid state or in solution in the *EZE*-conformation (**7**). A similar conjugated core, having the fixed *ZZE*-conformation, contained in 5-aminomethylene-2,2-dimethyl-1,3-dioxane-4,6-diones (**5**) is most probably planar or nearly planar. The *EZE*- and *ZZE*-alignments of the enamino-diketones can be distinguished by their spectral properties, and, particularly, by their vibrational spectra. Some features of the i.r. and Raman spectra indicate vibrational coupling between the two ν(C=O) vibrations, the effect being more marked in the cyclic enamino-diketones (**4**) and -diesters (**5**) than in their open-chain analogues. On the other hand, the coupling of the ν(C=O) with the ν(C=C) and the δ(N–H) modes seems to be less efficient in these enaminodione systems than in the related simple enaninones. Further arguments are presented questioning the criteria established to ascertain the planarity of enamino-diones and of other enamines having two strong electron-acceptor groups at C-2.

The vibrational spectra of 2,2-diacylethenamines ('enamino-diones') (**1**) are interesting because of the information they provide on the electron distribution inside these mesomeric systems and on the conformations they can adopt. Previous studies have shown that the intramolecularly bonded *EZE*-conformation‡ (**2a**) is preferred in the crystal lattices of 2-alkoxycarbonyl-3-aminoacrylic esters.[1] while in solutions of non-polar solvents these compounds exist as temperature- and concentration-dependent equilibria of this conformer and the *ZZE*-form (**2b**); the two conformations can be easily distinguished by their spectra.[1,2] Some features of the i.r. and Raman spectra suggested[1] that a weak vibrational coupling between the carbonyls occurs, the effect being stronger in the *ZZE*-conformation (**2b**).[1] It has also been concluded[2] that the position and intensity of the i.r. and Raman mixed ν(C=C) + δ(N–H) band are indicative of the degreee of planarity of these, and related, electron-delocalized systems, and that the near-zero Raman intensity of this band in the planar compounds is due to the low availability of polarizable π-electrons in the carbon double bond; these conclusions have been questioned.[1] In order to get a better understanding of the relationship between the vibrational spectra and conformations of enamino-diones, we have investigated the spectra of a variety of 2,2-diacetylethenamines (**3**), 2-aminomethylene-5,5-dimethylcyclohexane-1,3-diones (**4**), and 5-aminomethylene-2,2-dimethyl-1,3-dioxane-4,6-diones (**5**) (Table 1). A parallel *X*-ray crystallography study[3,4] of compounds (**3b**), (**3c**), (**4c**), and (**4f**) has been performed.

There are some data on the i.r. spectra of the cyclic enamino-diones. Bihlmayer *et al.*[9] noted the anomalous high carbonyl frequencies of the dioxanes (**5**; R = H, Et, cyclo-C_6H_{11}, and Ph), and excluded intramolecular hydrogen bonding between the C=O and N–H groups. Smith and Taylor[2] studied compounds (**4e**) and (**5c**) and suggested coupling between the

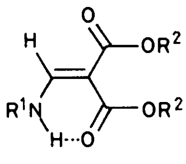


(**1**)



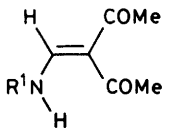
EZE

(**2a**)

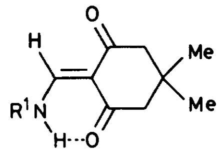


ZZE

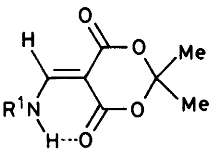
(**2b**)



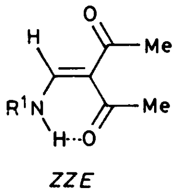
(**3**)



(**4**)

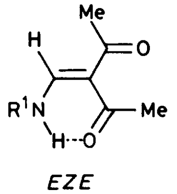


(**5**)



ZZE

(**6**)



EZE

(**7**)

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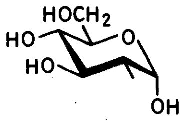
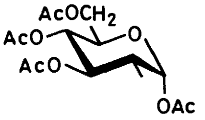
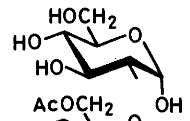
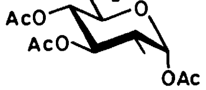
† Presented at the XVII European Congress on Molecular Spectroscopy, Madrid, 1985.

‡ The symbols indicate, in the order shown, the alignments of the free C=O, the bonded C=O, and the R^1 group with respect to the carbon–carbon double bond.

Table 1. Analytical data for the enamino-diones (3)—(5)

Compound (Formula)	R^1	Yield (%)	Solvent	M.p. (°C) Observed	M.p. (°C) Literature	Found (%) (Required) C	H	N
(3a) ($C_7H_{11}NO_2$)	Me	45	Et_2O	110—111		59.4 (59.6)	8.1 (7.85)	9.6 (9.9)
(3b) ($C_{10}H_{17}NO_2$)	Bu^n	59	C_6H_{12}	64—65		65.5 (65.55)	9.7 (9.35)	7.3 (7.6)
(3c) ($C_{12}H_{19}NO_7$)		98	EtOH	204—205	204—205[a]			
(3d) ($C_{20}H_{27}NO_{11}$)		80	EtOH	137—138	137—138[a]			
(3e) ($C_{12}H_{13}NO_2$)	Ph	51	Et_2O	89—90	90—91[b]			
(4a) ($C_{10}H_{15}NO_2$)	Me	88	EtOH	171—173		66.5 (66.5)	8.7 (8.35)	7.8 (7.7)
(4b) ($C_{13}H_{21}NO_2$)	Bu^n	91	EtOH	157—158		70.0 (69.9)	9.7 (9.5)	6.5 (6.3)
(4c) ($C_{15}H_{23}NO_7$)		75	EtOH	225—227	225—227[c]			
(4d) ($C_{23}H_{31}NO_{11}$)		72	EtOH	168—170	168—170[c]			
(4e) ($C_{15}H_{17}NO_2$)	Ph		EtOH	135—136	124—125[d]	74.0 (73.9)	5.75 (6.1)	7.0 (7.2)
(4f) ($C_{15}H_{16}N_2O_4$)	$p-NO_2C_6H_4$	53	EtOH	190—191		62.5 (62.5)	5.6 (5.6)	9.7 (9.7)
(5a) ($C_8H_{11}NO_4$)	Me			175—176		51.9 (51.9)	6.05 (6.0)	7.3 (7.6)
(5b) ($C_{11}H_{17}NO_4$)	Bu^n	67	C_6H_{14}	110—111		58.4 (58.1)	7.8 (7.5)	6.45 (6.1)
(5c) ($C_{13}H_{13}NO_4$)	Ph	60	CCl_4	155—156	157[e]			

[a] Ref. 5. [b] Ref. 6. [c] Ref. 7. [d] Ref. 8*a*. [e] Ref. 9

carbonyls to explain their anomalous absorption; both carbonyl groups were considered to be twisted out of the plane of the vinylamino group, the distortion being more severe for (**4e**). The similarity between the ^1H n.m.r. spectra of the open-chain (**3e**) and cyclic diketone (**4e**) led Wolfbeis *et al.*[8b] to consider that the former compound has the *ZZE*-conformation (**6**; R^1 = Ph).

Experimental

Spectra.—I.r. spectra were taken with a Perkin-Elmer 599B spectrophotometer. The measurements were performed in the solid state and in solution at 0.01—0.15M concentration, depending on the solvent, using 1—0.03 mm cells. Spectra for very dilute carbon tetrachloride solutions in the 3 800—2 400 cm^{-1} region were registered with 1 and 4 cm quartz cells. Raman spectra were obtained for solid samples and for carbon tetrachloride and/or [^2H]chloroform solutions using a Ramanor U-1 000 (5 145 Å) spectrophotometer. ^1H N.m.r. spectra were obtained on a Perkin-Elmer R-12B or a Varian XL-200 instrument using tetramethylsilane as internal standard. M.p.s were determined using open capillaries and are uncorrected. *N*-Deuteriation experiments were performed as described.[1]

Preparation of Compounds.—Compounds (**3c**—**e**), (**4c**—**e**), and (**5c**) were synthesized according to the literature (see Table 1). Compounds (**3a**) and (**3b**) were prepared from 3-acetylethoxybut-3-en-2-one[6] and the appropriate amine. Transamination of (**4e**) with an excess of methylamine or n-butylamine (absolute methanol as solvent) gave (**4a** and **b**), respectively. Compounds (**5a** and **b**) were prepared from 2,2-dimethyl-5-methoxymethylene-1,3-dioxane-4,6-dione and the appropriate amine by the established procedure.[9] Compound (**4f**) was obtained from 5,5-dimethylcyclohexane-1,3-dione, triethyl orthoformate, and *p*-nitroaniline as described[8a] for (**4e**).

Results and Discussion

The most significant features of the ^1H n.m.r. spectra of compounds (**3**)—(**5**) are in Table 2. Key data for the i.r. and Raman spectra are in Table 3.

The ^1H n.m.r. spectra of (**3**)—(**5**) are very simple and have all

Table 2. ^{1}H N.m.r. data[a] (δ; J/Hz in parentheses) for compounds (3)—(5)

Compound	=CH	NH	COMe or $COCH_2$
(**3a**)[b]	7.77d (14.0)	10.08br	2.23s, 2.44s
(**3b**)	7.75d (13.4)	11.07br	2.27s, 2.48s
(**3c**)[c]	8.02d (13.5)	10.80dd,br (13.5; 8.7)	2.17s, 2.30s
(**3d**)	7.67d (12.5)	10.95dd (12.5; 10.7)	2.30s, 2.45s
(**3e**)	8.24d (12.7)	12.75d (12.7)	2.38s, 2.56s
(**4a**)	8.11d (14.1)	11.00m,br	2.20s, 2.25s
(**4b**)	8.11d (14.0)	11.17m,br	2.35s, 2.35s
(**4c**)[c]	8.04d (14.3)	10.86m,br	2.25s, 2.30s
(**4d**)	8.02d (13.0)	10.99dd (13.0, 8.0)	2.33s, 2.35s
(**4e**)	8.62d (13.7)	12.88d (13.7)	2.41s, 2.46s
(**4f**)	8.61d (13.2)	12.93d,br (13.2)	2.46s, 2.51s
(**5a**)[b]	8.20d (14.0)	9.50m,br	
(**5b**)	8.12d (14.9)	9.57m,br	
(**5c**)	8.66d (14.4)	11.26d,br (14.4)	

[a] At 200 MHz in $CDCl_3$ unless otherwise indicated. [b] At 60 MHz. [c] In $[^{2}H_6]Me_2SO$.

the characteristics of those of intramolecularly bonded enamines.[8b,9,10] Some differences observed for the three types of compounds are significant. Compounds (**3**) show well separated (Δδ 0.11—0.22) singlets due to the two non-equivalent COMe groups, while in the diketones (**4**) with fixed *ZZE*-conformation the chemical shift between the two $COCH_2$ signals is much smaller (Δδ 0—0.07). This is attributed to differences in conformation, and as the bonded COMe in compounds (**3**) must have the *Z*-conformation, it follows that the free COMe group takes the *E*-disposition. Therefore, compounds (**3**) exist in solution in the *EZE*-conformation (**7**); the bonded COMe having the methyl group flanked by two carbonyls is the one appearing at lowest field. Concomitantly, the olefinic proton of the cyclic diketones (**4**) appears more deshielded (δ 8.0—8.1 for the compounds with an alkylamino group; δ 8.5—8.6 for the *N*-arylamino-derivatives) than in compounds (**3**) (*N*-alkylamino-derivatives, δ 7.85—8.0, *N*-arylamino-derivatives, δ 8.2), the effect being more apparent when pairs of compounds having the same nitrogen substituent are compared. Similarly, the olefinic signal of (**5**) with fixed *ZZE*-conformation appears at lower field (δ 8.2—8.65) than that of 2-alkoxycarbonyl-3-aminocrylic esters (**2**) (δ 7.99—8.43);[1] the chemical shifts measured for the latter compounds are the averaged values corresponding to conformers (**2a** and **b**) in rapid equilibrium.[1] The cyclic compounds (**4**) and (**5**) also show the bonded NH signal at a field slightly lower than do the analogous open-chain compounds (**3**) and (**2**), respectively; this can be associated with a stronger hydrogen bond in the former compounds.

The *X*-ray crystallographic study[3,4] of (**3b** and **c**) indicates that these compounds adopt the *EZE*-conformation (**7**) in the solid state and shows the presence of the intramolecular hydrogen bond between the *cis* NH and C=O groups. The (diacetylvinyl)amino group is essentially planar except for the intramolecularly bonded acetyl which is tilted [*ca.* 2° for (**3b**) and *ca.* 9° for (**3c**)] with respect to the rest of the delocalized system, and this is due to contacts between the methyl group of the chelated COMe and the carbonyl of the other COMe, and between the bonded NH and C=O groups. Electron delocalization is clearly reflected in the interatomic distances and affects both COMe groups almost equally. The equivalence in the i.r. frequencies observed for solid samples and for solutions of these two compounds provides evidence that they have the *EZE*-conformation irrespective of the medium. Furthermore, as the other compounds of type (**3**) exhibit the same pattern of absorption, it follows that all of them have the *EZE*-conformation, either as a solid or in solution, and that some small deviation from planarity that may exist, as observed in compound (**3c**), does not significantly alter the spectra. This absorption can be considered characteristic of the *EZE*-conformation.

The *X*-ray structure analysis[4] of (**4c** and **f**) shows that the *ZZE*-enaminodione system is strictly planar, and that the cyclohexane-1,3-dione ring adopts a half-boat conformation, with C-1—C-4 and C-6 on one plane, and C-5 above it. The interatomic distances also indicate the presence of an intramolecular C=O ··· HN bond, and that electron delocalization affects both carbonyl groups almost equally. The close similarity between the i.r. spectra for solid samples and for solutions of these two compounds, and for the other compounds (**4**) examined, indicates that the 2-(2-aminomethylene)-5,5-dimethylcyclohexane-1,3-dione moiety of all of them has the same conformation. This pattern of absorption, which is quite different from the one exhibited by compounds (**3**), can be associated with the planar *ZZE*-conformation.

The presence of the strong intramolecular hydrogen bond in all the compounds is evidenced by the frequency of ν(N–H). This band appears at 3 215—3 160 cm^{-1} in the diketones (**3**) and (**4**) (2 360—2 340 cm^{-1} in the *N*-deuteriated derivatives), and at 3 290—3 218 cm^{-1} in the cyclic diesters (**5**) (2 400—2 230 cm^{-1} in the *N*-deuteriated species); the lower frequencies observed for the former compounds indicate that they are stronger chelates than the diesters.

All the enaminodiones studied have three bands in the 1 750—1 500 cm^{-1} region both in the i.r. and in Raman. As in simple enaminones,[11,12] the band at lowest frequency, usually of medium or strong intensity, is assigned as a coupled vibration having a minor component of the ν(C=O) mode and strong components of ν(C=C) and δ(N–H) [referred to hereinafter as the enamine band, ν(C=C) + δ(N–H)]; on treatment with deuterium oxide, this band is replaced by another at still lower frequency, also medium or strong, which is mainly due to the ν(C=C) vibration of the *N*-deuteriated species. The frequency value, 1 595—1 569 cm^{-1}, of the enamine band of the diketones (**3**) and (**4**) is higher than that of the nearest simple enaminoketones (1 560—1 573 cm^{-1}).[11] The introduction of a second acyl group in the enaminone system would be expected to produce a fall in the frequency of this band; the opposite shift observed can be ascribed to less efficient coupling of the ν(C=O) with the ν(C=C) and δ(N–H) vibrations. Smith and Taylor, who noticed[2] this effect in compound (**4e**), attributed it to the twisting of the carbonyls out of the plane of the C=C–NH group, on the basis of their postulate that two planar acyl groups instead of one lower the frequency and intensity of the enamine band; the evidence now presented demonstrates that the twisted conformation attributed to (**4c**) on this basis is incorrect (see below). On the other hand, the frequency of the enamine band of the cyclic diesters (**5**) (1 632—1 620 cm^{-1}) is only slightly higher than that of their open-chain analogues (**2**) (1 622—1 608 cm^{-1}),[1] and that of 3-alkylaminoacrylic esters (*ca.* 1 615 cm^{-1}).[13] This almost constancy can be attributed to less effective coupling of the ester carbonyl with the rest of the enamine

Table 3. I.r. and Raman frequencies (in italics) (cm^{-1}) of compounds (3)—(5)

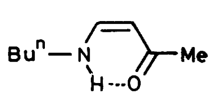
			ν(C=O)			
Compound	Medium	ν(N–H)	Sym.	Antisym.	ν(C=C) + δ(N–H)	ν(C=C)[a]
(3a)	CCl_4	3 185vw[b]	1 660sh	1 632vs	1 590m	1 547m
	$CDCl_3$	3 165vw	1 653m	1 624vs	1 585m	
	Me_2SO	3 200vw	1 655m	1 621vs	1 582m	
	KBr	3 200w	1 658s	1 620vs	1 595vs	
	Solid	*c*	*1 657*m	*1 630*vs 1 617m	*1 560*vs	
(3b)	CCl_4	3 190vw	1 657w	1 633vs	1 587m	1 544 m
		c	*1 660*vs	*1 632*m	*1 587*m	
	$CDCl_3$	3 180vw	1 655sh	1 625vs	1 588m	1 544m
		c	*1 657*vs,p	*1 629*s,pp	*1 584*m,pp	*1 546*m,pp
	KBr	3 190w	1 657m	1 615vs	1 592vs	1 555m
	Solid	*c*	*1 657*s	*1 622*vs *1 610*sh	*1 560*vs	
(3c)	Me_2SO	*d*	1 658sh	1 622vs	1 578m	
	KBr	*d*	1 649m	1 615vs	1 569s	
	Solid	*d*	*1 651*m	*1 617*m	*1 563*w	
(3d)	$CDCl_3$	*c*	1 658w	1 630vs	1 585m	1 542m
	Me_2SO	*c*	1 650sh	1 627vs	1 582m	
	KBr	3 185vw	1 655sh	1 630vs	1 590s	
	Solid	*c*	*1 654*vs	*1 635*m	*1 591*w	
(3e)	$CDCl_3$	3 180vw	1 655w	1 631vs	1 579s	1 534s
	KBr	3 180vw	*c*	1 632vs	1 586s	
(4a)	CCl_4	3 185vw	1 676s	1 614vs	1 589m	1 548m
	$CDCl_3$	3 190vw	1 673s	1 604s	1 590sh	1 549w
		c	*1 672*m,p	*1 608*vs,dp	~*1 590*sh	
	$[^{2}H_{6}]Me_{2}SO$	*e*	1 670vs	1 605vs	1 585s	
	KBr	3 190w	1 668s	1 605vs	1 587vs	
	Solid	*3 215*vw	*1 664*m	*1 604*vs	*1 565*m	
(4b)	CCl_4	~3 190vw	1 672s	1 607vs	1 585m	1 540m
		c	*1 671*vs,p	*1 606*s,dp	*1 583*s,pp	*e*
	$CDCl_3$	3 195vw	1 667s	1 597s	1 580sh	1 543w
		c	*1 667*vs,p	*1 597*s,dp	*1 580*sh	*1 545*m
	$[^{2}H_{6}]Me_{2}SO$	*e*	1 663vs	1 598vs	1 582sh	
	KBr	3 205w	1 667s	1 588vs	*f*	
(4c)	Me_2SO	*d*	1 662vs	1 597vs	1 575s	
	KBr	*d*	1 662vs	1 592vs	1 572sh	
	Solid	*c*	*1 654*vs	*1 580*vs	*1 566*m	
(4d)	$CHCl_3$	3 190vw	1 670s	1 603vs	1 582s	1 535s
		c	*1 669*vs,p	*1 603*vs,dp	*1 579*s,p	*1 536*s,pp
	Me_2SO	*e*	1 665vs	1 601vs	1 579s	
	KBr	*c*	1 663s	1 605vs	1 577s	
	Solid	*c*	*1 661*vs	*1 603*vs	*1 576*s	
(4e)	CCl_4	3 190vw	1 676s	1 610vs[g] 1 595vs[g]	1 572vs[g]	
	$CDCl_3$	*c*	1 668s	1 610s[g] 1 595vs[g]	1 575vs[g]	1 531s
	KBr	~3 190vw	1 674s	1 600s[g] 1 592vs[g]	1 581s[g]	1 536m
	Solid	~*3 185*vw	*1 673*s	*1 600*m[g] *1 588*vs[g]	*1 569*vs[g]	
(4f)	CCl_4	*c*	1 680s	1 617s[g] 1 601m[g]	1 676vs[g]	1 522vs
	$CDCl_3$	*c*	1 675s	1 613s[g] 1 599s[g]	1 573vs[g]	1 525vs
	KBr	*c*	1 668s	1 606s[g] 1 598s[g]	1 574vs[g]	
	Solid	*c*	*1 676*w	*1 611*vs[g] *1 602*sh[g]	*1 572*s[g]	
(5a)	CCl_4	3 268vw 3 215vw	1 732m	1 685vs	1 631m	
	$CDCl_3$	3 275vw 3 218vw	1 719m	1 673vs	1 627m	1 598m
		b	*1 726*s,p	*1 678*w,pp	*1 632*w,pp	
	$[^{2}H_{6}]Me_{2}SO$	*e*	1 722s	1 680vs	1 623s 1 605m	
	KBr	3 290m	1 723s	1 675vs	1 640s	
	Solid	*c*	1 726s	1 678m	1 615s	

Table 3 (*continued*)

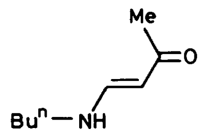
			ν(C=O)			
Compound	Medium	ν(N–H)	Sym.	Antisym.	ν(C=C) + δ(N–H)	ν(C=C)[a]
(**5b**)	CCl_4	3 265vw	1 731m	1 681vs	1 624s	
		3 210vw				
	$CDCl_3$	3 268vw	1 720m	1 672vs	1 622s	1 588s
		3 210vw				
	$[^2H_6]Me_2SO$	*e*	1 723s	1 679vs	1 620s	
					1 598m	
	KBr	3 280w	1 730m	1 669vs	1 637m	1 610
					1 615sh	
	Solid	*c*	1 725vs	1 692m	1 606m	
(**5c**)	CCl_4	3 180vw	1 735m	1 685vs	1 624vs	1 566vs
	$CDCl_3$	*h*	1 724m	1 680vs	1 626s	1 566s
		~*3 190*vw	*1 727*m,p	*1 680*w,dp	*i*	*1 565*
	$[^2H_6]Me_2SO$	*e*	1 729s	1 689vs	1 625vs	
	KBr	3 218w	1 732s	1 689vs	1 637vs	
	Solid	~*3 210*w	*1 732*m	*1 687*m	*i*	

[a] Measured in the *N*-deuteriated derivative. [b] Abbreviations: s, strong; m, medium; w, weak; v, very; sh, shoulder; p, polarized; pp, partially polarized; dp, depolarized. [c] Not detected. [d] Overlapped by the OH bands. [e] Obscured by the solvent. [f] Overlapped by the strong band at 1 588 cm^{-1}. [g] Large contribution of ring ν(C=C). [h] Not assigned. [i] Overlapped by the strong ring band at *ca.* 1 600 cm^{-1}.

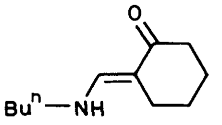
system relative to that operating in the enamino-ketones, the coupling being least in the cyclic diesters (**5**); the enamine band of the latter compounds does not differ much from that of a typical enamine (*ca.* 1 645 cm^{-1}).[14]



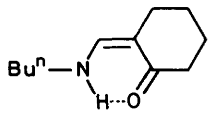
(**8a**)



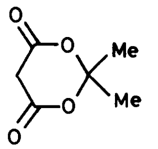
(**8b**)



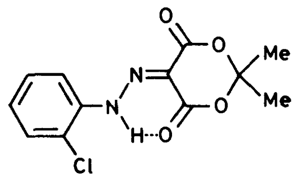
(**9a**)



(**9b**)



(**10**)



(**11**)

The other two bands in the double-bond region, insensitive to the *N*-deuteriation, are associated with the carbonyl stretchings. The position and intensity of these bands are different for the three classes of compounds studied. In the open-chain diketones (3), the i.r. band at the higher frequency (1 660—1 653 cm^{-1}) is of medium, or even weak, intensity in comparison with the low-frequency (1 632—1 615 cm^{-1}) band. In the Raman spectra, the reverse relationship is often observed; the high-frequency band is polarized and appreciably stronger than the other band that is depolarized. These two carbonyl bands have frequencies fairly close to those of the chelated *Z*-form and the *E*-form of simple enamino-ketones, but they differ greatly in intensity. For example, the bands (in carbon tetrachloride) at 1 657 (weak) and 1 633 cm^{-1} (very strong) of compound (**3b**) are quite near the carbonyl bands* (in tetrachloroethylene) at 1 646 (very strong) and 1 628 cm^{-1} (medium) for the chelated *ZZ*-form (**8a**) and *EE*-form (**8b**), respectively, of 4-n-butylaminobut-3-en-2-one.[11b] Furthermore, the difference between the two carbonyl frequencies of (**3b**) is slightly larger than that existing between the ν(C=O) bands of (**8a** and **b**). On this basis, it is concluded that the two C=O groups of compounds (3) are mechanically coupled, the high-frequency band being assigned as the symmetric mode with a large contribution from the stretching of the bonded C=O group, and the low-frequency band as the antisymmetric mode with a predominant contribution from the ν(C=O) of the free carbonyl.

The carbonyl bands of the *ZZE*-enamino-diones (**4**) are further apart (Δν *ca.* 65 cm^{-1}) than those of compounds (**3**) (Δν *ca.* 24 cm^{-1}), and have a different intensity pattern. The high-frequency band, at *ca.* 1 670 cm^{-1}, strong in the i.r., is also strong and polarized in the Raman, and the other band, at *ca.* 1 615 cm^{-1}, very strong or strong in the i.r., is strong and depolarized in the Raman. These results are indicative of strong mechanical coupling between the ν(C=O), and the large strength of the interaction in this class of compounds can also be seen by comparing their carbonyl absorptions with those of the nearest enaminones; for example, the bands at 1 672 (strong) and 1 607 cm^{-1} (very strong) of (**4b**) with those[11a] of the *ZE*-form (**9a**) (1 661 cm^{-1}, strong) and chelated *ZZ*-form (**9b**) (1 646 cm^{-1}, strong) of 2-n-butylaminomethylene-5,5-dimethylcyclohexanone in tetrachloroethylene solution. Consequently, the high-frequency carbonyl band of compounds (**4**) is assigned as the symmetric mode and the low-frequency band as the antisymmetric mode of the two strongly coupled ν(C=O) vibrations. Coupling between the carbonyls then occurs in both *EZE*- and *ZZE*-conformations of enamino-diketones, the effect being stronger in the latter, as foreseen.[2]

2,2-Dimethyl-1,3-dioxane-4,6-dione (**10**) has been shown to adopt a boat conformation either as a solid[15] or in solution,[16] with O-1, O-3, C-4, and C-6 being planar, C-2 and C-5 above the plane, and the two carbonyl oxygens below it. This conformational preference is a consequence of (**10**) containing two identical, planar lactone groups (C-O-CO-C) and the absence of

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* The vinyl analogue amide band (AV) I, in Dabrowski's terminology.[11a]

significant 1,4-steric interactions.[15] The introduction of a double bond conjugated with the carbonyls at position 5 would be expected to widen the C-4–C-5–C-6 angle and to flatten considerably the C-5 end of the boat; in the limit, the conformation would be a half-boat, with all the delocalized system in a plane, and C-2 above it, similar to that found in the diketones (**4**). In accord with this, the two strong bands at 1 785 and 1 753 cm^{-1} for compound (**10**), due to the in-phase and out-of-phase coupling of the ν(C=O) vibrations,[17] are shifted [18] 25—30 cm^{-1} to lower frequency in the chelated phenylhydrazone derivative (**11**); the *X*-ray crystallographic study of this compound reveals a very shallow boat conformation, as described above, and the presence of an intramolecular hydrogen bond.[18] Compounds (**5**) show bands at 1 735—1 719 cm^{-1}, of medium intensity in the i.r., and strong and polarized in the Raman, and 1 689—1 669 cm^{-1}, very strong in the i.r. and much weaker and depolarized in the Raman, which correspond to the symmetric and antisymmetric modes of the coupled ν(C=O); the further shift observed to lower frequency is due to the increased conjugation which must also result in a further flattening of the whole conjugated system. Compounds (**5**) most likely have, therefore, a half-boat or near half-boat conformation similar to that of the diketones (**4**), or of compound (**11**). It is noteworthy that both carbonyl bands of the compounds under study, and particularly, those of the cyclic compounds (**4**) and (**5**) in which coupling between the carbonyls is more effective, are sensitive to the solvent polarity. This can be due to the mixing of the vibrations, which disperses the effect of the solvent, and of chelation, among the different resulting modes.

The carbonyl bands of the cylic diesters (**5**) appear at frequencies higher than those of the *ZZE*-form (**2b**) of the open-chain analogues, as can be seen by comparing the absorption of (**5b**) with the bands at 1 713 and 1 641 cm^{-1} in the spectrum of (**2b**; $R^1 = Bu^n$, $R^2 = Et$) in carbon tetrachloride solution.[1] Similar shifts are observed [9,17,18] in other compounds containing the 1,3-dioxane-4,6-dione system when compared with similar open-chain diesters. This may be due in part to the special structure of the 1,3-dioxane-4,6-dione system in which each ester function acts as an electronegative substituent with respect to the other,[2] and also to the enhanced efficiency of the coupling between the coplanar carbonyls when they are included in a ring; the latter effect also operates in compounds (**4**).

The above results, and those previously reported,[1,2] suggest that the coupling between the carbonyls is stronger in the cyclic compounds (**4**) and (**5**) than in their open-chain counterparts (**3**) and (**2**), and is also stronger in the *ZZE*-conformation than in the *EZE*-alignment. Furthermore, the coupling of the ν(C=O) with the ν(C=C) and δ(N–H) vibrations seems to be weaker in the enamino-diones than in the nearest related enaminones, and in the cyclic diesters (**5**) than in the 2-alkoxycarbonyl-3-aminoacrylates (**2**). The strong coupling between the two ν(C=O) seems to inhibit their further coupling with other vibrational modes.

In the light of the above results, the criteria enunciated [2] for the planarity of the enamino-dione system should be reconsidered. The first establishes that the presence of two planar acyl groups instead of one at C-2 of an enamine will lower both the frequency and intensity of the enamine band. As said above, the frequency of this band in the planar diketones (**3**) and (**4**) is always higher than that [11] of the most similar enaminone with the same *N*-substituent [*i.e.*, 1 587 cm^{-1} (medium) for (**3b**) in carbon tetrachloride solution compared with the bands observed [11b] at 1 577 cm^{-1} for (**8a**) and at 1 583 cm^{-1} for (**8b**) in tetrachloroethylene]. According to the second criterion, planar enamines having two acyl groups at C-2 have a very weak, or absent, Raman enamine band; the Raman data contained in Table 3 indicate that the intensity of this band is variable, more often is of medium intensity, and can even be strong for solid samples.

In conclusion, the results show that the enamino-dione system contained in the diketones (**3**) and (**4**) is essentially planar irrespective of the medium, and that the former compounds adopt the *EZE*-conformation (**7**) either in the solid state or in solution. The alternative *ZZE*-conformation (**6**) must be much more unstable, probably because of the large steric hindrance between the parallel methyl groups which would produce a severe twisting of the delocalized system. The *EZE*- and *ZZE*-conformations give rise to quite distinct i.r. and Raman spectra. The cyclic diesters (**5**) are most probably planar, or nearly planar. Coupling between the carbonyl stretchings occurs, being stronger in the cyclic compounds (**4**) and (**5**) than in the open-chain analogues (**3**) and (**2**). Finally, the results also show that the planarity criteria established for enamino-diones, and for other enamines having two strongly electron-attracting substituents at C-2, lack generality and have doubtful diagnostic value.

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