# INFRARED SPECTRA AND STRUCTURE OF SUBSTITUTED UNSATURATED CARBONYL COMPOUNDS XII. β-AMINOACROLEIN

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(Received April 1st, 1969)

#### ABSTRACT

The IR spectra of  $\beta$ -aminoacrolein, the simplest amide vinylogue, have been studied. The solid compound has the trans configuration and this form prevails in solution in polar solvents. Of the two rotational isomers of the trans form, the s-trans seems to predominate in solution. In chloroform and other non-polar solvents, intense bands of the cis form were observed after the trans-cis equilibrium had been established. The band pattern of the cis form is very similar to that of cis-enamino ketones. The absorption bands were assigned on the basis of deuterium substitution and by comparison with previous data on alkylaminoacroleins.

### INTRODUCTION

In a series of studies<sup>1</sup>, many characteristic spectroscopic features of the interesting amide vinylogue system O=C-C-C-N-H have been accounted for. However, a number of absorption bands of these compounds still cannot be unambiguously assigned. Apart from the unavoidable problem of coupling of vibrations in such conjugated systems, there are two major sources of difficulty. Firstly, the simultaneously occurring cis, trans-s-cis and trans-s-trans forms in solution usually give rise to a rather complicated band pattern; secondly, the alkyl groups attached to the amide vinylogue grouping produce absorption bands liable to be confused with those of the amide vinylogue system proper.

In these respects,  $\beta$ -aminoacrolein (I) is of interest because, as for a highly polar compound, its predominant form is trans-s-trans and its molecule carries no alkyl substituents.

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## EXPERIMENTAL

 $\beta$ -Aminoacrolein (I). One gram of propargyl aldehyde, 2 ml ethanol, 2 ml ether, and 2 ml ammonia were placed in a tube cooled to  $-60^{\circ}$ , sealed, allowed to warm up to  $-10^{\circ}$  and kept at this temperature for 8 h, and finally kept at room temperature for 24 h. The tube was then opened, the solvents evaporated, and the residue dissolved in acetone-ethanol (10 : 1) and passed through a short silica gel column to remove tars. Finally the product was purified by a threefold high-vacuum sublimation  $(10^{-4} \text{ mm Hg})$  to yield 0.2 g of white crystals melting at  $105-106^{\circ}$  (lit.  $105-106^{\circ 2}$ ).

For deuteration, (I) was dissolved in 99.6 % heavy water used in hundredfold molar excess and the heavy water was distilled off at 1 mm Hg; the process was repeated and the residue sublimed. The deuterium content of the amino group was estimated by comparing the intensities of the v(NH) and v(ND) bands.

IR spectra were recorded with a Hilger H-800 double-beam spectrometer with sodium chloride optics. The NMR spectrum was recorded at 60 MHz with a Varian V-4300 C spectrometer.

Chloroform, bromoform, ethylene chloride, and acetonitrile used as spectroscopic solvents were purified by conventional methods. Solutions were investigated immediately after dissolution of the samples; this, however, took about 3 min. Isomerisation was then followed in terms of subsequently recorded spectra.

The spectra are shown in Figs. 1-5 and listed in Table 1.

### **RESULTS AND DISCUSSION**

Solid  $\beta$ -aminoacrolein has the trans configuration and this form prevails



Fig. 1. IR spectrum of solid  $\beta$ -aminoacrolein in KBr.

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also in its solutions in polar solvents, e.g. DMSO, acetonitrile, etc. The NMR spectrum of (I) in DMSO reveals signals of the  $\alpha$ -vinyl,  $\beta$ -vinyl, and formyl protons at  $\tau = 4.89$ , 2.70, and 1.29, respectively. The coupling constant of the vinyl protons, J = 12.3 Hz, is characteristic of the trans isomer<sup>3</sup>. The coupling constant of the formyl and  $\alpha$ -vinyl protons was 8.80 Hz.



Fig. 2. (---) IR spectrum of a freshly prepared saturated (0.003 M) solution of  $\beta$ -aminoacrolein in CHCl<sub>3</sub>; cell thickness 1 mm. (---) The same solution after 24 h.



Fig. 3. (----) The 1700-750 cm<sup>-1</sup> region of the spectrum of a 0.1 *M* solution of  $\beta$ -aminoacrolein in CH<sub>3</sub>CN; cell thickness 0.1 mm. (---) The same spectrum of the N-deuterated compound; deuterium content of the amino group ~ 65 %.

The IR spectrum of a freshly prepared, saturated (~ 0.003 *M*) chloroform solution of (I) exhibits bands attributable to asymmetric and symmetric vibrations of the NH<sub>2</sub> group at 3550 and 3440 cm<sup>-1</sup>, respectively, which are almost exactly consistent with the values obtained for trans enamino ketones<sup>4</sup>. After the cis-trans equilibrium has been established, a new band of the intramolecularly hydrogenbonded N-H group of the cis form appears at 3310 cm<sup>-1</sup> and the band of the free N-H group protruding outside the chelate occurs at 3520 cm<sup>-1</sup>; these band positions also are close to those observed with cis enamino ketones<sup>4</sup>. The strong absorption persisting at 3550 and 3440 cm<sup>-1</sup> proves that, at equilibrium, the dilute chloroform solution contains both the cis and the trans forms in considerable quantities.

The bands corresponding to stretching of the vinylic C-H linkages appear at a rather low value of  $2985 \text{ cm}^{-1}$ , whereas the characteristic aldehyde bands occur at 2810 and 2735 cm<sup>-1</sup> (Fig. 2).

In the double-bond region, the saturated (~ 0.003 *M*) chloroform solution produces "v(C = O)" bands of the trans-s-cis (AV-I-trans-s-cis; for nomenclature see ref. 1) and the trans-s-trans forms (AV-I-trans-s-trans) at 1675 and 1634 cm<sup>-1</sup>, respectively. As the latter is many times as strong as the former, it seems highly probable that of these two rotational isomers of the trans form the s-trans one prevails.

The  $1610 \text{ cm}^{-1}$  band is presumably assignable to an AV-II-trans-s-trans vibration, i.e. to the mode including the N-H deformation, for it does not occur in the spectrum of the compound with the deuterated amino group (cf. Figs. 4 and 5).

Alternatively, the  $1610 \text{ cm}^{-1}$  band may well be the inception of the AV-II-cis band which appears in the spectrum of the equilibrium mixture of both isomers at 1607 cm<sup>-1</sup>. However, an unresolved band of similar intensity at 1614 cm<sup>-1</sup> in the spectrum of a 0.1 *M* solution of (I) in CH<sub>3</sub>CN (Fig. 3), where the cisisomer is in negligible concentration, militates against the latter alternative.

The band which should correspond to the AV-III-trans vibration, i.e. to the mode dominated by the C=C stretch, is also hard to be found because of its low intensity which is characteristic of the s-trans conformer of many  $\alpha$ ,  $\beta$ -unsaturated carbonyl compounds<sup>5, 6</sup>. It may be assumed that this vibration is manifested by one of the very weak bands in the 1580–1540 cm<sup>-1</sup> region.

Of the five following bands appearing in the spectrum of solid (I) (Fig. 1) at 1389, 1322, 1297, 1276 and 1186 cm<sup>-1</sup>, the first is assigned to the bending mode of the formyl C-H bond. The band at 1297 cm<sup>-1</sup> is presumably due to the in-plane bending of the vinylic hydrogens<sup>7</sup>. The very strong band at 1186 cm<sup>-1</sup>, shifted in chloroform solution to  $1170 \text{ cm}^{-1}$ , is assigned to the next skeletal AV-IV-trans vibration likely to be dominated by the C-C stretch. The origin of the two remaining bands, 1322 and 1276 cm<sup>-1</sup>, appears obscure. Nevertheless, it should be assumed that they are characteristic of the trans-enamino system because the

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Fig. 4. (a) IR spectrum of a freshly prepared, saturated solution of  $\beta$ -aminoacrolein in CHCl<sub>3</sub>; cell thickness 0.2 mm. (b) The same solution after 24 h.



Fig. 5. (a) IR spectrum of a freshly prepared, saturated CHCl<sub>3</sub> solution of  $\beta$ -aminoacrolein after deuteration; cell thickness 0.2 mm. (b) The same solution after 24 h. Deuterium content of the amino group ~ 80 %.

spectra of the trans isomer of alkyl- $\beta$ -aminovinyl ketones also show two bands in this narrow region. Thus, the trans ethyl- and isopropyl- $\beta$ -aminovinyl ketones show bands at 1322 and 1255 cm<sup>-1</sup> and at 1331 and 1256 cm<sup>-1</sup>, respectively<sup>\*</sup>.

In the lower wavenumber region the band appearing at 979 cm<sup>-1</sup> (in CH<sub>3</sub>CN) is assigned to the out-of-plane vibration of vinylic hydrogens and that

<sup>\*</sup> Unpublished data.

Trans								Cis			
нсосн	-CHNH2		nenovale sa cingén a propaga a para na	nema and a second a	нсосн	(D)=CHND;		HCOCH=	•CHNH2		HCOCD_ CHND <sub>2</sub>
Solid in KBr	Liquid a r°+110°	In CH <sub>3</sub> CN <sup>b</sup>	In CHCI <sub>3</sub> °	In C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub>	Solid in nujol	In CH <sub>3</sub> CN <sup>b</sup>	In CHCl <sub>3</sub>	Liquid t°+110°	ln CHCl <sub>3</sub>	In C <sub>2</sub> H4Cl <sub>2</sub>	CHCI
1665s		1660s	1675s	1672s	1 N MARY AND	1660s	1660s	na a tring a su da anna a' fa si a ta ta anna amh a su	1648vs <sup>d</sup>	1647sh	1642vs
1620sh	1620sh	1637vs	1634vs	1637vs		1623vs	1625vs	1 2/2	1607vs <sup>d</sup>	1607vs	1529vs
1585vs	1590vs	10145 1564vw	1580vw sh <sup>d</sup>	1580vw sh		1569vw		1450w	1450wd	SAKACT	14/1111
			1560vw <sup>d</sup>	1560vw							1419vw
1389s	1395s		1402w	1402vw	1387vs		1405m		1383s <sup>d</sup>	1382s	1383s
1322s	1324s	1324s	1318s <sup>d</sup>	1316s	1333vs	1322s	1326sh				
1297s	1297s	1303s			1302m	1303s	1314s		1293vs <sup>d</sup>	1292s	1309vs
1276s		1271m			1282vs	1276m	1276m	1124sh	1124vw		
					1250m	1226m			1100w	1105w	
1186vs	1175vs	1170vs	1170s	1171s	1187vs	1169vs	1170s		1033vw		
-0101					11165	1133m	1119m				
10/UII 1078e	IMAm	1074m	1010w d	1073w	1020E	1018m					
976m	975m	m201	970m <sup>d</sup>		9758	978m			968s		
852m					854m						
832s	824m	830m			835s	828s					
781m		769w			784m	778w		745sh	761s °		
698s	710m				727s						
677s					698s						

at 830  $\text{cm}^{-1}$  probably corresponds to the same type of vibration of the formyl hydrogen.

Upon deuteration in the amino group (which is accompanied by exchange of the  $\alpha$ -hydrogen<sup>9</sup>), the 1614 cm<sup>-1</sup> band disappears from, and two new bands at 1226 and 1136 cm<sup>-1</sup> arise in, the spectrum of the acetonitrile solution. Although the former band corresponds fairly well to the isotopically shifted AV-II-trans band (1614/1226 = 1.32) both bands appear to be unassignable at the moment.

As the trans  $\rightarrow$  cis conversion proceeds in chloroform solution, the absorption bands of the cis isomer appear and comply in number, position, and intensity with those observed for cis-alkyl- $\beta$ -aminovinyl ketones<sup>4,8</sup>. The AV-I-cis, AV-II-cis, and AV-III-cis bands appear at 1648, 1607 and 1511 cm<sup>-1</sup>, respectively. The remaining characteristic bands of the cis -CO-CH=CH-NH<sub>2</sub> system appear at 1450 and 1293 cm<sup>-1</sup>. The band occurring at 1383 cm<sup>-1</sup> corresponds certainly to the bending of the formyl C-H bond, whereas the 761 cm<sup>-1</sup> band (CHBr<sub>3</sub> solution) is due to the out-of-plane vibration of the vinyl hydrogens of the cis isomer.

Deuteration in the amino group causes changes analogous to those observed in the spectra of cis-alkyl- $\beta$ -aminovinyl ketones<sup>4,8</sup>. The AV-I-cis band is slightly lowered (1648  $\rightarrow$  1642 cm<sup>-1</sup>) whereas the 1607 cm<sup>-1</sup> band is replaced by a new one at 1529 cm<sup>-1</sup> [v(H)/v(D) = 1.05]. This, however, seems to correspond to a vibration mode different from that of the parent band at 1607 cm<sup>-1</sup> (ref. 8). The AV-III-cis band is shifted down to 1471 cm<sup>-1</sup> and the 1293 cm<sup>-1</sup> band up to 1309 cm<sup>-1</sup>. Simultaneously a new low intensity band appears at 1419 cm<sup>-1</sup>; its origin is not clear, but a similar band is known, fairly characteristic of N-deuterated cis enamino ketones<sup>8</sup>. The band at 1568 cm<sup>-1</sup> corresponds to the admixture of the compound deuterated to 50 % in the amino group<sup>8,10</sup>, whose presence cannot be avoided during the experiment. The remaining bands of cis-aminoacrolein can not be observed for want of solvents sufficiently transparent below 1200 cm<sup>-1</sup> and able to contain this isomer in adequate concentrations.

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