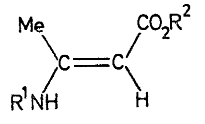
Infrared and Nuclear Magnetic Resonance Absorption and Isomerism o 3-Aminocrotonic Esters. Part III [1]

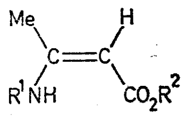
By **Antonio Gómez Sánchez,*** Departamento de Química Orgánica, Universidad de Sevilla, and Instituto de l
Grasa y sus Derivados, C.S.I.C., Seville, Spain
Juana Bellanato, Instituto de Optica, C.S.I.C., Madrid, Spain

The i.r. and ^{1}H n.m.r. spectra of 3-(dialkylamino)crotonates indicate that these substances exist as the isomer wit the (E)-configuration; the i.r. spectra also show the presence of minute amounts of the sterically more hindere (Z)-form. The low temperature ^{1}H n.m.r. spectra reveal the existence of barriers to rotation around the C–N which amount to *ca.* 11—14 kcal mol^{-1}. Some complexities in the i.r. spectra suggest in addition the existenc of smaller energy barriers to rotation around the C–CO$_2$R single bond.

IN previous Parts [1-3] it has been shown that i.r. and ^{1}H n.m.r. spectroscopy can be used to distinguish between the (E)- and (Z)-forms (I and II, $R^1 = H$ or alkyl) of 3-aminocrotonates with a primary or secondary amino-group, and to study the interconversion between these isomers. The formation of an intramolecular hydrogen bond [as in (III) or (IV)] was found to be the main stabilizing factor of the (Z)-form in such a way that in the derivatives with a primary amino-group this isomer is overwhelmingly predominant. The difference of energy between the two isomeric forms of 3-(alkylamino)-crotonates is smaller; while these compounds are stronger chelates than the unsubstituted 3-amino-crotonates, they exist as equilibrium mixtures of the chelated (Z)-forms (III) and (IV) and the (E)-form (I), the position of the equilibrium depending mainly on the polarity of the solvent, the (Z)-form being the most stable. Thus the introduction of an alkyl substituent on the nitrogen destabilizes the (Z)-form, and this effect was considered to be due to the steric compression arising between the N-alkyl group and the =CMe group that can balance the chelation energy. On the other hand, the data existing on 3-aminocrotonates bearing an electron-withdrawing substituent on the nitrogen,[4-6] indicate that the chelated (Z)-form is again much more stable than the (E)-form; apparently the very strong hydrogen bond existing in these compounds overcomes all other unfavourable factors.

In order to have a complete picture of the influence of the N-substituents on the isomerism, it was considered of interest to study the i.r. and ^{1}H n.m.r. spectra of 3-aminocrotonates with tertiary amino-groups. In addition to the (E)- and (Z)-forms (V) and (VI), the electron delocalization inherent to this conjugated, planar system makes the occurrence of rotational isomers possible for each of these forms [*e.g.*, the *s-cis*- and *s-trans*-rotamers (VIII) and (IX) respectively for the (E)-form]; the existence of hindered rotation around the C–N bond could also be anticipated. Th data existing [4,7] on the i.r. absorption of N-disubstitute


(I)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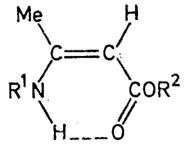
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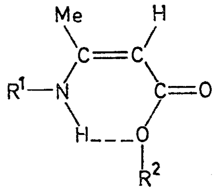
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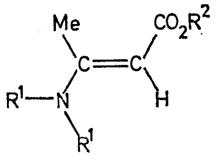
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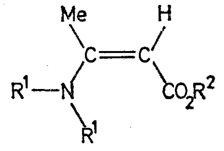
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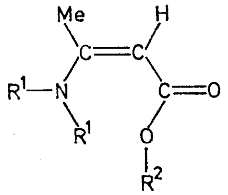
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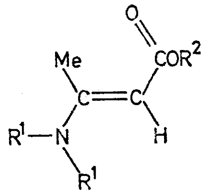
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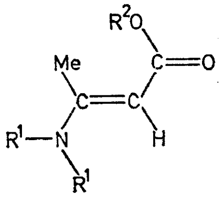
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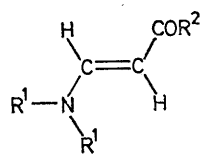
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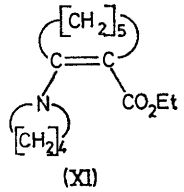
(XI)

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[5] W. Werner, *Tetrahedron*, 1971, **27**, 1755.

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

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3-aminocrotonates are very scarce and fragmentary; ethyl 3-(diethylamino)crotonate has been reported[4] to show bands at 1 677 (strong) and 1 655 cm^{-1} (weak) attributed to the carbonyl groups of the predominating (*E*)- and the (*Z*)-form, respectively. On the other hand, some preliminary data[2,8] on the ^{1}H n.m.r. spectra have been taken as evidence of the existence of these compounds in the (*E*)-form exclusively. Studies[9] on the dipole moments of ethyl 3-(dimethylamino)crotonate in cyclohexene and dioxan solutions at different temperatures confirmed the (*E*)-configuration and indicated the existence of an equilibrium between the *s-cis-* and the *s-trans*-conformers, the proportion of the latter increasing with the polarity of the solvent. The u.v. and i.r. results[10] for the related alkyl dialkylaminovinyl ketones (X) indicate that they exist as equilibrium mixtures of the *s-cis-* and *s-trans*-rotamers [similar to (VIII) and (IX)] of the *trans*-form. Variable tem-

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[8] J. Ulrich and P. Vay, *Chim. analyt.*, 1966, **48**, 549.

[9] P. Vay, *Compt. rend.*, 1967, **264C**, 1617.

[10] (*a*) J. Dabrowski and K. Kamienska-Trela, *Spectrochim. Acta*, 1966, **22**, 211; (*b*) C. F. Huebner, L. Dorfman, M. M. Robison, E. Donoghue, W. G. Pierson, and P. Strachan, *J. Org. Chem.*, 1963, **28**, 3134.

TABLE 1

I.r. data of compounds $R^1_2N{-}CMe{=}CH{-}CO_2R^2$ *

Substance		Medium	C=O				C=C							
R$^1_2$	R^2		ν	10^{-1} ε	Δν	10^{-3} *E*	ν	10^{-1} ε	Δν	10^{-3} *E*	ν(C–N)[a]	ν(C–C–O)	ν(O–R^2)	γ(=C–H)
[CH$_2$]$_4$	Me	C$_6$H$_{14}$	1 699vs[b]	84	8	12	1 628sh[c]				1 422s	*d*	1 186w	795m
			1 656vw[c]				1 584vs[e]	(111)	(23)	35		1 267vw	1 148vs	
		C$_6$H$_{12}$	1 698vs	107	7	15	1 627sh[c]				1 423s	1 299vw	1 186w	794m
			1 685sh				1 583vs[e]	(116)	(22.5)	36		*d*	1 146vs	
			1 660vw[c]											
		CCl$_4$	1 691s	52	20	15	1 628sh[c]				1 426s	1 298vw	1 185w	*d*
							1 581vs	97	23	33		1 268vw	1 147vs	
												1 251vw		
		CS$_2$	1 688vs	73	15	16	1 627sh[c]				1 425s	1 299vw	1 187w	792m
							1 584					1 267vw	1 143vs	
												1 250vw		
		CHCl$_3$	1 675sh	37	37	17	1 569vs	120	22.5	43	1 431s	1 302vw	1 186w	*d*
			1667m									1 278vw	1 149vs	
												d		
		EtOH	1 690w				1 635sh				1 433s	*d*	1 187m	793w
			1 661s				1 583sh						1 159vs	
							1 569vs						1 148sh	
		Dioxan	1 686s				1 626sh[c]				1 430	*d*	1 185w	792w
							1 576vs						*d*	
		Me$_2$SO	1 676s	47	24	19	1 623sh[c]				*d*	*d*	1 184w	789w
							1 568vs	123	25.5	44		1 270vw	1 146vs	
												1 255vw		
		C$_5$H$_5$N	1 681s	60	21	18	*d*				*d*	1 301vw	1 184m	789w
												1 268vw	1 141vs	
												1 255vw		
		Melted	1 683s				1 632sh[c]				1 429s	1 301vw	1 183w	787w
							1 579vs					1 268vw	1 164sh	
												1 252vw	1 138vs	
		Nujol	1 695s				1 630vw[c]				1 423	1 300vw	1 186w	792m
			1 653vw[c]				1 589s					1 254vw	1 162sh	777m
							1 580sh						1 146vs	
		KBr	1 677s				1 625sh[c]				1 427sh	1 301vw	1 180w	784m
							1 590s					1 257vw	1 165sh	
							1 568sh						1 151s	
[CH$_2$]$_4$	Et	C$_6$H$_{14}$	1 694vs	91	9	15	1 625sh[e]				1 422s	1 300vw	1 184w	794m
			1 654vw[c]				1 583vs[e]	(107)	(24.5)	37		1 264vw	1 142vs	
												1 250vw		
		C$_6$H$_{12}$	1 695vs	101	8	15	1 625sh[c]				1 423s	1 301vw	1 183w	794m
			1 654vw[c]				1 583vs[e]	(104)	(23.5)	35		*d*	1 141vs	
		CCl$_4$	1 686s	60	18	15	1 581vs	115	22	36	1 426s	1 298vw	1 183w	*d*
												1 266vw	1 144vs	
												1 251vw		
		CHCl$_3$	1 668s	36	37	17	1 635sh[c]				1 431s	1 301vw	1 182m	*d*
			1 664sh				1 568vs	127	22.5	43		1 276vw	1 145vs	
												1 252vw		
		Dioxan	1 681s	58	16		1 576vs	106	25		1 432	*d*	1 184	791m
													d	
		Me$_2$SO	1 671s	58	22	19	1 635sh[c]				*d*	1 301vw	1 183w	788w
							1 568vs	125	23.5	45		1 269w	1 142vs	
												1 253vw		
		C$_5$H$_5$N	1 676s	75	21		*d*				*d*	1 299vw	1 182m	790w
												1 265w	1 139vs	
												1 253vw		
		Liquid	1 678s				1 577vs				1 431s	1 299vw	1 182m	788m
												1 265w	1 139vs	
												1 253vw		

TABLE 1 (*Continued*)

Substance medium			C=O				C=C							
R^1_2	R^2		ν	$10^{-1}\varepsilon$	$\Delta\nu$	$10^{-3}E$	ν	$10^{-1}\varepsilon$	$\Delta\nu$	$10^{-3}E$	ν(C–N) [a]	ν(C–C–O)	ν(O–R^2)	γ(=C–H)
Me_2	Et	C_6H_{14}	1 698vs	72	10	12	1 591vs	100	20	29	*d*	1 302vw	1 192m	802w
			1 654vw [c]									1 273vw	1 139vs	
												1 245w		
		C_6H_{12}	1 698vs	80	9	12	1 589vs	94	21	28	*d*	1 302vw	1 192m	802w
			1 658sh [c]									*d*	1 139vs	
												1 245w		
		CCl_4	1 690s	56	18	15	1 585vs	112	20	32	1 434w	1 301vw	1 193m	*d*
												1 275vw	1 141vs	
												1 245w		
		$CHCl_3$	1 673s	34	36	17	1 575vs	109	24	38	1 435m	1 298sh	*d*	*d*
												1 281vw	1 144vs	
												d		
		Dioxan	1 685s	62	17	16	1 582vs	104	24.5	36	*d*	*d*	1 193m	797w
		Me_2SO	1 675s	50	23	15	1 574vs	107	25	39	*d*	*d*	1 193w	794w
			1 654sh									1 276vw	1 140vs	
												1 241vw		
		C_5H_5N	1 680s	55	20		*d*				*d*	1 300vw	1 193w	796w
												1 277vw	1 141vs	
												1 243vw		
		Liquid	1 683s				1 582vs				1 436s	1 301vw	1 193m	795m
												1 274w	1 137vs	
												1 243w		
Et_2	Et	C_6H_{14}	1 696vs	86	8	13	1 634vw [c]				1 432m	1 298vw	1 175s	801w
			1 657vw [c]				1 582vs	116	17.5	32		1 281vw	1 136vs	
												1 257vw		
		C_6H_{12}	1 695vs	83	9.5	13	1 634vw [e]				1 432m	1 300vw	1 176s	801m
			1 656vw [c]				1 580vs	114	16	30		1 281vw	1 137vs	
												1 260vw		
		CCl_4	1 687s	58	17.5	15	1 577vs	109	21	35	1 433m	1 298vw	1 176s	*d*
												1 281vw	1 137vs	
												1 260vw		
		$CHCl_3$	1 670m	35	36	17	1 635sh [c]				1 439m	1 299vw	1 177s	*d*
			1 664sh				1 567vs	123	21	43		1 282vw	1 141 vs	
												1 263vw		
		Dioxan	1 682s	56	16		1 572vs	114	20		*d*	*d*	1 176s	797w
													d	
		Me_2SO	1 673s	47	22	16	1 566vs	119	18	38	*d*	*d*	1 176s	794w
												d	1 137vs	
												1 263vw		
		C_5H_5N	1 678s	52	20		*d*				*d*	1 297vw	1 176m	797w
												1 282vw	1 137vs	
												1 261vw		
		Liquid	1 682s				1 582vs				1 436m	1 298vw	1 176s	796w
												1 282vw	1 135vs	
												1 261vw		
Et_2	Me	C_6H_{12}	1 699vs	83	8	12	1 632vw [c]				*d*	1 298vw	1 176s	800m
			1 659vw [c]				1 581vs	124	14	30		*d*	1 138vs	
		CCl_4	1 691s	58	17	15	1 635vw [c]				1 433m	1 298vw	1 177s	*d*
							1 576vs	113	20	35		1 281vw	1 143vs	
												1 262vw		
		$CHCl_3$	1 677m	34	37	17	1 635sh [c]	117	18	39	1 437m	1 300vw	1 177s	*d*
			1 671sh				1 567vs					1 283vw	1 143vs	
												1 265vw		
		EtOH	1 691w				1 635sh				1 438	*d*	1 182s	798w
			1 662s				1 566vs	112	25	43			1 151vs	
													1 140sh	
		Me_2SO	1 676s	50	23	17	1 623sh [c]				*d*	*d*	1 177s	794w
							1 567vs	116	18	36		*d*	1 139vs	
												1 263vw		
		C_5H_5N	1 682s	54	18	13	*d*				*d*	1 297vw	1 176s	796w
												1 283vw	1 138v	
												1 264vw		
		Liquid	1 686s				1 640sh [e]				1 436s	1 297vw	1 177s	794m
							1 571vs					1 283vw	1 138vs	
												1 263vw		

* Assigned to the (*E*)-form (V) unless otherwise indicated; frequencies in cm^{-1}.

[a] CH_3 and CH_2 groups also absorb at this region. [b] Abbreviations: v, very; s, strong; m, medium; w, weak. [c] Assigned to a small proportion of the (*Z*)-form (VI). [d] Obscured by the solvent. [e] Double band.

perature ^1H n.m.r. measurements[11] for 4-dimethylaminobut-3-en-2-one (X; $R^1 = R^2 =$ Me) confirmed the existence of these equilibria and gave a free energy difference between the conformers of 0.4 kcal mol^{-1}, the *s-cis*-rotamer being most stable; the free energies of activation for rotation around the =C–C=O single bond and around the C–N bond were *ca.* 11.5 and 14 kcal

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[11] J. Dabrowski and L. Kozerski, *J. Chem. Soc.* (*B*), 1971, 346.

mol^{-1}, respectively. In this paper we discuss the results of an investigation of the i.r. and ^{1}H n.m.r. spectra of several 3-(dialkylamino)crotonates; the ^{1}H n.m.r spectra at low temperatures of some of the compounds have also been taken in order to reveal the possible hindered rotations around the C–CO$_2$R^2 single bond and C–N bond.

EXPERIMENTAL

I.r. and ^{1}H n.m.r. spectra were recorded as indicated in refs. 2 and 3. ^{1}H N.m.r. spectra at low temperature were recorded at 90 MHz on a Perkin-Elmer R-32 spectrometer or at 100 MHz on a Varian XL-100 instrument. The following compounds were prepared by standard procedures, their physical properties being in agreement with those reported: methyl 3-(diethylamino)crotonate,[12] ethyl 3-(dimethylamino)crotonate,[13] ethyl 3-(diethylamino)crotonate,[14] and ethyl 3-(pyrrolidino)crotonate.[15] *Methyl* 3-(*pyrrolidino*)*crotonate*, m.p. 68—69° (from light petroleum) (Found: C, 64.1; H, 9.0; N, 8.4. $C_9H_{15}NO_2$ requires C, 63.9; H, 9.0; N, 8.3%), was prepared in a way similar to that indicated [15] for the ethyl ester. All substances were distilled or recrystallized before use.

Intensity Measurements.—The apparent integrated intensity (E value) in cm^{-2} l mol^{-1} was calculated from the expression $E_{\nu_1}^{\nu_2} = \int_{\nu_1}^{\nu_2} \varepsilon_\nu d\nu$, where $\varepsilon_\nu = 1/cl \log (T_0/T)_\nu$ and the symbols have their usual significance. Spectra were recorded on a Beckman IR-7 spectrophotometer having a spectral slit width of 2—3 cm^{-1} in the range 1 700—1 550 cm^{-1}. The measurements were carried out in solution at 0.05—0.35M concentration, according to the solvent.

Deuteriation Experiments.—Aliquot portions of 0.1—0.4M solutions of methyl 3-(diethylamino)crotonate and methyl 3-(pyrrolidino)crotonate in the appropriate solvent (carbon tetrachloride, cyclohexane, carbon disulphide) were shaken with deuterium oxide for different periods. The organic phase was then removed, dried by filtration through a thick filter paper, and transferred for measuring to the i.r. cell or the ^{1}H n.m.r. tube.

RESULTS AND DISCUSSION

Data for the i.r. spectra of 3-(dialkylamino)crotonates, including the apparent half-band width in cm^{-1}, and the band assignments are in Table 1. ^{1}H N.m.r. results are in Table 2; these data complement those previously reported.[2,8]

TABLE 2

^{1}H N.m.r. data [a,b] for compounds $R^1_2N–C(Me)=CH–CO_2R^2$

			δ(*J*/Hz)						
R^1_2	R^2	Solvent	=CH	=CMe	N-Me or N-CH$_2$	R^2	T_c(°C ± 2)	Δν(Hz ± 0.5) (*t*/°C)	Δ*G*‡/kcal mol^{-1} ±0.5
Et$_2$	Me	(CD$_3$)$_2$CO	4.54	2.43	3.31q (7.0)	3.50	−60	7.2 (−70)	11.4
Me$_2$	Et	CDCl$_3$ [c]	4.55	2.44	2.94	4.1q, 1.25t (7.0)	−45	11.0 (−65)	11.8
		(CD$_3$)$_2$CO [d]	4.46	2.41	2.91	3.97q, 1.16t (7.1)	−62	20.0 (−90)	10.7
[CH$_2$]$_4$	Me	CCl$_4$ [c]	4.35	2.39	3.30t (6.9)	3.50			
		CHCl$_3$ [d]	4.38	2.37	3.25t (7.0)	3.48			
		CDCl$_3$	4.54	2.43	3.26t (7.0)	3.58	7	26.0 (−20)	14.1
[CH$_2$]$_4$	Et	Liquid [d]	4.29	2.35	3.20t (6.5)	3.92q, 1.13t (7.1)			
		CCl$_4$ [d]	4.26	2.33	3.23t (6.8)	3.91q, 1.15t (7.0)			
		CDCl$_3$ [d]	4.41	2.42	3.27t (6.9)	4.04q, 1.22t (7.0)			
		(CD$_3$)$_2$SO [d]	4.30	2.36	3.22t (6.8)	3.92q, 1.12t (7.1)			

[a] At 90 MHz unless otherwise indicated. [b] Referred to internal tetramethylsilane. [c] At 60 MHz. [d] At 100 MHz.

The i.r. spectra show that the 3-(dialkylamino)-crotonates studied in this work exist almost exclusively in a single configuration and that no isomeric change can be induced either by raising the temperature or by changing the polarity of the solvent. These compounds presented two strong bands in the double bond region in the ranges 1 695—1 699 and 1 581—1 589 cm^{-1} (in cyclohexane). The band at the highest frequency is assigned as a carbonyl stretching because of its position, intensity, and large displacement to lower frequency on increasing the polarity of the medium. By comparing the frequencies of this absorption in different solvents with those corresponding to the ν(C=O) band of the (*E*)- and (*Z*)-forms of 3-(alkylamino)crotonates,[3] it can be concluded that the predominating form of 3-(dialkylamino)crotonates has the (*E*)-configuration (V). The slight shift (6—12 cm^{-1} in cyclohexane) to lower fre-

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quency observed in these compounds can be attributed to the larger $+I$ effect of the double N-substitution; the increased electron delocalization induced by this effect will reduce the C=O bond order and the carbonyl frequency. The second strong band in the double bond region appeared at the same frequency as the ν(C=C) band of the N-dideuteriated derivatives of 3-aminocrotonates[1] and is similarly assigned; the position of this band seems to be common to both the (E)- and (Z)-forms[1,3] and has no diagnostic value. The absolute intensity of the ν(C=O) band was smaller than that of the ν(C=C) band, the ratio between them being *ca.* 0.4; this intensity relationship, which was also observed in ethyl (E)-3-(benzylamino)crotonate, seems to be characteristic of the (E)-isomeric form of 3-aminocrotonates. The lack of strong absorption of the compounds studied in the 1 200—1 300 cm^{-1} region and the strong ν(O–R^2) band at *ca.* 1 140 cm^{-1} was also a common feature with the (E)-form of 3-(alkylamino)crotonates. Additionally, the presence of the γ(:C–H) absorption at *ca.* 795 cm^{-1} as compared with the same band of the (E)- and (Z)-forms of 3-aminocrotonates previously studied[1,3] (795 and 785 cm^{-1}, respectively) provided further confirmation of the (E)-configuration.

Two additional, very weak bands, at *ca.* 1 660 and 1 630 cm^{-1}, were observed in some solvents, the latter band appearing usually as a shoulder of the stronger absorption at *ca.* 1 580 cm^{-1}. The absorption at *ca.* 1 660 cm^{-1} corresponds to that previously observed[4] in ethyl 3-(diethylamino)crotonate. These bands are assigned as the ν(C=O) and ν(C=C) vibrations of minute amounts of the (Z)-isomer (VI); there are data[10b] from cyclic β-dialkylamino αβ-unsaturated esters with fixed (Z)-configuration, such as ethyl 2-pyrrolidinocyclohept-1-enecarboxylate (XI), which show the carbonyl stretching at *ca.* 1 660 cm^{-1}. Thus the ν(C=O) band of the (Z)-isomer of 3-(dialkylamino)crotonates and that of compound (XI) appears at the same frequency as that of the intramolecularly bonded (Z)-form of 3-aminocrotonates with a primary or a secondary amino-group, in spite of the fact that the former compounds are not chelated and that the increased nitrogen substitution will cause deviation from coplanarity and inhibition of resonance. A possible explanation for this similarity of frequencies is that the (Z)-form of 3-aminocrotonates with a primary or a secondary amino-group usually has the *s-cis*-conformation (III), which is expected to be a stronger chelate than the *s-trans*-conformer (IV), whereas the (Z)-3-(dialkylamino)crotonates [and (XI)] may adopt the *s-trans*-conformation (VII) that in other αβ-unsaturated carbonyl compounds[16] shows lower carbonyl frequency than the *s-cis*-form; the shift to lower frequency caused by the (Z)-3-(dialkylamino)crotonates and compound (XI) adopting the *s-trans*-conformation would be approximately the same as, or larger than, that produced by the intramolecular hydrogen bond in the *s-cis*-(Z)-3-aminocrotonates with a primary or a secondary amino-group. The failure to observe these (Z)-bands in polar solvents may be due to their being overlapped by the broader and stronger (E)-bands.

As indicated above, the ν(C=O) band of the predominating (E)-isomer of 3-(dialkylamino)crotonates was very sensitive to the polarity of the solvent, the frequency varying in an interval (Δν 37 cm^{-1}) larger than that usually found[17] in esters. Furthermore, the band showed a marked asymmetry that in some solvents became resolved, or almost resolved, into two bands. We consider that this complex absorption has two components differing slightly in frequency, each of them associated to one of the conformational isomers (VIII) and (IX) present in an equilibrium. Bowles *et al.*[18] have also admitted the existence of similar *s-cis*- and *s-trans*-rotamers in acrylates and *trans*-crotonates and concluded that the difference between their carbonyl frequencies would be of the order of 3 cm^{-1} and the bands would not be distinguishable unless they were exceptionally sharp. The changes in the equilibrium (VIII) $\rightleftharpoons$ (IX) associated with changes in the polarity of the solvent would contribute to the large frequency shifts observed. In the spectra of methyl 3-(pyrrolidino)crotonate in chloroform, the main component of the carbonyl band was the one of lower frequency, as opposed to that observed with the other esters, and it is considered to arise from the *s-trans*-conformation (IX); this rotamer is expected[16] to absorb at lower frequency than the *s-cis*-conformer (VIII), to be stabilized by a sterically favourable hydrogen bond with the solvent, and to be less hindered than the *s-trans*-conformer of the ethyl esters. Likewise, the ethanol solutions of all the compounds examined showed two bands, the one at the lowest frequency also being assigned to the *s-trans*-rotamer stabilized by formation of a strong hydrogen bond of the type C=O · · · H–OEt. In non-polar solvents the main component of the carbonyl band was the one at the highest frequency because of the predominance of the *s-cis*-rotamer.

The broad, strong ν(C=C) band of the (E)-isomer was also asymmetric in all the compounds studied, and for the hexane and cyclohexane solutions of the 3-(pyrrolidino)crotonates was clearly resolved into two bands. However, in these cases the band, or the component of the band, at the highest frequency [at 1 592 and 1 591 cm^{-1} in methyl and ethyl 3-(pyrrolidino)crotonate, respectively] disappeared when the vinyl hydrogen was exchanged for deuterium (see below) and, therefore, the splitting, or the asymmetry, is attributed to a Fermi resonance which most likely involves the overtone of the γ(:C–H) band near 790 cm^{-1}.

A further characteristic of the i.r. spectra of 3-(dialkylamino)crotonates is a strong band near 1 430 cm^{-1} which partially overlaps the CH$_2$ and CH$_3$ absorptions in this region. Its exact position depended also on the

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polarity of the solvent, the frequency shifts being of opposite sign to those of the ν(C=O) and ν(C=C) bands. In the case of ethyl 3-(dimethylamino)crotonate this band, at 1 436 cm^{-1}, corresponds to the intense line, at 1 450 cm^{-1}, in the Raman spectrum.[19] On this basis, it is considered that it arises from a mixed vibration which has contributions from the ν(C–N) mode (the frequency of which has been enhanced by the electron delocalization) and a bending mode.

Confirming previous findings,[2,8] the ^1H n.m.r. spectra (Table 2) of 3-(dialkylamino)crotonates were very simple and indicative of a single isomeric form. That this has the (*E*)-configuration followed from the chemical shift of the :C–Me signal (δ *ca.* 2.40) as compared with those of the (*E*)- and (*Z*)-forms [(I) and (II); δ 2.2—2.4 and 1.8—1.9, respectively] of 3-(alkylamino)crotonates.[2] The δ-value of the olefinic signal (*ca.* 4.55, in [^2H]chloroform) agreed very closely with that calculated by the use of additive increments[20] for the (*E*)-configuration (δ 4.51); however, this value is not significantly different from that calculated (δ 4.62) for the (*Z*)-isomer, and actually the predicted resonance positions are in inverted order from those observed[3] for 3-(alkylamino)crotonates with the (*E*)- and (*Z*)-configurations (δ *ca.* 4.52 and 4.45, respectively). No signals that could be ascribed to the (*Z*)-isomer were detected.

Single signals were observed at room temperature for both the NR^1_2 and CO_2R^2 groupings, which pointed to rapid rotations around the C–N and C–CO_2R^2 single bonds. On cooling, the *N*-methyl, or *N*-methylene, signals became split due to lowering of rotation around the C–N bond. Data of the coalescence temperatures (T_c), the maximum separation of the peaks (Δν) at the temperature indicated (*t*), and the free energy of activation ($\Delta G^‡$) at T_c for three of the compounds are given in Table 2. The observation of the coalescence was straightforward in ethyl 3-(dimethylamino)crotonate which gave two fairly sharp *N*-methyl singlets below the coalescence point; in the compounds containing the *N*-diethyl or pyrrolidino-groups, the collapsing signals were multiplets, and in order to avoid uncertainty in the measurement of T_c, the spectra were previously simplified by spin decoupling irradiating the methyl or the methylene groups β to the nitrogen, the merging of singlets being thus observed. The free energy of activation found for the two non-cyclic compounds (*ca.* 11 kcal mol^{-1}) are lower than those observed for 4-dimethylaminobut-3-en-2-one (X; $R^1 = R^2 =$ Me)[11] and ethyl *trans*-3-(dimethylamino)acrylate (X; $R^1 =$ Me, $R^2 =$ OEt)[21] (*ca.* 14 kcal mol^{-1}) which indicates a lower C–N bond order in the former; the $\Delta G^‡$ value for methyl 3-(pyrrolidino)crotonate being approximately the same. Further lowering of the temperature to −90° (in [$^2H_6$]acetone) failed to show additional splitting which could be attributed to frozen rotation around the C–CO_2R^2 single bond.

By analogy with observations[22] for other β-dialkylamino αβ-unsaturated carbonyl compounds, it was expected that, on reaction with deuterium oxide, 3-(dialkylamino)crotonates would slowly exchange the olefinic hydrogen for deuterium. In order to reveal the effect of the isotopic substitution on the i.r. spectra, the exchange reaction was performed by treating solutions of methyl 3-(diethylamino)crotonate and methyl 3-(pyrrolidino)crotonate in different solvents with deuterium oxide. The i.r. spectra showed the anticipated slow decrease of the ν(=C–H) band at *ca.* 3 090 cm^{-1} (in carbon disulphide, cyclohexane, and carbon tetrachloride solutions), the decrease of the γ(=C–H) band (in carbon disulphide and cyclohexane), and the formation of the ν(C–D) band at *ca.* 2 290 cm^{-1}. A significant change occurred in the double bond region where the ν(C=C) absorption sharpened, the asymmetry, or the splitting, of the band disappearing as indicated above; the ν(C=O) band remained unchanged. The parallel ^1H n.m.r. measurements showed the concomitant decrease of the olefinic signal.

In conclusion, 3-aminocrotonates have a clear-cut stereochemistry as revealed by i.r. and ^1H n.m.r. spectroscopy. The compounds with a primary amino-group are the chelated (*Z*)-isomers; the *N*-disubstituted derivatives adopt the sterically less hindered (*E*)-configuration; in the latter case the more sensitive i.r. technique allows the detection of trace amounts of the other geometric isomer. The *N*-monosubstituted 3-aminocrotonates are in an intermediate situation being mixtures of both isomers. There is hindered rotation around the C–N bond, the energy barrier being 11—14 kcal mol^{-1} in the *N*-disubstituted derivatives; in the remaining compounds the barrier is higher because of the hydrogen bond. Most likely there are also smaller barriers ($\Delta G^‡ < 10$ kcal mol^{-1}) to rotation around the C–CO_2R^2 single bond as suggested by the i.r. spectra.

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