

Infrared and Nuclear Magnetic Resonance Absorption and Isomerism of 3-Aminocrotonic Esters. Part II.¹

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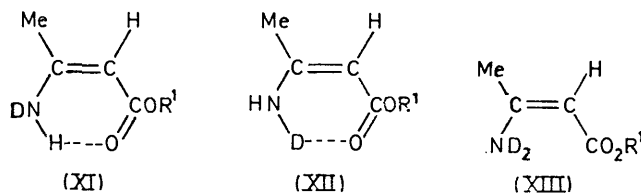
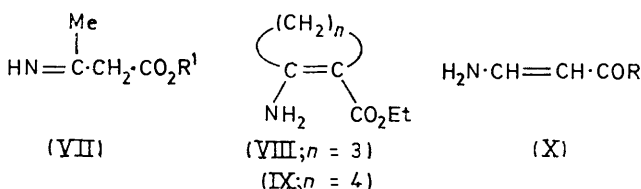
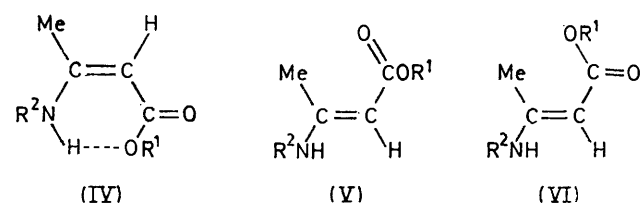
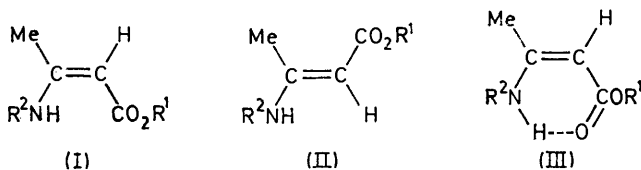
The i.r. and ¹H n.m.r. spectra of 3-aminocrotonic esters with primary amino-groups indicate that these substances exist, in the liquid state and in solution, almost exclusively as the isomers with the chelated (*Z*)-configuration. Some complexities of the i.r. spectra are interpreted in terms of the existence of conformational isomers arising from restriction of rotation around the C-CO₂R single bond. The strength of the hydrogen bond in these compounds is less than that in 3-(alkylamino)crotonates. The i.r. spectra of *N*-monodeuteriated 3-aminocrotonates also reveal the existence of conformers arising from restriction of rotation around the C-N single bond. The spectra of the *N*-dideuteriated derivatives show the existence of strong mechanical couplings which affect mainly the ν(C=C), ν(C-N), and δ(NH₂) vibration modes. Some very weak bands observed in the ν(N-H) region in certain solvents are attributed to a small concentration of non-chelated molecules.

3-(ALKYLAMINO)CROTONIC esters exist^{1,2} either in the liquid state or in solution as equilibrium mixtures of the isomers with the (*Z*)- and (*E*)-configurations (I) and (II). Each isomeric form has characteristic, easily distinguishable spectroscopic (¹H n.m.r., i.r.) properties which can be used in assigning compounds of this type to their correct geometric configuration. The position of the equilibrium is solvent-dependent, and the energy difference between the isomers varies from *ca.* 1.75 kcal mol⁻¹ in non-polar solvents to *ca.* 0.20 kcal mol⁻¹ in dimethyl sulphoxide, the intramolecularly bonded (*Z*)-form (III) and/or (IV) being the most stable. The i.r. data also suggest that rotational isomerism involving the C-N and C-CO₂R single bonds also occurs but that the energy barriers between the isomers are very low. The i.r. spectra of the *N*-deuteriated derivatives indicate that there exist mechanical couplings which affect mainly the ν(C=C), ν(C-N), and δ(N-H) vibrations of the mesomeric HN=C-C=O system.

When 3-aminocrotonic esters bear an electron-withdrawing substituent, such as the aryl or glycosyl groups, on the nitrogen,^{3,4} the chelated (*Z*)-form (III) and/or (IV) is the only one observed even in polar solvents. Dudek⁵ found that linear relationships exist between the chemical shift of the amino-proton and the ν(N-H) and ν(C=O) frequencies of the chelated (*Z*)-form of 3-aminocrotonates and other β-amino-αβ-unsaturated esters and ketones.

In order to get further knowledge of the influence of structure on the isomerism of 3-aminocrotonic esters, it seemed of interest to study the i.r. spectra of compounds of this structure with a primary amino-group. Owing to the partial equalization of single and double bonds produced by electron delocalization, geometrical and rotational isomers (III)–(VI) (R² = H) are possible in these substances in addition to the tautomeric imino-ester form (VII); the existence of hindered rotation around the C-N bond can also be expected. There are data on the i.r.^{5,6} and Raman⁷ spectra of ethyl 3-

aminocrotonate. The i.r. spectrum indicates that the substance exists in the intramolecularly bonded (*Z*)-form (III) and/or (IV) (R² = H); on the other hand, the Raman spectrum shows complexities in the double-bond



region which were explained by assuming the existence of the chelated (*Z*)-form (III) and/or (IV) (R² = H) in the presence of an isomer tentatively considered to be the imino-form (VII). The ¹H n.m.r. spectra of methyl and

¹ Part I, A. Gómez Sánchez, A. M. Valle, and J. Bellanato, *J. Chem. Soc. (B)*, 1971, 2330.

² A. Gómez Sánchez, M. Tena Aldave, and U. Scheidegger, *J. Chem. Soc. (C)*, 1968, 2570.

³ W. Werner, *Tetrahedron*, 1971, **27**, 1755.

⁴ A. Gómez Sánchez, M. Tena Aldave, and U. Scheidegger, *Carbohydrate Res.*, 1969, **9**, 335.

⁵ G. O. Dudek, *J. Org. Chem.*, 1965, **30**, 548.

⁶ (a) B. Witkop, *J. Amer. Chem. Soc.*, 1956, **78**, 2873; (b) F. Korte and K. Trautner, *Chem. Ber.*, 1962, **95**, 295; (c) G. DeStevens, B. Smolinski, and L. Dorfman, *J. Org. Chem.*, 1964, **29**, 1115.

⁷ K. W. F. Kohlrausch and A. Pongratz, *Ber.*, 1934, **77**, 976.

ethyl 3-aminocrotonate have been reported^{2,5,8,9} and interpreted in terms of the chelated (*Z*)-isomer (III) and/or (IV) ($R^2 = H$) only. The existence of the non-equivalent amino-groups was deduced from the presence in the spectrum of two amino-signals; of these the one which appears at lower field (δ 7.5—8.0 p.p.m.) is ascribed to the intramolecularly bonded proton. Data for the i.r. and 1H n.m.r. spectra of the related cyclic compounds (VIII) and (IX) with a fixed (*Z*)-configuration have been published¹⁰ and taken as evidence of the existence in these substances, and, by extension, in 3-aminocrotonates, of a free amino-group. The i.r. spectra of alkyl β -aminovinyl ketones (X) have shown that these substances are mixtures of the chelated *cis*-form and the *trans*-form, and that extensive mechanical couplings exist in these molecules which affect mainly the $\nu(C=C)$, $\nu(C-N)$, and $\delta(NH_2)$ vibrations.¹¹

In this paper we discuss the results of a reinvestigation of the i.r. spectra of several 3-aminocrotonates and those of ethyl 2-aminocyclohexene-1-carboxylate (IX). Measurements on their *N*-deuteriated derivatives have also been made to reveal the possible hindered rotation around the C-N bond and the mechanical couplings of group vibrations inside the enamino-ester system.

EXPERIMENTAL

I.r. and 1H n.m.r. spectra were recorded as indicated in refs. 1 and 2. The following compounds were prepared by the published procedures, their physical properties being in agreement with those reported: methyl 3-aminocrotonate,¹² ethyl 3-aminocrotonate,¹³ and ethyl 2-aminocyclohexene-1-carboxylate.^{6a}

New 3-aminocrotonates were prepared from the appropriate acetoacetate and ammonia by conventional methods:^{12,13} *isopropyl 3-aminocrotonate*, m.p. 26—27 °C (from light petroleum) (Found: C, 59.1; H, 9.3; N, 9.6. $C_7H_{13}NO_2$ requires C, 58.7; H, 9.1; N, 9.8%); *t-butyl 3-aminocrotonate*, m.p. 39—40 °C (from light petroleum) (Found: C, 61.2; H, 9.7; N, 9.1. $C_8H_{15}NO_2$ requires C, 61.1; H, 9.6; N, 8.9%).

All substances were distilled or recrystallized before use, and their purity was checked by g.l.c. *N*-Deuteriations were performed as indicated in Part I.¹

RESULTS AND DISCUSSION

Data for the i.r. spectra of 3-aminocrotonic esters and their corresponding assignments are in Table 1. For comparison, data for ethyl 2-aminocyclohexene-1-carboxylate (IX) are included. The 1H n.m.r. spectra of 3-aminocrotonic esters are in Table 2; these complement those previously reported.^{2,5}

The i.r. and 1H n.m.r. spectra show that 3-aminocrotonic esters with primary amino-groups exist almost exclusively, either in the liquid state or in solution, in a

single isomeric form, and that no isomerization occurs on changing the temperature or the polarity of the solvent. By comparing the frequencies and chemical shifts observed with those corresponding to the (*Z*)- and (*E*)-forms of 3-(alkylamino)crotonates and with those of cyclic compound (IX) with a fixed (*Z*)-configuration, it can be concluded that the predominant isomeric form of 3-aminocrotonates has the (*Z*)-configuration (*I*; $R^2 = H$). The study of the $\nu(N-H)$ region in different solvents and at different concentrations showed also the presence of an intramolecular hydrogen bond. All the compounds studied presented two or three main bands in this region, according to the conditions. The spectra of dilute solutions in non-polar solvents showed a band above 3500 cm^{-1} , which is assigned as the $\nu(N-H)$ vibration of a free N-H group; when the concentration was increased, another band at *ca.* 3450 cm^{-1} , attributed to the intermolecularly associated N-H group, became visible. A third band, which appeared at *ca.* 3335 cm^{-1} and was almost insensitive to the changes of concentration and of polarity of the medium, is assigned to the N-H group intramolecularly bonded to the ester group. In basic solvents, such as dimethyl sulphoxide and pyridine, a band appeared at *ca.* 3400 cm^{-1} due to the N-H group intermolecularly bonded to the solvent, in addition to the chelated $\nu(N-H)$ band. On the other hand, the 1H n.m.r. spectra show two N-H signals that can be assigned to the chelated and free (or intermolecularly bonded) N-H groups.

The chelated $\nu(N-H)$ frequency of 3-aminocrotonates is *ca.* 50 cm^{-1} higher than that corresponding¹ to the (*Z*)-form of 3-(alkylamino)crotonates (III) and/or (IV); also the bonded N-H proton of the former substances resonates at higher field than that of the *N*-monosubstituted derivatives. These results indicate that 3-aminocrotonates with primary amino-groups form a weaker hydrogen bond than their *N*-monosubstituted derivatives.

On the basis of the 1H n.m.r. and i.r. spectra, Dürbeck *et al.*¹⁰ concluded that in cyclic compounds (VIII) and (IX) the amino-group is free whereas in their *N*-alkyl and *N*-aryl derivatives the amino-group is intramolecularly bonded to the ester group. This conclusion was based on the observation that the amino-group of the unsubstituted compounds gave a single, two-proton resonance signal and two stretching bands of approximately the same chemical shift and frequencies as those of the amino-group of 3-amino-5,5-dimethylcyclohex-2-enone, a compound with fixed (*E*)-configuration in which chelation is not possible. Although the authors emphasized the mesomeric character and the planarity of these unsaturated systems, they did not seem to have realized that the two non-equivalent protons of the primary amino-group should give two distinct signals even in the absence of chelation. Exchange of sites between the two

⁸ 'High Resolution N.M.R. Spectra Catalog,' Varian Associates, Palo Alto, 1963, vol. 2, No. 442.

⁹ J. Ulrich and P. Vay, *Chim. analyt.*, 1966, **48**, 549.

¹⁰ H. W. Dürbeck and L. L. Duttka, Colloquium Spectroscopicum Internationale XVI, Heidelberg, October 1971, preprints, vol. I, p. 271, Adam Hilger, London, 1971; H. Wamhoff, H. W. Dürbeck, and P. Sohá, *Tetrahedron*, 1971, **27**, 5873.

¹¹ J. Dabrowski, *Spectrochim. Acta*, 1963, **19**, 475.

¹² P. C. Anderson and B. Staskun, *J. Org. Chem.*, 1965, **30**, 3033.

¹³ A. D. Josey and E. L. Jenner, *J. Org. Chem.*, 1962, **27**, 2466.

amino-protons produced by the partially hindered rotation of the NH₂ group around the C-N bond could cause broadening of the signals or their coalescence into a single

well as proton exchange between neighbouring molecules might also contribute to the incomplete separation and the broad nature of the signals. There can be little

TABLE I
I.r. vibrational frequencies ^a/cm⁻¹ of compounds H₂N·CMe=CH·CO₂R

R	Medium	Free ν(N-H)		Bonded		ν(C=O)	C=C-NH ₂			ν(C-O)	ν(O-R ¹)	τ(NH ₂)	γ(=C-H)
Me	C ₆ H ₁₂	3520w b, c		3447 d	3327w	1678s	1636m	1616m	1563m	1310m	1166vs	1119vw	789w
Me	CCl ₄	3513w e	3410vw f, g	3452 d	3339w 3290sh	1673s	1634m	1615s	1564s	1311m 1273w	1168vs	1122vw	e
Me	CHCl ₃	3508w e	3410vw g	3490sh h	3346w	1665s	1629m	1613s	1564s	1311m 1275w	1169s	1119vw	e
Me	EtOH			e	e	1672m 1652s		1629s	1569s	1310s 1289sh	1172vs 1164sh	e	789w
Me	Dioxan			3437w h	3333w 3295sh	1671s	sh	1623s	1571s	1290s	1167vs	e	788w
Me	Me ₂ S ^o			3400w h	3307w h 3280sh	1663s		1627s	1568s	1308m 1293m	1164vs	1143sh 1117sh	787w
Me	C ₆ H ₅ N			3402w h	3331sh 3315w h 3282sh	1667s		1627s	e	1307sh 1292m	1165vs	e	787w
Me	Molten			3455w d	3340w	1671s 1662sh	1638sh	1620s	1566s	1305sh 1286m	1167s	1116sh	787w
Et	C ₆ H ₁₂	3515w e		3447 d	3343sh 3325vw	1675s 1662sh	1632sh	1620m	1565m	1307m	1173sh 1163vs	1118vw	789w
Et	CCl ₄	3513w e	3407vw f, g	3448 d	3335w	1672s	1631sh	1619s	1567s	e	1174sh 1163vs	1119w	e
Et	CHCl ₃	3510w e	3411vw g	3490sh h	3344w	1661s	1632sh	1614s	1563s	1306m 1271m	1173sh 1167s	1117w	e
Et	Dioxan			3438w h	3332w	1666s		1624s	1571s	e	1170sh 1163s	e	788m
Et	Me ₂ SO			3400w h	3310w h 3285sh	1660s		1627s	1567s	1283m	1161s	e	787w
Et	C ₆ H ₅ N			3397w h	3320w 3310sh h 3280sh	1663s		1629s	e	1291m	1168sh 1161s	e	788w
Et	Liquid			3446m d	3338m	1668sh 1657s 1649sh		1635s	1566s	1290s	1173sh 1163s	1116vw 1112vw	788m
Pr ^l	C ₆ H ₁₂	3514w e 3500sh		3447 d	3333sh 3326w	1671vs 1659sh	1630sh	1620s	1563s	1311m 1290sh	1166vs † 1114s †		790m
Pr ^l	CCl ₄	3513w e	3423vw f, g 3405vw f, g	3455 d	3333w	1667s	1630sh	1618s	1563s	1304m 1269m	1168vs † 1113s †		e
Pr ^l	CHCl ₃	3511m e	3410vw g	3490sh h	3343w	1659s	1630sh	1616s	1563s	1303m 1274m	1173s † 1111s †		e
Pr ^l	Dioxan			3436w h	3330w	1663s		1619s	1570s	e	1166s †		789w
Pr ^l	Me ₂ SO			3403m h	3308w h	1659s		1628s	1568s	1292s	1166vs † 1114s †		788w
Pr ^l	C ₆ H ₅ N			3400m h	3320w	1661s		1628s	e	1291s	1167vs † 1113s †		788w
Pr ^l	Liquid			3444s h	3335m	1665sh 1656s		1622vs	1563vs	1287vs	1166vs † 1109vs †		788s
But ^t	C ₆ H ₁₂	3514w e		3500sh	3325vw	1670s	1638sh	1620s	1563m	1312m 1273w	1152vs	1118vw	791w
But ^t	CCl ₄	3512w e	3401vw f, g	3455 d	3331w	1667s	1641sh	1618s	1563m	1312m 1274w	1152vs	1120vw	e
But ^t	CHCl ₃	3508w e	3406vw g	3497sh h 3451sh d	3343vw	1658s		1616s	1562m 1557sh	1313m 1282w	1151vs	1118vw	e
But ^t	EtOH			e	e	1666m 1647s		1627s	1566s	1306s	1152vs		791w
But ^t	Me ₂ SO			3400w h	3307w h 3272sh	1658s		1626s	1567s	e	1149vs		788w
But ^t	C ₆ H ₅ N			3397w h	3317w	1659s		1624s	e	1297m	1149vs		788w
But ^t	Molten			3450m d	3338w	1664s 1655s		1620vs	1566s	1298s	1149vs	1113sh	790m
j	C ₆ H ₁₂	3504w e	3409vw g	3453 d	3335sh 3321w	1673s		1619s 1588sh	1539m	1282m 1254s 1248s	1212s		
j	CCl ₄	3501w e	3425vw f, g 3403vw f, g	3450 d	3326w	1668s		1616s	1538m	1282m 1255s 1243s	1211s		
j	CHCl ₃	3500w e	3405vw g		3340w	1659s		1613s	1538s	1282m 1259s 1250sh	e		
j	Dioxan			3439w h	3324w	1666s		1618s	1545m	e	1215s		
j	Me ₂ SO			3404m h	3304w h	1658s		1621s 1590sh	1544m	1278m 1253s 1247sh	1220s		
j	Molten			3450m d	3328m	1666s		1616s	1540s	1280m 1254s 1247sh	1212s		

^a Assigned to the chelated (Z)-form (III) and/or (IV) (R² = H) unless otherwise indicated. ^b Abbreviations: s, strong; m, medium; w, weak; sh, shoulder; v, very. ^c Assigned to the free N-H group. ^d Assigned to the intermolecularly bonded N-H group, increasing with concentration. ^e Obscured by the solvent. ^f Measured at dilute solutions. ^g Assigned to the symmetrical N-H stretching vibration of a non-bonded form or to the =NH group of the imino-form (VII). ^h Assigned to the N-H group associated with the solvent. ⁱ Coupled with CH₂ rocking modes. ^j Ethyl 2-aminocyclohexene-1-carboxylate.

signal. Indeed, both effects are commonly observed in the ¹H n.m.r. spectra of 3-aminocrotonates (see Table 2 and refs. 2 and 5); lowering of the temperature results, in some cases, in a slower exchange and a better resolution.¹⁴ The quadrupole coupling of the ¹⁴N nucleus as

doubt that a similar situation prevails in cyclic enamino-esters (VIII) and (IX). On the other hand, the band at ca. 3350 cm⁻¹ observed in the i.r. spectra of compounds (VIII) and (IX) has a frequency too low to be assigned as

¹⁴ P. Vay, *Compt. rend.*, 1967, C, **264**, 1617.

the symmetrical stretching vibration of a free NH_2 group; from the data by Dabrowski¹¹ for several $\alpha\beta$ -unsaturated β -amino-ketones (X) with the *trans*-configuration, the frequency ranges for the asymmetrical and symmetrical stretching vibrations of the free NH_2 group are 3540—3515 and 3450—3415 cm^{-1} (in chloroform) respectively. The large displacement to lower frequency observed in enamino-esters (VIII) and (IX) must then be due to chelation; the band at 3365 cm^{-1} observed by Dürbeck and Duttka in 3-amino-5,5-dimethylcyclohex-2-enone arises most likely from an intermolecularly associated amino-group; it is known¹¹ that *trans*- β -amino- $\alpha\beta$ -unsaturated ketones form dimers even in comparatively dilute solution, and show a band at *ca.* 3400 cm^{-1} attributed to an intermolecularly bonded form.

3-Aminocrotonates and the cyclic compound (IX) also showed two or three weak bands in the $\nu(\text{N-H})$ region which disappeared on deuteration (Table 1). Two of

at the highest frequency (1680—1650 cm^{-1}) is assigned as the $\nu(\text{C=O})$ of the chelated (*Z*)-form (III) and/or (IV) ($\text{R}^2 = \text{H}$) from considerations of its position and its displacement to lower frequency on increasing the polarity of the medium. The frequency of this band is significantly higher than that corresponding to the same vibration of (*Z*)-3-(alkylamino)crotonates; this indicates again the presence of a weaker hydrogen bond in the compounds with primary amino-group than in their *N*-substituted derivatives.

The remaining two or three bands which appeared in the double-bond region are considered to arise from skeletal vibrations of the group C=C-NH_2 . Owing to the partial equilization of double and single bonds in this system, it could be expected that the $\nu(\text{C-N})$ and $\delta(\text{NH}_2)$ frequencies would be raised and the $\nu(\text{C=C})$ frequency lowered, and, consequently, that extensive mechanical coupling occurs between them. Three mixed vibrations

TABLE 2
¹H N.m.r. data ^{a,b} for compounds $\text{H}_\alpha\text{H}_\beta\text{N}\cdot\text{CMe}=\text{CH}\cdot\text{CO}_2\text{R}$ ^c (*J*/Hz in parentheses)

R	Solvent	δCH	δCMe	NH		R
				α	β	
Me	(CD_3) ₂ SO	4.44	1.78	6.93 ^d	7.66 ^d	3.49
Et	(CD_3) ₂ SO	4.37	1.84	6.87 ^d	7.67 ^d	1.17t, 4.02q (7.1)
Pr ^t	None	4.45	1.85		6.70 ^e	1.14d, 4.95 (7.0)
Pr ^t	CDCl_3	4.46	1.86		6.54 ^e	1.18d, 4.99 ^f (7.2)
Pr ^t	(CD_3) ₂ SO	4.35	1.80	6.85 ^d	7.72 ^d	1.13d, 4.94 ^f (1.71)
Bu ^t	None	4.41	1.81		6.44 ^e	1.42
Bu ^t	CCl_4	4.34	1.82		6.40 ^e	1.42
Bu ^t	CDCl_3	4.45	1.85		6.25 ^e	1.44
Bu ^t	(CD_3) ₂ SO	4.25	1.78	6.83 ^d	7.62 ^d	1.38
Bu ^t	(CD_3) ₂ CO ^g	4.34	1.76	6.72 ^d	7.98 ^d	1.39

^a At 60 MHz unless otherwise indicated. Referred to internal tetramethylsilane. ^c NH_2 and CO_2R *cis*. ^d Broad. ^e Very broad two proton singlet. ^f Septuplet. ^g At 100 MHz.

these bands, at *ca.* 3425 and 3410 cm^{-1} , were observed in very dilute carbon tetrachloride solutions by use of 1—4 cm cells; the second one was also observed in chloroform solutions. It is likely that these bands arise from the symmetrical $\nu(\text{NH}_2)$ vibration of a free primary amino-group and/or from the $\nu(\text{N-H})$ vibration of an imino-group, and could, therefore, be associated with the presence of minute amounts of an isomer, (I) or (II) ($\text{R}^2 = \text{H}$), with the free amino-group, or the imino-ester form (VII), in equilibrium with the overwhelmingly predominant chelated (*Z*)-form (III) and/or (IV) ($\text{R}^2 = \text{H}$). It is noteworthy that the band at 3410 cm^{-1} has approximately the same frequency as the symmetrical $\nu(\text{NH}_2)$ band of *p*-aminobenzoic acid¹⁵ and ethyl *p*-aminobenzoate.¹⁶ The third weak band appeared around 3230 cm^{-1} and is considered to be an overtone of the band at *ca.* 1620 cm^{-1} (see below) reinforced by Fermi resonance with the chelated $\nu(\text{N-H})$ band at *ca.* 3335 cm^{-1} ; this absorption has not been included in Table 1.

Three or four bands were observed in the double-bond region of the spectra of 3-aminocrotonates. The band

would then result to each of which the $\nu(\text{C=C})$, $\nu(\text{C-N})$, and $\delta(\text{NH}_2)$ modes would contribute. As previously indicated, similar couplings have been observed in amides,¹⁷ thioamides,¹⁸ $\alpha\beta$ -unsaturated β -amino-ketones,¹¹ and 3-(alkylamino)crotonates.¹ Of these mixed vibrations, the one appearing at *ca.* 1620 cm^{-1} in non-polar solvents has a predominantly $\delta(\text{NH}_2)$ character, as was deduced from its displacement to higher frequency when the polarity of the solvent was increased. On the other hand, the Raman spectrum of ethyl 3-aminocrotonate shows 7 bands at 1615 and 1560 cm^{-1} which correspond with the two i.r. absorptions of approximately the same frequencies; the strong intensity of these Raman lines indicates that the double-bond stretchings make a great contribution to both of them.

As was the case with 3-(alkylamino)crotonates, more strong or medium bands were observed in several regions of the spectra of 3-aminocrotonic esters than could be expected for a single conformation of the predominant (*Z*)-form (I). The complexity of the chelated $\nu(\text{N-H})$

¹⁵ J. Bellanato, *Optica pura aplicada (Madrid)*, 1968, **1**, 73.

¹⁶ J. Bellanato, unpublished results.

¹⁷ C. N. R. Rao, 'Chemical Applications of Infrared Spectroscopy,' Academic Press, New York and London, 1963, p. 259.

¹⁸ Ref. 17, p. 300.

band in cyclohexane and, particularly, the splitting of the $\nu(\text{C}=\text{O})$ of the liquid or molten substances can be attributed to the presence of the two rotamers (III) and (IV) ($\text{R}^2 = \text{H}$). Two $\nu(\text{C}=\text{O})$ absorptions were also observed in ethanol solution and, as in the *N*-monosubstituted derivatives, the one at highest frequency is assigned to the *s-cis*-rotamer (III; $\text{R}^2 = \text{H}$), and the second one to the *s-trans*-conformer (IV; $\text{R}^2 = \text{H}$) which is stabilized

the early and intermediate stages of deuteration and are attributed to the $\text{C}=\text{C}-\text{NH}$ grouping of the *N*-monodeuterated derivatives in two different conformations. It should be noted that the *N*-monodeuterated compounds show an absorption in the double bond region strongly reminiscent of that corresponding to the chelated (*Z*)-form of the *N*-monoalkyl derivatives (III) and (IV).¹

TABLE 3

I.r. vibrational frequencies/ cm^{-1} of compounds $\text{DHN}\cdot\text{CMe}=\text{CH}\cdot\text{CO}_2\text{R}$ and $\text{D}_2\text{N}\cdot\text{CMe}=\text{CH}\cdot\text{CO}_2\text{R}$ in carbon tetrachloride

R	$\nu(\text{N}-\text{H})^a$		$\nu(\text{N}-\text{D})^a$		$\nu(\text{N}-\text{D})^b$		$\nu(\text{C}=\text{O})$	$\text{C}=\text{C}-\text{NH}^a$		$\nu(\text{C}=\text{C}-\text{N})^b$	$\gamma(\text{C}-\text{H})^c$
	Free	Bonded	Free	Bonded	Free	Bonded					
Me	3496	3357	2579	2478	2630	2454sh ^d	1669	1607 1482 1592	1584	788	
Et	3494	3356	2577	2477	2627	2452sh	1669	1611 1483 1593	1584	<i>e</i>	
Pr ^f	3496	3353	2578	2478	2628	2453sh 2443	1664	1611 1482 <i>e</i>	1587	<i>e</i>	
<i>f</i>	3483	3352	2568	2484	2617	2441	1666	1600 1466 <i>e</i>	1575		

^a Monodeuterated compound. ^b *N*-Dideuterated compound. ^c In CS_2 . ^d sh, Shoulder. ^e Not measured. ^f Ethyl 2-amino-cyclohexene-1-carboxylate.

by formation of a strong intermolecular bond between the carbonyl group and the solvent. The presence of several bands in the 1300 cm^{-1} region might also have the same cause.

The *N*-deuteration of 3-aminocrotonic esters is a step-wise process which could be easily followed spectroscopically. In the early stages, the i.r. spectra showed the gradual decrease of the free and chelated $\nu(\text{N}-\text{H})$ bands of the starting substance and the appearance of the $\nu(\text{N}-\text{H})$ bands and the $\nu(\text{N}-\text{D})$ bands of the *N*-monodeuterated species (XI) and (XII). As the reaction proceeded, these bands also decreased as two new $\nu(\text{N}-\text{D})$ bands, owing to the *N*-dideuterated compound (XIII), appeared. The position of these bands and their assignments are given in Table 3. The existence of the two rotational isomers (XI) and (XII) in the *N*-monodeuterated compound indicates again the existence of hindered rotation around the $\text{C}-\text{N}$ bond, and, also, the splitting of the chelated $\nu(\text{N}-\text{D})$ band in the *N*-dideuterated derivative is most likely due to the restricted rotation around the $\text{C}-\text{CO}_2\text{R}$ bond which results in the two rotamers similar to (III) and (IV) ($\text{R}^2 = \text{H}$). Similar results have been reported with primary aromatic amines bearing a carbonyl group in *ortho*-position.¹⁹

N-Deuteration also affected the absorption in the double bond region. The frequency and intensity of $\nu(\text{C}=\text{O})$ changed very little, whereas the three bands between 1635 and 1550 cm^{-1} decreased in intensity and were gradually replaced by new bands. This confirms that the $\nu(\text{C}=\text{O})$ and $\delta(\text{NH}_2)$ vibrations are not strongly coupled to each other, and that the other three bands are mixed vibrations to each of which the $\delta(\text{NH}_2)$ mode strongly contributes. The positions and assignments of the new bands are indicated in Table 3. Of these bands, the two which appeared at *ca.* 1600 cm^{-1} were visible in

The prolonged treatment of 3-aminocrotonates with deuterium oxide resulted finally in the exchange of the olefinic proton as was indicated by the disappearance of the $\gamma(\text{:CH})$ absorption (in carbon disulphide solution) and the :CH resonance signal.

The above results demonstrate that 3-aminocrotonates with primary amino-groups have a greater tendency to adopt the (*Z*)-configuration than their *N*-monoalkyl derivatives in spite of the fact that the former are weaker chelates. The *N*-substituent can alter the strength of the hydrogen bond by changing the polarities of the carbonyl oxygen and the nitrogen atom. Substituents such as the alkyl groups, having a $+I$ effect, will increase the electron delocalization in the unsaturated system, thus promoting a high electron density on the carbonyl oxygen atom and reducing the $\text{C}=\text{O}$ and $\text{C}=\text{C}$ bond orders; this will result in a strong hydrogen bond, a low $\nu(\text{C}=\text{O})$ frequency, and a low energy barrier to the (*Z*) \rightleftharpoons (*E*) conversion. On the other hand, molecular models show that in 3-(alkyl-amino)crotonates with the chelated (*Z*)-configuration there exists some steric hindrance between the $=\text{C}-\text{Me}$ group and the *N*-alkyl group; this interaction might force the $\text{N}-\text{H}$ group to bend toward the CO_2R group, strengthening still further the hydrogen bond, but will, at the same time, destabilize the (*Z*)-form. The balance of these effects may be a slight destabilization of the (*Z*)-form relative to the strainless *s-trans*-conformation of the (*E*)-form in the *N*-monoalkyl derivatives. Consequently, the population of the intramolecularly bonded (*Z*)-isomers in the equilibrium will diminish, but still the strength of the hydrogen bond will be larger than in the unsubstituted compounds. Similar situations in other kinds of compounds have been described.²⁰ The weaker $\text{NH}\cdots\text{O}=\text{C}$ interaction in the *s-cis*-isomer of the

¹⁹ A. N. Hambly and B. V. O'Grady, *Austral. J. Chem.*, 1963, **16**, 459 and references therein.

²⁰ L. P. Kuhn, *J. Amer. Chem. Soc.*, 1958, **80**, 5950; E. L. Eliel, 'Stereochemistry of Carbon Compounds,' McGraw-Hill, New York, 1962, p. 132.

unsubstituted derivatives will also allow a higher population of the more polar *s-trans*-rotamer (IV; $R^2 = H$) in the isomeric equilibrium, particularly in polar solvents. The ratio of isomers (III) and (IV) ($R^2 = H$) will then depend markedly of the polarity of the solvent. This

reasoning provides an explanation of the comparatively large solvent effect observed in the $\nu(C=O)$ band of the unsubstituted derivatives.

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