Vibrational Spectroscopy and Conformations of 2-Alkoxycarbonyl-3-aminoacrylic Esters †
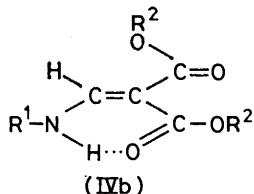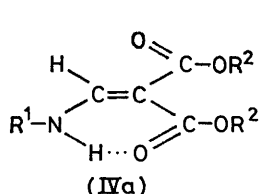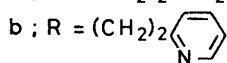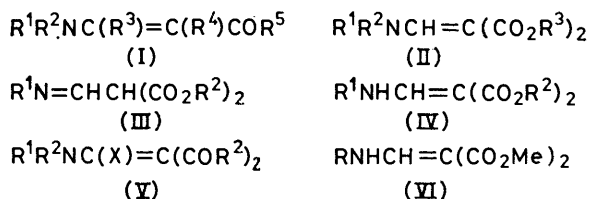
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The i.r., Raman, and ^1H n.m.r. spectra of 2-alkoxycarbonyl-3-aminoacrylic esters (IV; $R^1 = H$, alkyl, aryl) and those of their *N*-deuteriated derivatives show that these substances exist in the enamino-ester form with a strong intramolecular hydrogen bond between the *cis*-NH (or -ND) and CO_2R^2 groups. Some complexities in the i.r. and Raman bands, and their dependence on solvent polarity, temperature, and aggregation state, indicate the existence of rotational isomerism: conformers (IVa and b) predominate in non-polar media; an additional rotamer (IVd) is also probably present in polar solvents. Conformation (IVb) is preferred in the solid state. Some features of the $\nu(C=O)$ bands suggest a weak vibrational coupling between the carbonyls. The validity of the criteria established by Smith and Taylor to ascertain the planarity of these and related substances is discussed, and no significant difference in this respect is considered to exist between compounds (IV) with primary and secondary amino-groups.

ENAMINO-ESTERS and -ketones ('enaminones')[1] of formula (I) are planar, or nearly planar, mesomeric systems which can exist in several configurational and conformational isomeric forms due to restrictions to

$$R^1R^2NC(R^3)=C(R^4)COR^5$$
$$(I)$$

$$R^1N=CHCH(CO_2R^2)_2$$
$$(III)$$

$$R^1R^2NC(X)=C(COR^2)_2$$
$$(V)$$

$$R^1R^2NCH=C(CO_2R^3)_2$$
$$(II)$$

$$R^1NHCH=C(CO_2R^2)_2$$
$$(IV)$$

$$RNHCH=C(CO_2Me)_2$$
$$(VI)$$

a ; R = $(CH_2)_2NEt_2$

b ; R = $(CH_2)_2$⟨N⟩

(IVa)

(IVb)

rotation around the olefinic double bond and the C–N and C–C=O single bonds. This isomerism is well suited to spectroscopic study,[2-5] and the results obtained allow the different isomers to be distinguished in most cases and have led to the formulation[5c] of rules to predict the $\nu(C=O)$ and $\nu(C=C)$ frequencies. As in the parent enones[5b,6a] and other β-substituted enones[5a,6b] mechanical couplings exist in these compounds which affect the $\nu(C=O)$, $\nu(C=C)$, and $\nu(C-N)$, and, in the enaminones with primary and secondary amino-groups, the $\delta(N-H)$ modes.[3-5] In continuation of our studies[4] on the absorption and isomerism of β-amino-αβ-unsaturated esters, we have examined the i.r. spectra of 2-alkoxy-

carbonyl-3-aminoacrylic (aminomethylenemalonic) esters (II). These trisubstituted ethylenes can only exist in a single configuration, but due to the presence of three restricted rotations, the occurrence of $2^3 = 8$ (4 when $R^1 = R^2$) rotational isomers is theoretically possible. The tautomeric imino-form (III) can also exist for derivatives with primary or secondary amino-groups. In addition to the complexity which the coexistence of these, or some of these, isomers could confer to the spectra, the presence of the β-dicarbonyl system could result in coupling of the two $\nu(C=O)$ vibrations and the further perturbation of the absorption. Complex patterns of carbonyl bands have been observed in malonic esters and β-diketones[7,8] and have been explained in terms of the occurrence of vibrational coupling and/or rotational isomerism.
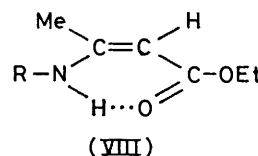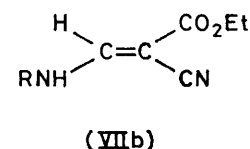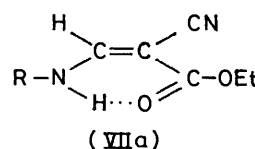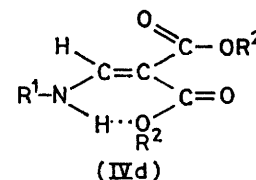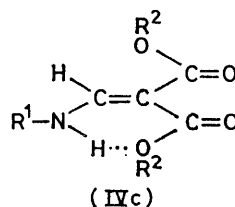
(IVc)

(IVd)

(VIIa)

(VIIb)

(VIII)

There were few data[9] on the i.r. spectra of 2-alkoxycarbonyl-3-aminoacrylic esters (IV) when this investigation was started. Extensive dynamic ^1H n.m.r. studies[10] on the *N*-disubstituted derivatives had

revealed the existence of enhanced energy barriers to rotation around the C–N bond and the concomitant reduction of the energy of rotation around the C=C bond. This paper deals with the i.r. spectra of compounds (IV; R^1 = H, alkyl, aryl) with primary and secondary amino-groups; some Raman and ^{1}H n.m.r. data, which can assist in the interpretation of the i.r. spectra, have also been included. When this work was complete, a report [11] appeared on the i.r. absorption of substances of formula (V; X = H or an electron-donating group), including ethyl 3-amino-2-ethoxycarbonylacrylate (IV; R^1 = H, R^2 = Et) and its two N-substituted derivatives (VIa and b); the results were interpreted in terms of the existence of the two chelated conformers (IVa and b) which were considered to be fully planar in the compound with the primary amino-group and to have the plane of the free ester group twisted from the plane of the ring of the chelate in derivatives (VIa and b). Criteria were also established to assign conformation and to decide the issue of planarity. Our results, while confirming the existence of rotational isomerism, as indicated by Smith and Taylor,[11] and providing additional arguments for many of their assignments, cast doubts on some others as well as on the validity of their planarity criteria. Mechanical coupling between the ν(C=O) vibrations is considered to occur and to be responsible for some peculiarities of the spectra. Moreover, the present data suggest the existence of more complex conformational equilibria in polar media and the operation of extensive mechanical couplings which affect the whole of the conjugated system.

EXPERIMENTAL

Spectra.—I.r. spectra were recorded on a Perkin-Elmer 457 spectrophotometer. The measurements were performed in the solid and/or the liquid state, and in solution at 0.001—0.5M concentration, depending on the solvent, using 1—0.03 mm cells. Spectra for very dilute carbon tetrachloride solutions in the 3 600—3 000 cm^{-1} region were taken with 1 and 4 cm quartz cells. Indene and polystyrene were used for instrument calibration, and the reported wavenumbers are estimated to be accurate to within ±3 cm^{-1}. Variable-temperature experiments were carried out with a Beckmann-R.I.I.C. unit VLT-2, using carbon tetrachloride and tetrachloroethylene solutions. Raman spectra were taken for liquid and solid samples, and for carbon tetrachloride and chloroform solutions using Jarrell-Ash 25-300 and Ramanor H-G, 2S (5145 Å) spectrometers. ^{1}H N.m.r. spectra were measured at 60 MHz and 26—28 ° for neat liquids or 0.5M solutions on a Perkin-Elmer R-12B instrument using tetramethylsilane as internal standard.

Compounds.—The following compounds were prepared by published procedures, with properties in agreement with those reported: ethyl 3-amino-2-ethoxycarbonylacrylate,[12] ethyl 3-anilino-2-ethoxycarbonylacrylate,[9c,12] ethyl 2-ethoxycarbonyl-3-toluidinoacrylate,[13] ethyl 2-ethoxycarbonyl-3-p-nitroanilinoacrylate.[13]

The following new compounds were prepared from ammonia or the appropriate amine and alkyl 3-alkoxy-2-alkoxycarbonylacrylate by conventional procedures:[4d,12] *methyl 3-amino-2-methoxycarbonylacrylate*, m.p. 124—125°

(from ethanol) (Found: C, 45.45; H, 5.85; N, 9.35. $C_6H_9NO_4$ requires C, 45.3; H, 5.7; N, 8.8%); *methyl 3-n-butylamino-2-methoxycarbonylacrylate*, m.p. 47—48° (from ethanol) (Found: C, 56.05; H, 8.1; N, 6.45. $C_{10}H_{17}NO_4$ requires C, 55.8; H, 7.95; N, 6.5%); *ethyl 2-ethoxycarbonyl-3-ethylaminoacrylate*, b.p. 86—87° at 0.04 mmHg, liquid at room temperature, n_D^{23} 1.503 5 (Found: C, 55.45; H, 7.9; N, 6.5. $C_{10}H_{17}NO_4$ requires C, 55.8; H, 7.95; N, 6.5%); *ethyl 3-n-butylamino-2-ethoxycarbonylacrylate*, b.p. 110—111° at 0.02 mmHg, liquid at room temperature, n_D^{23} 1.495 6 (Found: C, 59.3; H, 8.65; N, 6.15. $C_{12}H_{21}NO_4$ requires C, 59.3; H, 8.9; N, 5.95%); *ethyl 3-cyclohexylamino-2-ethoxycarbonylacrylate*, b.p. 115—116° at 0.02 mmHg, n_D^{29} 1.513 5 (Found: C, 62.6; H, 8.6; N, 5.45. $C_{14}H_{23}NO_4$ requires C, 62.4; H, 8.6; N, 5.2%); *ethyl 3-p-chloroanilino-2-ethoxycarbonylacrylate*, m.p. 79—80° (from ethanol) (Found: C, 56.5; H, 5.35; N, 4.75. $C_{14}H_{16}ClNO_4$ requires C, 56.45; H, 5.45; N, 4.7%); *ethyl 3-benzylamino-3-ethoxycarbonylacrylate*, m.p. 68—69° (from ethanol) (Found: C, 65.0; H, 7.0; N, 5.05. $C_{15}H_{19}NO_4$ requires C, 64.95; H, 6.9; N, 5.05%).

N-*Deuteriation Experiments.*—Aliquot portions of solutions of compounds (III) in the appropriate solvent were shaken with deuterium oxide for different periods. The organic phase was then removed and transferred to the i.r. cell or the ^{1}H n.m.r. tube.

RESULTS AND DISCUSSION

Data for the i.r. and Raman spectra of 3-alkoxycarbonyl-3-aminoacrylic esters with primary and secondary amino-groups and the band assignments are in Tables 1 and 2, respectively. The most significant features of the ^{1}H n.m.r. spectra of both types of compounds appear in Table 3.

The existence of these substances in the enaminoester form and the presence of a strong intramolecular hydrogen bond followed straightforwardly from the ^{1}H n.m.r. spectra. The compounds with a secondary amino-group had a one-proton signal at low field (δ 9.1—9.4, for the compounds with an alkylamino-group; δ 11.1—11.3, for the N-arylamino-derivatives) which is assigned to the intramolecularly bonded NH proton. This signal was rather broad, an effect most likely due to ^{14}N-quadrupole relaxation, but in most cases its multiplicity was apparent: in the N-arylamino-derivatives it was a doublet ($J_{:CH,NH}$ *ca.* 14 Hz); in the compounds with an alkylamino-group, it was a more complex multiplet due to the additional coupling between the NH proton and the proton(s) at the α-carbon of the N-alkyl group. The clear cut, one-proton doublet ($J_{:CH,NH}$ 13—14 Hz) at δ 8.0—8.5 is assigned to the olefinic proton; the high value of the coupling indicated a *trans*-relationship between the amino and vinyl protons and hindrance to rotation around the C–N bond imposed by chelation. Compounds with a primary amino-group showed very broad signals attributable to the NH protons; in the diethyl ester (IV; R^1 = H, R^2 = C_2H_5) there were two, one of them, at δ *ca.* 7.3 (1 H), assigned to the free amino-proton (H_α), and the second, which was an unresolved doublet (J *ca.* 15 Hz), at δ *ca.* 8.5, ascribed to the intramolecularly bonded amino-proton (H_β).

TABLE 1

I.r. and *Raman* frequencies (cm^{-1}) of compounds H$_2$N–CH=C(CO$_2$R)$_2$

R	Medium (molarity, M)	ν(N–H) Free	(c)	ν(N–H) Bonded	ν(C=O) Free s-cis	Free s-trans	Bonded s-cis	Bonded s-trans	C=C–NH$_2$	C=C–NH$_2$	ν(C–O) a	ν(C–O) a	ν(O–R)	τ(NH$_2$)	b	γ(=C–H)
Me	CCl$_4$	3 510m d	3 405W	3 315w	1 730s e	1 700s f	1 673L f 1 665L e 1 650L		1 621s	g	1 320L 1 298m 1 277m	1 233s	1 188s	1 127s	1 063s	g
	CDCl$_3$ (0.1)	3 500m 3 400W f		3 410W h 3 323w	1 740L 1 710L e 1 700S i	~1 690 f	1 640L f	1 670S i	1 629s	1 565W 1 530w 1 510w	1 321m 1 302m 1 288m	1 239s	1 190m	1 130s	1 068s	807m
	KBr			3 360s h 3 325s		1 688 f	1 664S f		1 640s	1 535w 1 510m 1 502m	1 335s 1 297s 1 287s	1 224s	1 196s	1 143s	1 075s	782m
Et	CCl$_4$ (0.001)	3 510m	3 405W	3 315w	1 720S e	1 697s f	1 665S f 1 650L e		1 624S	g	1 313L 1 295M 1 273m	1 232S	1 172s 1 096m	1 125s	1 065s	g
	CCl$_4$ (0.1)	3 510w		3 400w,b h 3 310w,b	1 718L e	1 692s f	1 665S f		1 638L 1 624S	1 575L,b 1 521w,b	1 315L 1 293s	1 228s	1 172w 1 096w	1 130s	1 063s	g
	CCl$_4$ (0.5)	*g*	*g*	*3 390W h* *3 300w,b*	*1 720L e,p*	*1 690s f,p*	*1 668L f,dp* *1 640L e,dp* *1 665L e* *1 648L e*		*1 625m,p*	*1 525s,p*	*1 280m,p*	*1 228m,p*	*1 172w,p*	*g*		*g*
	C$_2$Cl$_4$ (0.01)	3 510m	3 405W	3 310w	1 725m e	1 697s f	1 665S f		1 623S	1 522w,b	1 312L 1 293s 1 273m	1 231S	1 167 *g*	g	1 063s	g
	C$_2$Cl$_4$ (0.1)	3 505w		3 395w,b h 3 305w	1 720w e	1 694s f	1 665S f		1 635L 1 625S	1 570L,b 1 520w,b	1 320L 1 293L 1 281s	1 225S	1 170w 1 094w	g	1 064s	g
	CDCl$_3$ (0.1)	3 502m 3 400W f		3 410W h 3 323w	1 740L 1 710L e 1 692s i	1 685L f	1 640m f	1 665S i	1 625S	1 527w 1 510w	1 315L 1 298m 1 283s	1 230s	1 170w 1 094w	1 130M	1 065s	805W
	CHCl$_3$ (0.2)	3 495W		3 393W h 3 315w	*1 710L e* *1 690 i*	*1 690s f*	*1 635L f*	*1 660L i*	*1 620s*	~1 520 *g*	*1 285s*	*g*	*g*	*1 130L*		
	EtOH	*g*	*g*		*1 725M e* *1 695S i*	*1 671S f*	*1 648L f,i*	*1 660S i*	1 640L	1 585L,b 1 530w,b	1 298L 1 281s	1 225s	*1 091W*	1 140s		~805
	Me$_2$SO (0.5)			3 380w,b k 3 205w,b k	1 730L 1 703s e,i	1 684s f	1 644 f,e,i	1 662s i	1 644s	1 582w,b 1 532w,b	1 328w 1 291s 1 275s	1 223s	1 170w 1 095w	1 135s	g	805W
	KBr			3 370S h 3 220s		1 675s f	1 658S f		1 630L	1 530L 1 511M	1 328s 1 298m 1 283s	1 213s	1 170w 1 098w	1 152s	1 073s	808w
	Solid			3 367W h 3 215w		1 682S f	1 654M f		1 630L	1 505m	1 324m 1 294w 1 270s	1 208s	1 162w 1 093W	*1 130L*		806w

ª Also, contribution of ν (=C–C). ᵇ Coupled mode; according to Smith and Taylor,[11] γ(NH$_2$). ᶜ Tentatively assigned to a small concentration of the imino-form (III). ᵈ Abbreviations: S, very strong; s, strong; M, medium strong; m, medium; w, weak; W, very weak; L, shoulder; b, broad; P, polarized; dp, depolarized; ν(N–H) of a non-chelated form. ᵏ Assigned to solvent bonded N–H groups. ˡ Overlapped by the skeletal vibration. ᵉ Assigned to rotamer (IVa). ᶠ Assigned to rotamer (IVb). ᵍ Obscured by the solvent. ʰ Assigned to the intermolecularly bonded N–H group. ⁱ Asssigned to rotamer (IVd). ʲ Assigned to the symmetrical ν(N–H) of the imino-form (IVd).

TABLE 2

I.r. and *Raman* frequencies (cm⁻¹) of compounds R¹NH–CH=C(CO₂R²)₂

Compound R¹	R²	Medium	ν(N–H) d	ν(N–H) Bonded	ν(C=O) e	Free s-cis	Free s-trans	Bonded s-cis	Bonded s-trans	C=C–NH	a	b	ν(C–O)		ν(O–R²)		γ(=C–H)
PhCH₂	Et	C₆H₁₂				1728M f,g	1695s h	1658s h / 1643S g		1612s	i	1313m / 1305m	1282s / 1257M	1234S / 1214S	1200M	1102L 1092M 1089L 1076m	801m
		CCl₄		3268W		1718M g	1689s h	1657S h / 1646S g		1611s	1432m	1313m / 1303m	1283m / 1256m	1236S / 1216S	1200M	1096m 1086m 1075m	*i*
				3270W,p		*1713M g,p / 1690w h,p*		*1655L h / 1644w g,dp*	*1656S k*	*1604s,p*	*1430SJ,p*	*1310m*	*1282w / 1255m*	*1235m,p / 1215L*	*1198M,p*	*1110w,p / 1095W,p*	*i*
		CDCl₃	3378W	3275W		1710L g / 1695s k / *1695s g,k*	1685s h / *1680L h*	1648L h,g / 1639s g / *1635s h,g*	1655S k / *1660W k*	1610s / *1605s*	432m / *430SJ*	1317m / *1302m*	1285m / 1263m / *1265m*	1240s / *1216S*	1202L	1091m 1078m *1115W 1095W*	804m
		EtOH	*i*			1722m g / 1692s k / 1713s g	1677s h	1646L h,g	1661S k	1627L / 1614s / 1608s	1423 i	1314m / *1315M / 1303m*	1287s / 1270L / *1255S*	1238 / 1216	1204L		806m
		Dioxan	*i*				1687s h	1657S h / 1645S g / 1608s		*i*	1320			1202L		803m
		Me₂SO		3290w	1728w	1702s g / 1697L k / *1707s g,k*	1684s h	1648L h,g / *1645s h,g*	1656S k	1606s	1422m i	1319m i / *1318m*	1281m i / 1259s i / 1283m	1205 / 1233s / 1211S / 1235s	1198L	089m	804m
		C₅H₅N	3380W	3270W	1735W		1686s h		1656S k	~1607s	*i*	*1300L*	*1300L*	1202L	089m	803m
		Molten	3380L	3273W	1737L	1711s g	1687s h	1655S h / 1642L g / 1633S h		1611s	1428m	1317m / 1298m	1283m / 1259m	1234S / 1213S	1200L	1093m 1072m *1104m 1072W*	802m
		Solid		3285w			1682s h			1605s	1428s	1316s	1291s	1230S	1198s	1109w 1096m 1084L 1073M 1095m 1084L 1073M 1080L 1072m 1094L 1078s	805m
Et	Et	CCl₄		3290W / 3268W		*1718M g*	*1677s h / 1689s h*	*1635S h / 1658s h / 1644S g*		*1605s / 1612s*	*1425SJ / 1431m / 1420L*	*1314m / 1315M / 1303m*	*1287s / 1270L / 1255S*	*1222s / 1231S*	*1192m / 1153s*	*1109w / 1096m / 1084L 1073M 1095m*	794w / *i*
		C₂Cl₄		3265W		1721m g	1689s h	1658s h / 1644S g		1611s	1431m / 420L	1315M / 1308m	1270L / 1254S	1230S	1152s	1095m 1072m	
		CDCl₃	3383W	3280W	1728w	1710L g / 1692L k	1682s h	1647L h / 1638s g / 1645s h,g	1654S k	1611s	431m / 423m	309s / 303m / 321m / 301m	1278L / 257S / 280L / 255S	1233S	1153s	1096m 1073m *1093w 1080s*	804m
		Me₂SO	3380W	3268W	1728L	1700s g,k	1683s h	1655S h / 1636s g	1658S k	1608s	*i* / 425s / 430SJ	1321s / 302m / 327m	321s / 302m / 327m / 282m	1222s	1161s	1096m 1055s *1096w*	804w
		Liquid	3380L	3280w	1738L	1710s g / 1690L k	1688S h / *1690L h*	1655S h / 645s g / *1656L h / 1646m g*		1612s / *1609m*	321s / 298m / 327w / 298m	1298m / 298m	1275L / 282m / *1275L / 282m*	1295m / *1228m*	1152s / *1151w*		804m / *804w*
Buⁿ	Et	CCl₄		3270W		1713m g	1685s h	1656s h / 648L h / 1635s g		1609s	430L / 420L	1318m / 310m	1275s / 248L / 1255s	1233s / 212S	1149m	1073m	
		CDCl₃	3380W	3278W		1710L g / 1690L k	1681s h	1648L h / 635s g	1651S k	1609s	430m / 422m	1322m / 313w	1275L / 266m / 250L	212S / 236s / 213s	1151m	1093w 080s	*804*
		Me₂SO			1728L / 1735L	1701s g,k / 1712s g	1683s h / 1685S h	1648L h,g / 655S k / 646S g / 1653m g / 658L k	1657S k	1609s / 1612S	*i* / 425L / 429SJ / 423L	1325m / 324S / 313L / 324L	1257m / 277s / 255s / 258	213s / 224S / 216S / 232s / *215m*	1151m / 152s / *150w*	1095s 076s *1097W 1071m*	804m / 803m
		Liquid				*1711m g*	*1690m h*	*1644m g / 1659L k*	*1657S k*	*1610m*	*1429SJ / 423L*	*1324s*	*1275L / 231*	*1215m / 231S*	*150w*	*1074m*	805w / *i*
cyclo-C₆H₁₁	Et	CCl₄		3270W		1715m g	1684s h	1655S h / 640S g		1608s	431m / 423L	319m / 312m	1274s / 261s	213m / 236s	1153m	1096m 074m	*i*
		CDCl₃	3378W	3280W		1710L g / 1690L k	1682s h	1648L h / 636m g	1654S k	1608s	431L / 423m	327m / 313m	1273s / 262s	1236m / 229L	1154m	1096L 090m *1075m*	803m
		Me₂SO		3260W	1730L	1701s g,k	1681s h	1640L h,g	1652S k	1606s	*i* / 431s	1327m / 304w	1274s / 259s	1236s / 222s	1151m	1095s	808m
		Liquid		3285w	1738L	1712s g	1688S h	1655S h / 649S g		1612S	431s / 423L	324s / 313L / 303M	1277s / 255s	1224S / 216S	1154m	1095s 076s	808m
						1714s g	*1688m h*	*1655L h / 1645m g*		*1610L / 1606s*	*1429SJ*	*1323L / 310s*	*1275L / 260s*	*1237s / 1223L*	*1150m*	*1095m 1077m*	803s

TABLE 2 (continued)

Compound R¹	Rᵃ	Medium	ν(N–H) d	ν(N–H) Bonded	ν(C=O) e	Free s-cis	Free s-trans	Bonded s-cis	Bonded s-trans	C=C–NH	a	b	ν(C–O)	ν(C–O)ᵉ	ν(O–R²)	ν(O–R²)	γ(=C–H)
Buⁿ	Me	CCl₄		3 270W		1 721s ᵍ	1 690s ʰ	1 660S ʰ, 1 649S ᵍ		1 612s	1 446S	1 321m, 1 303L	1 277s	1 238S, 1 214S	1 149m	1 092L, 1 081m	i
		CDCl₃	3 380W	3 278W		1 715L ᵍ, 1 695s ᵏ	1 687L ʰ	1 655L ʰ, 1 642L ᵍ	1 661S ᵏ	1 615s	1 447S	1 327m, 1 306L	1 276s, 1 255L	1 238s, 1 215s	1 149m	1 088s	808m
		Me₂SO		3 270w	1 730L	1 708s ᵍ,ᵏ	1 687s ʰ	1 653L ʰ,ᵍ	1 662S ᵏ	1 611s	i	1 326m, 1 302w	1 275s, 1 260L	1 222s, 1 212s	1 148m	1 082s	807m
		KBr		3 305m			1 692S ʰ	1 628S ʰ		1 615L	1 442S	1 303m	1 249s, 1 255S	1 225S	1 151s	1 089s	811s
C₆H₅	Et	CCl₄		3 268W		1 721M ᵍ	1 692s ʰ	1 655s ʰ, 1 648L ᵍ		1 622s	1 425s	1 326s, 1 303m	1 259S	1 239S, 1 228L	1 304m	1 094m, 1 083L, 1 073m	i
		CDCl₃	3 365W	3 268W		1 710L ᵍ, 1 698s ᵏ	1 688S ʰ	1 640L ʰ,ᵍ	1 653S ᵏ	1 622s	1 424M	1 314m	1 258S	1 233S	1 306M	1 094L, 1 084L, 1 076s	806m
		Me₂SO		3 270W	1 730L	1 710s ᵍ,ᵏ	1 690s ʰ	1 645L ʰ,ᵍ	1 653s ᵏ	1 621s	i	1 314L, 1 298L, 1 322L	1 270L	1 229S	1 305m	i	803w
		KBr		3 270W			1 691S ʰ	1 643S ʰ		1 621s	1 428s		1 260m	1 260S, 1 250L	1 310m	1 100s, 1 083w	802s
		Solid					1 684m ʰ	1 647m ʰ		1 622L, 1 615S ⁿ, 1 610S ⁿ	1 425S ʲ	1 323m	1 257S	1 241S	1 309w	1 113W, 1 084W	807W
p-Me-C₆H₄	Et	CCl₄		3 260W		1 720s ᵍ	1 692s ʰ	1 650S ʰ,ᵍ		1 620s, 1 610S ⁿ	1 439m	1 303m, 1 293w	1 260S	1 240S, 1 220L	1 313m	1 095m, 1 083L, 1 073m	i
		CDCl₃	3 360W	3 268W		1 710L ᵍ, 1 698s ᵏ	1 690L ʰ	1 640L ʰ,ᵍ	1 653S ᵏ	1 620s, 1 605S ⁿ	1 438S	1 300w, 1 293m	1 259S	1 236S	1 314w	1 094m, 1 080s	807w
		KBr		3 270W			1 684S ʰ	1 635S ʰ		1 618S	1 438m	1 296m	1 255S		1 312m	1 100m	805m
p-Cl-C₆H₄	Et	CCl₄		3 260W		1 724m ᵉ	1 693s ʰ	1 652S ʰ, 1 647L ᵍ		1 618S	1 441m	1 289m	1 255S	1 234S	1 303M	1 095s, 1 083L, 1 072m	i
		CDCl₃	3 360W	3 268W		1 712L ᵍ, 1 698s ᵏ	1 687S ʰ	1 647L ʰ,ᵍ	1 651s ᵏ	1 616S	1 437m	1 310L, 1 282m	1 255S	1 230S	1 303s	1 094s	803w
		Me₂SO		3 250W	1 730L	1 708s ᵍ,ᵏ	1 691m ʰ	1 645L ʰ,ᵍ	1 652s ᵏ	1 614S	i	1 312L, 1 285m	1 254S	1 239S	1 304m	1 078m	803w
		KBr		3 260W			1 680S ʰ	1 635S ʰ			1 436s	1 317m, 1 286m	1 255S		1 299s	1 091s	808m
p-NO₂-C₆H₄	Et	CCl₄		3 260W		1 728s ᵍ	1 695s ʰ	1 656s ʰ,ᵍ		1 623s, 1 589S ⁿ	1 450m	1 310L	1 255S ʲ	1 242S ʲ, 1 230L	1 293s	1 094m, 1 083L, 1 073m	i
		CDCl₃	3 355L	3 268W		1 718L ᵍ, 1 708s ᵏ	1 691s ʰ	1 645L ʰ,ᵍ	1 657s ᵏ	1 626s, 1 589S ⁿ	1 448w	1 310L	1 256S	1 241S, 1 230L	1 294s	1 094m	805w
		Me₂SO		3 265W	1 735L	1 710s ᵍ,ᵏ	1 694s ʰ	1 659s ʰ	1 659s ᵏ	1 623s, 1 586S ⁿ	i	i	1 256S	1 234S, 1 210L	1 296s	1 078M	i
		KBr		3 270W			1 688s ʰ	1 641s ʰ		1 623s, 1 580S ⁿ	1 452m		1 260S	1 248S	1 303w	1 100m	809m

ᵃ Large contribution of ν(C=N). ᵇ Mixed vibration with contribution of ν(=C–C), ν(C–O), and δ(NH). ᶜ Also contribution of ν(=C–C). ᵈ Probably, non-chelated NH group. ᵉ Tentatively assigned to a small concentration of the imino-form (III). ᶠ Abbreviations: as in Table 1. ᵍ Assigned to rotamer (IVa). ʰ Assigned to rotamer (IVb). ⁱ Obscured by the solvent. ʲ Remarkably strong. ᵏ Assigned to rotamer (IVd). ˡ In (CD₃)₂SO. ⁿ Large contribution of δ(NH) and ring ν(C=C). See text.

TABLE 3

^{1}H N.m.r. chemical shifts and multiplicities [a,b] for compounds $R^1NHCH=C(CO_2R^2)_2$ (J/Hz in parentheses)

R^1	R^2	Solvent	=CH	NH	R^1	R^2
H	Me	CDCl$_3$–[^{2}H$_6$]Me$_2$SO	~8.1dd (8.0, 15)	~8.5br	~8.5br	3.65, 3.75
H ^{c}	Et	CDCl$_3$	8.10dd (8.5, 14.5)	8.5br ^{d}	7.3br ^{c}	1.34t (7.1), 1.29t (7.1), 4.16q, 4.26q
CH$_2$Ph	Et	CDCl$_3$	8.08d (13.5)	9.37br	4.49d (5.0), 7.33	1.28t (7.0), 1.32t (7.0), 4.22q, 1.25q
		[^{2}H$_6$]Me$_2$SO	8.13d (14.0)	9.35br, dq (14.0, 5.5)	4.58d (5.5), 7.35	1.20br,t (6.5), 4.09q (7.0), 4.15q (7.0)
Et	Et	None	8.04d (14.3)	9.17br, dt (14.3, 6.1)	1.24t (6.7), 3.40dq (6.1, 6.7)	1.24t (6.7), 4.14q, 4.18q
		CDCl$_3$	8.00d (14.0)	9.15br,dt (14.0, 7.0)	1.20t (6.9), 3.42dq (6.9, 7.0)	1.26t (7.0), 4.07q (6.90), 4.12 (6.90)
		[^{2}H$_6$]Me$_2$SO	7.95d (14.5)	9.10br,dt (14.5, 7.0)	1.20t (6.8), 3.38dq (6.8, 7.0)	1.20br,t (7), 4.04q (7.0), 4.10 (7.0)
Bu^n	Et	None	8.02d (14.0)	9.17br,dt (14.0, 5.7)	0.90m, 1.4m, 3.38dt (5.7, 5.3)	1.22t (7.0), 1.24t (7.0), 4.09q, 4.13q
		CDCl$_3$	7.99d (14.1)	9.17br,m	0.94m, 1.2m, 3.38dt (6.0, 6.3)	1.23t (6.8), 1.23t (6.8), 4.12q, 4.15q
		[^{2}H$_6$]Me$_2$SO	7.95d (14.1)	9.15br,m	0.88m, 1.3m, 0.35dt (6.0, 6.3)	1.18t (6.7), 1.20t (6.7), 3.99q, 4.03q
cyclo-C$_6$H$_{11}$	Et	CDCl$_3$	8.03d (14.3)	9.20br	1.2—2.2m, 3.2br,m	1.30t (7.1), 1.35t (7.1), 4.19q, 4.25q
Bu^n	Me	CDCl$_3$	8.05d (13.7)	9.25br,dt (13.7, 5.4)	0.96m, 1.4m, 3.35dt (5.4, 7.0)	3.69, 3.76
Ph	Et	CDCl$_3$	8.43d (13.4)	11.09br,d (13.4)	7.20m	1.29t (7.2), 1.35t (7.2), 4.20q, 4.28q
p-MeC$_6$H$_4$	Et	CDCl$_3$	8.45d (14.0)	11.04br,d (14.0)	2.30 7.08m	1.31t (7.1), 1.36t (7.1), 4.20q, 4.28q
p-ClC$_6$H$_4$	Et	CDCl$_3$	8.41d (13.5)	10.97br,d (13.5)	7.04d, 7.30d (8.5)	1.31t (7.0), 1.36t (7.0), 4.24q, 4.31q
p-O$_2$NC$_6$H$_4$	Et	CDCl$_3$	8.45d (13.4)	11.24br,d (13.4)	7.15d, 8.15d (8.5)	1.34t (7.2), 1.38t (7.2), 4.25q, 4.29q

^{a} At 60 MHz, referred to internal tetramethylsilane. ^{b} Abbreviations: br, broad; d, doublet; dd, double doublet; dq, double quartet; dt, double triplet; m, multiplet; q, quartet; t, triplet. The absence of any indication implies that a singlet was observed. ^{c} H$_\alpha$ (see text). ^{d} H$_\beta$ (see text).

This signal partly overlapped a double doublet ($J_{:CH,H\alpha}$ 7.5, $J_{:CH,H\beta}$ 15.0 Hz) at δ 8.10 due to the olefinic proton. In the dimethyl ester (IV; R^1 = H, R^2 = CH$_3$) the two amino-protons appeared as a single broad bump centred at δ 8.5, also overlapping the olefinic multiplet. Upon treatment with deuterium oxide there was a slow exchange of the amino-hydrogen(s) by deuterium as revealed by the disappearance of the NH signal(s) and the collapse of the :CH multiplet to a singlet. The appearance of this part of the spectra was almost identical with the absorption of the R^1NH$^-$CH= grouping of the (Z)-form (VII; R = H or alkyl) of 3-amino-2-cyanoacrylic esters,[4d,14] compounds for which both the configuration and the presence of a hydrogen bond have been established. The two different alkoxycarbonyl groups gave distinct signals. All these data are consistent with the existence of the compounds under study as one of the four chelated rotamers (IVa—d) or as mixtures of all, or some of them, in rapid equilibrium. No signals which could be assigned to the imino-form (III) were detected.

Confirming previous observations,[9,11] the i.r. absorptions of compounds (IV; R^1 = H, alkyl, aryl) were rather complex. The N-alkyl derivatives had, when examined in solutions of non-polar solvents, up to three weak bands in the 3 500—3 200 cm^{-1} region which are considered to arise from vibrations involving the NH group. Of these bands, the one at ca. 3 270 cm^{-1} was not affected by dilution or changes in temperature and is assigned to the stretching vibration of the amino-group intramolecularly bonded to the carbonyl group in the rotational isomers (IVa and b). This band usually had a shoulder at ca. 3 300 cm^{-1} which is considered to be a combination of the ν(C=O) band at ca. 1 650 cm^{-1} and the strong vibration at ca. 1 610 cm^{-1} due to the C=C–NH grouping (see below), reinforced by Fermi resonance with the ν(N–H) band. The third band in this region appeared at ca. 3 200 cm^{-1} and is considered to be the first overtone of the band at ca. 1 610 cm^{-1}, also reinforced by Fermi resonance with the ν(N–H) band. On N-deuteriation these three absorptions slowly disappeared as a single, usually asymmetric new band appeared at 2 432—2 410 cm^{-1}; this band is assigned as the ν(N–D) vibration of the N-deuteriated derivatives of conformers (IVa and b). Exceptionally, two bands at 2 448 and 2 410 cm^{-1} were observed in the N-deuteriated derivative of (IV; R^1 = R^2 = Et), but we assume that the second band in this compound, and probably the asymmetry in the others, is due to the first overtone of the band at ca. 1 230 cm^{-1} reinforced by Fermi resonance

Compound					
R^1	R^2	R^3	Solvent	ν/cm^{-1}	Reference
H	Me	D	CCl_4	1 584S [b]	4c
H	Me	Me	CCl_4	1 561S	4b
CN	H	D	$CHCl_3$	1 590S	14
CN	H	Et	CCl_4	1 592S	4e
CO_2Et	H	D	CCl_4	1 570S	c
CO_2Et	H	Et	CCl_4	1 570S	c

[a] Coupled with $\nu(C-N)$.   [b] Abbreviation: S, very strong.
[c] This paper.

with the neighbouring $\nu(N-D)$ band rather than to rotational isomerism. This pattern of NH(D) absorption is very similar to those observed in the chelated (Z)-forms of 3-alkylaminocrotonic [4b] (VIII; R = alkyl) and 3-alkylamino-2-cyanoacrylic [4f] (VIIa; R = alkyl) esters.

The similarities between the NH(D) absorptions of the N-aryl derivatives of compounds (IV) and (VIIa) [4f] are still closer: for example, a carbon tetrachloride solution of the anilino-derivative (IV; R^1 = Ph, R^2 = Et) showed bands at 3 268, 3 215, and 3 163 cm^{-1} which, upon deuteriation, were changed into a band at 2 408 cm^{-1} with a shoulder at 2 360 cm^{-1}. By analogy with the frequency of the $\nu(N-H)$ band of the N-alkyl derivatives and because it obeys better the $\nu(N-H){:}\nu(N-D)$ relationship, the band at the highest frequency is assigned as the stretching vibration of the chelated amino-group while the other two are considered to be combinations of the C=C-NH band at 1 622 cm^{-1} with each of the two benzene bands at 1 602 and 1 588 cm^{-1} which also have a $\delta(N-H)$ component. This behaviour is almost identical to that observed in compound (VIIa; R = Ph).[4f]

In very dilute (10^{-3}M) solutions of non-polar solvents compounds (IV) with a primary amino-group had weak bands at ca. 3 510 and 3 315 cm^{-1} assigned as the $\nu(N-H)$ of the free amino-group and the amino-group intramolecularly bonded to carbonyl, respectively, in rotamers (IVa and b); these two bands were accompanied by a band at ca. 3 240 cm^{-1}, which, as in the N-substituted derivatives, is the first overtone of the band at 1 624 cm^{-1}, and a very weak, sharp band at ca. 3 400 cm^{-1}, the origin of which is not completely clear. On increasing the concentration, a broader band appeared at ca. 3 400 cm^{-1} whose intensity increased at the expense of the 3 510 cm^{-1} band and is attributed to the intramolecularly associated N-H group All these bands were sensitive to isotopic exchange. The same pattern of absorption has been observed in the chelated (Z)-forms of primary 3-aminoacrotonic [4c] (VIII; R = H) and 3-amino-2-cyanoacrylic [14] (VIIa; R = H) esters. This interpretation is at variance with that given [11] by Smith and Taylor who assigned the bands at 3 510 and 3 400 cm^{-1} (observed by these authors in fairly concentrated solutions) as $\nu(N-H)$ of the free amino-group in rotamers (IVb; R^1 = H) and (IVa; R^1 = H), respectively, and the bands at 3 310 and 3 240 cm^{-1} as the same mode of the intramolecularly bonded amino-group in the

same rotamers. We consider that this view is untenable because it does not take into account the effects of dilution on the bands at 3 510 and 3 400 cm^{-1} and could not be applied to explain the almost identical absorptions of the related 3-aminoacrotonic and 3-amino-2-cyanoacrylic esters.

The effects due to rotational isomerism appeared more clearly in the 1 750—1 500 cm^{-1} region. Compounds (IV; R^1 = alkyl) had, when examined in solutions of non-polar solvents, five strong bands in this range. Of these bands, the one at the lowest frequency (ca. 1 610 cm^{-1} is assigned as a mixed vibration involving mainly the $\nu(C=C)$ and the $\delta(N-H)$ modes on the basis of its disappearance upon N-deuteriation and its analogy by position and intensity to the deuterium-exchange sensitive band observed in the chelated (Z)-form of related esters (VIIa; R = alkyl and (VIII; R = alkyl).[4b,e] This band was replaced upon isotopic exchange by a strong band at ca. 1 570 cm^{-1} due mainly to the $\nu(C=C) + \nu(C-N)$ vibration of the N-deuteriated species. The four bands at higher frequencies, the position of which remained unaffected upon deuteriation, are considered to arise from vibrations with a predominant $\nu(C=O)$ contribution and not strongly coupled with the $\delta(N-H)$ vibration. An additional band, also with a contribution from the $\delta(N-H)$ vibration, which might have been expected in this range, was absent, but it should be kept in mind that the absorption due to this mixed mode has medium to weak intensity in the (E)-form of 3-alkylaminocrotonates, is weak in the corresponding (Z)-isomers (VIII; R = alkyl),[4b] and is weaker still or absent in cyanoacrylates (VIIa; R = alkyl).[4e]

The shape of the carbonyl absorption was highly characteristic: it consisted of two pairs of bands, one of very close components at ca. 1 650 cm^{-1} and a second one, of better resolved components, lying between 1 730 and 1 684 cm^{-1}. The frequencies of the bands around 1 650 cm^{-1} did not change much on varying the polarity of the solvent or on dilution and are consequently assigned as stretchings of carbonyl groups intramolecularly bonded to the amino-group. The splitting is attributed, in agreement with Smith and Taylor,[11] to the presence of rotational isomers (IVa and b); the former, a stronger chelate because of steric compression between the OR^2 group and the bonded CO_2R^2, gives rise to the band at the lowest frequency (ca. 1 645 cm^{-1}).[11] The positions of the two bands in the range 1 730—1 685 cm^{-1} were more affected by the polarity of the solvent and by dilution and are ascribed to $\nu(C=O)$ of the free ester group in two different conformations. By analogy with other compounds of type (I),[3-5] and also in accord with Smith and Taylor,[11] the band at the highest frequency is attributed to conformer (IVa) with the C=O and the C=C in an s-cis (or quasi-s-cis) disposition, and the band at ca. 1 685 cm^{-1} to conformer (IVb) with these groups s-trans (or quasi-s-trans).* Variable-temperature measurements performed on some of the compounds also showed a slight temperature dependence

* These rotamers are further called s-cis and s-trans.

of the relative intensities of these bands, the absorbance ratio 1 718 : 1 689 increasing with temperature. This ratio also increased upon N-deuteriation and on dilution, thus indicating that all these processes were accompanied by readjustments in the conformational equilibrium with an increase of the concentration of the more crowded conformer (IVa).

Compounds (IV; R^1 = H) showed, in very dilute solutions of non-polar solvents, the same pattern of carbonyl absorption as the N-alkyl derivatives, and additional bands at ca. 1 624 (very strong in the i.r.; medium in Raman) and 1 520 cm^{-1} (weak in the i.r.; strong in Raman) due to mixed vibrations of the C=C–NH$_2$ group. Of these, the one at ca. 1 620 cm^{-1} moved to higher frequencies when the polarity of the solvent was increased; it has therefore predominant δ(NH$_2$) character. On increasing the concentration, two new weak absorptions appeared at ca. 1 640 and 1 575 cm^{-1} due to associated species. In the per-N-deuteriated derivatives these bands were replaced by a single band at 1 570 cm^{-1} assigned to a mixed vibration with a major ν(C=C) contribution.

Smith and Taylor [11] concluded that ethyl 3-amino-2-ethoxycarbonylacrylate (IV; R^1 = H, R^2 = Et) is fully planar while its N-substituted derivatives (VIa and b), and by extension compounds (IV; R $\neq$ H), have the CO$_2$Et trans to the NH twisted out of the plane of C=C and the chelated C=O groups. Molecular models reveal that, although there is some hindrance between the two CO$_2$R groups, no extra steric interaction is likely to be introduced by replacement of the free amino-hydrogen by alkyl.* Two properties were considered by these authors to be characteristic, and diagnostic, of the full planarity in these and related molecules. The first is a sharp drop ($\Delta\nu$ 40—80 cm^{-1}) in the frequency and intensity of the ν(C=C) band when compared with a related structure [for example, ethyl 3-amino-crotonate (VIII; R = H) for compounds (IV)] having a single electron-acceptor group. We believe that this criterion is unreliable on the following grounds.

(i) No real ν(C=C) frequencies are actually compared. It is generally agreed [3,5,11] that the stretching and deformation vibrations of the functional groups in system (I; R^1 = H, R^2 = H, or alkyl) are coupled, and the ν(C=C) component which any of these mixed vibrations may have for a particular class of compounds will be dependent on the nature of substituents R^2—R^5. It cannot be said with certainty that the mixed vibration at 1 564 cm^{-1} of reference compound (VIII; R = H) has the same weight for ν(C=C) as the vibration at 1 520 cm^{-1} of compound (IV; R^1 = H, R^2 = Et), although both bands may be predominantly ν(C=C).

* In P. J. Taylor's view (personal communication), cumulative in-plane bond angle deformations, induced by electronic repulsions between the C–O and C=O bonds, would bend the NHR group back towards the olefinic hydrogen giving rise to steric hindrance when R $\neq$ H. We consider that, although this effect may be operative and even contribute to maintaining the planarity, it is unlikely that its magnitude is large enough as to produce any steric interaction between =C–H and the N-substituent.

(ii) The (Z)-form of ethyl 3-amino-2-cyanoacrylate (VIIa; R = H) is an obviously planar structure which shows [14] (in chloroform) the ν(C=O) band at 1 690 cm^{-1} and bands at 1 640 (strong) and 1 535 cm^{-1} (weak) due to the C=C–NH$_2$ grouping, the latter having most likely a predominant ν(C=C) component. The low intensity and frequency of this band, when compared with (VIII; R = H) would be, according to Smith and Taylor, a reflection of the strong electron demand imposed by the two planar electron-acceptor groups on the enamine. On the other band, its N-monosubstituted derivatives (VII; R^1 = alkyl or aryl), which must also be planar as the replacement of one amino-hydrogen by alkyl [as indicated before for compounds (IV)] does not introduce any significant steric hindrance, show [4f] a strong band, considered to be mainly ν(C=C) + δ(N–H), at 1 625 cm^{-1} (see above). Here, the electron-demand of the planar CN and CO$_2$Et groups is not reflected in the frequency and intensity of the band which is supposed to have mainly ν(C=C) character. Moreover, the almost perfect parallelism between the absorptions of compounds (VII; R^1 = H, alkyl, aryl) and (IV; R^1 = H, alkyl, aryl) strongly suggest that they are all planar or nearly planar.†

Based on the above arguments, it could be considered that the coupled ν(C=C) + ν(C–N) frequencies of enaminones, measured for their per-N-deuteriated derivatives, could be used more advantageously than the more complex mixing ν(C=C) + δ(N–H) [or δ(NH$_2$)] + ν(C–N). Actually, the mixed ν(C=C) + ν(C–N) vibrations of the N-deuteriated enaminones (I) are often assigned [4,5,11] as ν(C=C) (see also above). The frequencies of this band for some typical representatives of the enamino esters under discussion have been set up for comparison in Table 4. It can be seen that there are no significant differences between them and indeed that the last two compounds, one planar and the other twisted according to Smith and Taylor, have the same value.

The second property considered [11] to be characteristic of planar enaminones having two electron-acceptor groups and one electron-donor group [as (II)] is the very weak, or absent, Raman ν(C=C). Here again comparison of mixed frequencies could lead to erroneous conclusions, and perhaps a revision of this criterion using ν(C=C) + ν(C–N) of the N-deuteriated derivatives, as for the i.r. frequencies, is required. Moreover, our Raman results (Table 1) for primary amino-compounds (IV; R^1 = H, R^2 = Et) show that even this mixed band, appearing at 1 525 cm^{-1} in solutions and at 1 505 cm^{-1} in the solid state, is medium or even strong; similarly, the fully planar compounds (VII; R = alkyl, aryl) exhibit weak to medium C=C–NHR absorptions [for instance, medium to strong, polarized at 1 626 cm^{-1} for chloroform solutions of (VIIa; R = CH$_2$Ph)].[14] The generality of this criterion is, in our view, doubtful.

The above considerations do not imply that compounds

† P. J. Taylor, personal communication, has expressed doubts about the generality of this criterion on the basis of its failure when applied to 3-amino-2-cyanoacrylic esters.

(IV) are planar; most likely some deviations from planarity occur, but the way and extent to which this takes place with the minimum cost of conjugation cannot be ascertained on the basis of the available data, and probably there is not much difference in this respect between the primary and secondary amino-compounds.

The intramolecularly bonded ester groups of compounds (IV; R^1 = alkyl) have lower $\nu(C=O)$ frequencies than the chelated (Z)-forms of 3-alkylaminoacrylic esters (1 665—1 660 cm^{-1}),[15] while the free ester group absorbs at slightly higher frequencies than the (E)-form of the same compounds $(ca.$ 1 690 cm^{-1}).[15] The introduction of the electron-attracting CO_2R at the α-position of a 3-alkylaminoacrylate would be expected [7a,11] to raise the $\nu(C=O)$ frequencies of both the (Z)- and (E)-forms of these compounds, and a similar effect for an α-CN group has been observed.[4e] The deviation found in the compounds under study is considered to be due to vibrational coupling inside the β-dicarbonyl system: although the free and bonded ester C=O groups are not subject to identical force fields, their stretching frequencies must be fairly similar and some degree of mixing will occur; this would result in a low frequency vibration with a strong contribution from the chelated $\nu(C=O)$ mode, and a high frequency vibration mainly due to the free $\nu(C=O)$. The small contribution of the chelated carbonyl stretching to the latter mixed mode is the explanation of its low frequency compared with the value observed [4e] for the (E)-form of 3-alkylamino-2-cyanoacrylates (VIIb; R = alkyl). The differences between the i.r. and Raman intensity patterns of these bands are in agreement with this interpretation: while the pair of bands at 1 650 cm^{-1} was stronger than the pair at $ca.$ 1 700 cm^{-1} in the i.r., the reverse relationship was observed in the Raman as expected if these vibrations were the mixed out-of-phase and in-phase modes, respectively; moreover, some polarized Raman measurements performed on compounds (IV; R^1 = CH_2Ph, H, R^2 = Et) in carbon tetrachloride solution showed that the band at 1 645 cm^{-1} was depolarized while the bands at 1 715 and 1 690 cm^{-1} were partly polarized. Enough coplanarity is retained to make the coupling possible and more apparent than in other malonic ester derivatives [7] where no strong restrictions to rotation exist.

The neat splitting of both the free and chelated ester bands of compounds (IV) contrasts sharply with what is usually observed in acyclic $\alpha\beta$-unsaturated esters [16] and their β-amino-derivatives [4b,e] where the s-cis and s-trans rotamers give rise to a single, broad (or asymmetric) band, and indeed Bowles et al.[16] concluded that the frequency difference between the two forms would be rather small (3—19 cm^{-1}) and the bands would not be resolved unless they were exceptionally sharp. We believe that the explanation for the greater separation (up to 32 cm^{-1}) in compounds (IV) also lies in the coupling between the carbonyls. As suggested,[11] the mutual alignment of the two groups would be expected to affect the extent of mixing and, by comparison with related

compounds of known conformation,[17] this would be larger for (IVa) than for (IVb). The superimposition of this effect on that due to rotational isomerism [in fact due to differences of coupling between the free $\nu(C=O)$ and the $\nu(C=C)$ [9b] in (IVa and b)] results in a still larger difference between the frequencies. Also, the chelated $\nu(C=O)$ of (IVa) would appear at lower frequency than that of (IVb) thus reinforcing the effect due to steric compression alluded to above.

Compounds (IV; R^1 = aryl) lacked splitting of the absorption at $ca.$ 1 650 cm^{-1} and showed instead a strong band, in most cases with a shoulder on its low-frequency side. On N-deuteriation there were the changes in the intensity ratios of the C=O bands associated with readjustments of the conformational equilibria; for example, in the anilino-derivative (IV; R^1 = Ph, R^2 = Et), the intensity ratio 1 721 : 1 692 increased as the shoulder at 1 645 cm^{-1} became a well resolved band. Exchange also affected the C=C–NH band at 1 622 cm^{-1} and the aromatic bands at 1 602 and 1 588 cm^{-1}, thus indicating the mixed character of these vibrations.

Some solvent effects on the NH(ND) and the double bond absorptions can also be associated with changes in the conformational equilibria. In chloroform solutions the bonded $\nu(N-H)$ band shifted slightly to higher frequency and the complexity of the carbonyl absorption increased: the high frequency free $\nu(C=O)$ band moved to lower frequency $(ca.$ 1 710 cm^{-1}) and weakened to become a shoulder of a stronger absorption having components at $ca.$ 1 695 (also a shoulder) and 1 680 cm^{-1}; concomitantly, the bonded $\nu(C=O)$ band at the lowest frequency also weakened and moved to still lower frequency $(ca.$ 1 640 cm^{-1}) as a strong absorption, with a maximum at $ca.$ 1 655 cm^{-1} and a shoulder at $ca.$ 1 650 cm^{-1}, developed. These changes could be due to an increase of the concentration of rotamer (IVb), which would give rise to the free s-trans $\nu(C=O)$ at $ca.$ 1 680 cm^{-1} and the bonded s-cis $\nu(C=O)$ at $ca.$ 1 650 cm^{-1}, and the participation in the equilibrium of another rotamer with the bonded carbonyl s-trans [most probably (IVd)] responsible for the new bands at $ca.$ 1 695 [free s-cis $\nu(C=O)$] and 1 655 cm^{-1} [bonded s-trans $\nu(C=O)$] and the shift of the $\nu(N-H)$ band; chloroform would stabilize these more polar conformations by dipolar interaction and by formation of intermolecular hydrogen bonds with the s-trans carbonyls, thus compensating for the loss of chelation energy in (IVd). Rotamer (IVc), less stable because of the parallel dipolar interaction between the carbonyls, is less likely to be present in the equilibrium. Similar observations were made for ethanol solutions of (IV; R^1 = CH_2Ph, R^2 = Et): the ester group trans to NH gave rise to three bands at 1 722 [s-cis in (IVa)], 1 692 [s-cis in (IVd)], and 1 677 cm^{-1} [very strong, solvent bonded s-trans in (IVb)], whereas the ester group intramolecularly bonded to NH gave a very strong band at 1 661 cm^{-1} mainly due to the solvated rotamer (IVd), with shoulders at lower frequencies attributable to (IVa and b). In the case of other polar solvents such as dimethyl sulphoxide, the frequency shifts and intensity

changes observed could also be explained by the existence of a solvated form of (IVd).

The spectra of the N-alkyl derivatives as neat liquids were also consistent with their being mixtures of conformers (IVa and b). The same applies to (IV; $R^1 =$ Bu^n, $R^2 = Et$) and (IV; $R^1 = CH_2Ph$, $R^2 = Et$) in the molten state; on resolidification of the sample, the spectrum of the latter substance simplified considerably and the positions of the bands indicated a strong predominance of conformer (IVb). The spectra of solid (IV; $R^1 = H$ or aryl) dispersed in KBr were also much simpler that the spectra in solution and showed only bands attributable to (IVb). This conformation seems to be the most stable in the crystal lattices of compounds (IV).

The region below $1\,450$ cm^{-1} also appeared very complex and most of the bands were affected by temperature, solvent polarity, and N-deuteriation, these facts pointing again to the presence of different mixtures of rotamers and the occurrence of vibrational couplings. One or two bands of variable intensity appearing in the $1\,450$—$1\,420$ cm^{-1} zone in the i.r. and the very strong, polarized Raman band in the same range, are considered to arise from a mixed vibration with a large contribution from $\nu(=C-N)$, its frequency being raised by electron delocalization. This assignation is supported by bond-length data [18] for the di-N-substituted derivative (II; $R^1 = R^2 = R^3 = Me$) which indicate extensive electron-delocalization.

In conclusion, the results show the strong tendency of 2-alkoxycarbonyl-3-aminoacrylic esters with primary and secondary amino-groups to adopt the enamino-ester form, the stability of which can be accounted for by conjugation and formation of a very strong chelate. In spite of the distortion which might occur due to hindrance between the CO_2R groups, enough planarity is retained to allow strong conjugation which affects the whole of the enamino-diester system. As a consequence of this, fairly high energy barriers to rotation develop in the nearly planar molecules giving rise to easily detectable rotational isomerism. The increased conjugation and the near-planarity of the two C=O, the C=C, and the N-H moieties, as well as the benzene ring in the N-aryl derivatives, allow couplings among these groups in such a way that the conjugated system could be better regarded as a vibrating unity rather than as an ensemble of independent oscillators.

Work on the i.r. spectra and conformations of other β-amino-αβ-unsaturated diesters and diketones is continuing and will be reported in due course.

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