Infrared Spectra and Structure of Substituted Unsaturated Carbonyl Compounds. XVIII. *N*-Alkyl-enamino Thiones

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Skeletal and N–H bending vibrations have been investigated in enamino thiones having the general formula $R^1C(S)CH{=}C(R^3)NHR^4$ (R=alkyl) and compared with those of the oxygen analogues (enamino ketones).

Previous work[1)] has shown that the interpretation of IR spectra of enamino ketones, in the region where absorptions due to skeletal vibrations occur, is made very difficult by the presence of strong vibrational coupling. The effect encompasses all the bonds present in the main chain of molecules of this type $(\mathrm{O{=}\underset{|}{C}{-}\underset{|}{C}{=}\underset{|}{C}{-}N{\langle}_{H}})$. This also applies to bending vibrations of the amino group: these are uncharacteristic, due undoubtedly to strong vibrational interactions with the skeleton.

Replacing oxygen by sulphur, whilst effectively not changing the mesomerism within the molecule, does lead to a change in the frequencies of skeletal vibrations. It seemed likely that this would afford a better opportunity of studying the absorptions corresponding to bending vibrations of the >NH group. Such was the main reason why the present work on the IR spectra of a number of secondary enamino thiones and their deuterated derivatives (listed in Table 1) was undertaken. Their oxygen analogues (enamino ketones) have been included for comparison. Moreover, an attempt has been made to assign the absorption bands for other vibrations of the above system, especially the stretching vibrations of the thione group. Previous assignments[2)] with $\nu_{C=S}=1260$—$1300\ \mathrm{cm}^{-1}$ are incorrect.[3)]

TABLE 1. ALIPHATIC ENAMINO THIONES AND ENAMINO KETONES $R^1C(X)CHCR^3{-}NR^4R^{4'}$

Compound No	X	R^1	R^3	R^4	$R^{4'}$
I	S	CH_3	H	H	C_2H_5
Ia	O	CH_3	H	H	C_2H_5
Id_1	S	CH_3	H	D	C_2H_5
II	S	C_2H_5	H	H	CH_3
IIa	O	C_2H_5	H	H	CH_3
IId_1	S	C_2H_5	H	D	CH_3
III	S	CH_3	H	H	C_3H_7
IIIa	O	CH_3	H	H	C_3H_7
IIId_1	S	CH_3	H	D	C_3H_7
IV	S	CH_3	CH_3	H	C_3H_7
IVa	O	CH_3	CH_3	H	C_3H_7
IVd_1	S	CH_3	CH_3	D	C_3H_7

Experimental

The syntheses of 4-ethylaminobuten-3-thione-2 (I) and 1-methylaminopenten-1-thione-3 (II) have been described in a previous paper.[2)] 4-Propylaminobuten-3-thione-2 (III) and 4-propylaminopenten-3-thione-2 (IV) were obtained in a similar way. Infrared spectra were recorded on a VEB Carl Zeiss (Jena) UR-20 double beam spectrometer using NaCl and KBr prisms. Solvents and concentrations are reported in Tables 2 and 3.

Results and Discussion

The >NH stretching region is specifically dealt with in a separate paper;[4)] in the present work the 1800—400 cm^{-1} region has been studied. Here, in theory, four bands due to skeletal stretching vibrations of the $\mathrm{S{=}\underset{|}{C}{-}\underset{|}{C}{=}\underset{|}{C}{-}N\langle}$ system are to be expected, together with two bands derived from >NH bending (assuming there is no strong interaction with other oscillators).

It has been considered appropriate to retain the nomenclature previously used for the skeletal bands, *i.e.* "Amide Vinylogue Bands," AV-I, AV-II, AV-III, and AV-IV.[1)] However, whereas in enamino ketones the AV-I frequency (mainly $\nu_{C=O}$) was the highest the analogous AV-I frequency in the thiones is the lowest of the four (Tables 2 and 3). AV-II is a skeletal vibration, chiefly of $\nu_{C=C}$ character but with a significant contribution from NH bending. AV-III and AV-IV are coupled vibrations dominated by C–C and C–N stretching. Apart from these four bands one other due to a vibration dominated by N–H bending has been identified. In recent papers Taylor[5,6)] has discussed our previous results, and in particular our nomenclature, obviously without being aware of some of the arguments presented in the references cited by him, and also of our subsequent papers[1c–h)] where the infrared spectroscopy of enamino carbonyl compounds has been further discussed. Thus, in contrast to Taylor's assesment,[5)] we were able in many cases to obtain a complete separation of isomers[1a,d,e)] and there is really no ground for the statement[5)] that: "Up to the present time no detailed infrared study based on compounds of known configuration has appeared." As to the nomenclature, Taylor supposed that our reason for not naming directly the bands $\nu_{C=O}$ and $\nu_{C=C}$ was due possibly to the "··· prejudice that existed, and still exists, against assigning the strongest band in the 6 μm region to anything other than carbonyl".[6)]

In fact we did not consider intensity as a factor in the discrimination between the $\nu_{C=O}$ or $\nu_{C=C}$ character of any of the bands under discussion. On the contrary, we showed, that a band, which is conventionally assigned $\nu_{C=C}$, can be both more intense than "$\nu_{C=O}$" (for the *trans-s-cis*[1c)] and *cis-s-cis* forms[1c,e)]) as well as less intense (for the *trans-s-trans* form[1e)]). The main reason for proposing a nomenclature similar to that employed for amides (*i.e.* the avoidance of a simplified

TABOE 2. THE MAIN INFRARED ABSORPTION BANDS OF ENAMINO THIONES AND THEIR *N*-DEUTERATED DERIVATIVES IN THE 1700—700 REGION

Compound No.	Solvent	Concn. mol/l	AV-II a)	δ_{NH}	AV-III a)	AV-IV a)	δ_{ND}	AV-I a) *trans*	AV-I a) *cis*	γ_{NH}
	MeC(S)CH=CHNHEt									
I	—	—	1628s	1585m	1497s	1271s	—	—	1107m	790s e)
Id_1	—	—	1592s	—	1487s	1290s	1158m	—	1074w	
I	C_2Cl_4	0.4	1622s	—	1492s	1266s	—	—	1110m	
Id_1	C_2Cl_4	0.4	1590s	—	1485s	1287s	1160w c)	—	1074w	
Id_1	CCl_4	0.2	1590s	—	1484s	1287s	1162w c)	—	1074w	
I	$(CH_3)_2SO$	1.5	1626s	1588s b)	1503s	1270s	—	1130sh d)	1108w c)	
	EtC(S)CH=CHNHMe									
II	—	—	1628s	1587m	1498s	1296s	—	—	1115m	802s e)
IId_1	—	—	1599s	—	1488s	1267m	1160w	—	1050w	
II	C_2Cl_4	0.4	1631s	—	1495s	1291s	—	—	1119m	
IId_1	C_2Cl_4	0.4	1597s	—	1486s	1262m	—	—	1050w	
II	$(CH_3)_2SO$	1.5	1630s	1593s b)	1503s	1285s	—	1135sh d)	1113w c)	
	MeC(S)CH=CHNHPr									
III	—	—	1628s	1587m	1498s	1276s	—	—	1106m	786s e)
IIId_1	—	—	1592s	—	1486s	1288s	1156w	—	1076w	
III	C_2Cl_4	0.4	1626s	—	1495s	1268s	—	—	1110m	
IIId_1	C_2Cl_4	0.4	1591s	—	1483s	1287s	1160w c)	—	1076w	
III	$(CH_3)_2SO$	1.5	1624s	1588s b)	1501s	1275s	—	1135sh d)	1105w c)	
	MeC(S)CH=C(Me)NHPr									
IV	—	—	1602s	1537s	—	1310s	—	—	1108m	786m e)
IVd_1	—	—	1556s	—	1476s	1305s	1216m	—	1133m	
IV	C_2Cl_4	0.4	1601s	1531s	—	1293s	—	—	1116m	

a) For nomenclature see text. b) The band is of higher intensity than in the neat compound. c) The band is of lower intensity than in the neat compound. d) Shoulder on a band with its maximum at about 1145 cm^{-1}. e) Intensity diminishes upon deuteration.

TABLE 3. THE MAIN BANDS OF ENAMINO KETONES IN THE 900—1700 cm^{-1} REGION; SOLUTIONS IN C_2Cl_4

Compound No.	AV-I	AV-II	AV-III	AV-IV	γ_{NH} a)
Ia	1644s	1583s	1486s	1261s	740s
IIa	1643s	1584s	1483s	1290s	730s
IIIa	1645s	1581s	1486s	1277s	740s
IVa	1616s	1586s	1519m	1288s	736s

a) Band position was determined for neat compounds.

group frequency nomenclature) was the pronounced vibrational coupling in amide vinylogues; the coupling manifests itself in both isotopic[1a,c—h] and solvent shifts[1a,b] of the bands and is unexplanable within a simple concept of characteristic group frequencies.

The skeletal bands of compounds I, II, and III manifest themselves as described below.

AV-II, dominated by C=C coordinate, appears in solution spectra (in C_2Cl_4) at frequencies between 1622—1631 cm^{-1}, *i.e.* 39—47 cm^{-1} higher than in the case with the oxo analogues (comparison of I, II, and III with Ia, IIa, and IIIa in Tables 2 and 3). This can be explained in terms of a "repulsive" interaction between C=O and C=C oscillators in the oxo compounds. At the same time, this frequency is lower by some 30 cm^{-1} than $\nu_{C=C}$ is in olefins since the conjugation with the thione group is comparable to that with the carbonyl group.

The positions of bands AV-III at 1492—1495 cm^{-1} and AV-IV at 1266—1291 cm^{-1} differ little from those of the corresponding bands in the enamino ketones. This is to be expected since, as has already been stated, there is no inherent difference in the bond orders within the two skeletons being compared. It should be added that under the conditions described above, both classes of compounds exist in the *cis* form.

As for the bending vibrations of the >NH group, with solution spectra (in C_2Cl_4) of the thioketones I, II, and III the appropriate band is not observed as a separate entity. On the other hand, the pure substances (which according to NMR data, also exist exclusively in the *cis* form) exhibit an additional band in the region 1585—1587 cm^{-1}. This disappears on deuteration while a new band arises at 1156—1160 cm^{-1} (see Figs. 1 and 2). This band is also absent in the Ni(II) complex of I. Another consequence of deuteration is the shift of AV-II to 1592—1599 cm^{-1}, *i.e.* 29—36 cm^{-1} towards lower frequencies.

The fact that two bands are affected by deuteration permits us to assume that both represent some complex form of vibration with contributions from skeletal and NH bending modes. In the. deutero derivative these

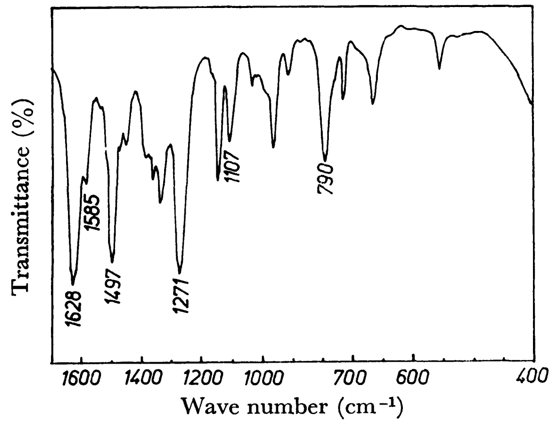

Fig. 1. Infrared spectrum of 4-ethylaminobuten-3-thione-2 (I); capillary film.

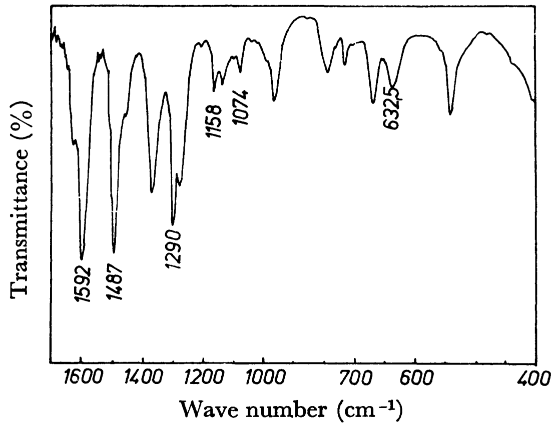

Fig. 2. Infrared spectrum of deuterated 4-ethylamino-buten-3-thione-2 (Id_1): capillary film.

vibrations are no longer coupled to an appreciable degree; thus, the band above 1500 cm^{-1} corresponds to a large extent to sketetal vibrations and the 1156—1160 cm^{-1} band to δ_{N-D} vibrations.

Remarkably, compound IV (having, β to the thiocarbonyl group, a methyl group instead of hydrogen) exhibits spectral characteristics which differ somewhat from those of compounds I, II, and III. The AV-II frequency is lowered by 26 cm^{-1} (for neat liquid) which indicates a lowered C=C bond order. Instead of two separate bands of the δ_{N-H} and AV-III type one band was found at 1537 cm^{-1} which exhibits features characteristic of both the skeletal stretching and NH bending vibrations. This assignment is based on the results of deuteration of the compound IV: in place of the disappeared 1537 cm^{-1} band two bands, *viz.*, a strong AV-IIId_1 band at 1476 cm^{-1} and a δ_{N-D} one at 1216 cm^{-1} occur. Obviously, a decoupling of the complex AV-III+δ_{N-H} vibration resulted from deuteration.

In order to understand the unusual spectral behaviour of compound IV one must take into account the great degree of stabilization achieved by the *cis* form. There is then a complementary increase in the strength of the intramolecular hydrogen bonding as compared with compounds I, II, and III (this has been shown in a previous paper[4)]). We can thus postulate greater intramolecular charge delocalization and further, an equalization of the bond energies within the skeleton. This may be the reason for the exceptional nature of the IR absorption of compound IV.

In the literature[7,8)] dealing with the absorptions of the thiocarbonyl group it is stated that the C=S band appears at 1170—1220 cm^{-1} in aromatic thioketones and at 1244—1270 cm^{-1} in aliphatic thioketones.[8)] Clearly the position of the band depends on the coupling present (assuming, of course, that the assignments are correct).

The problem is particularly difficult in the compounds here investigated because, due to the strong coupling of the skeletal vibrations, there cannot exist a vibration localized solely within the C=S group. For this same reason no resemblance to the spectra of thiones described in the literature is expected.

For the purpose of detecting such a band in which the contribution of C=S stretching predominates, (designated AV-I, according to our nomenclature) we utilized the changes that take place in the spectrum when, in a medium of dimethylsulphoxide, the *cis* form changes to the *trans*. NMR spectra have confirmed, unequivocally, that a partial *cis-trans* isomerisation takes place under these conditions. In the IR spectrum a new AV-I band is expected at higher frequencies, the hydrogen bonds, $\rangle$N–H···S=C$\langle$ having been broken by dimethylsulphoxide. In the region under discussion the 1106—1115 cm^{-1} band undergoes a definite change (*cf.* the spectra in Table 2). In dimethylsulphoxide solution this band contracts while at the same time a new band appears at higher frequencies (1130—1135 cm^{-1}). The first of these would thus correspond to the AV-I vibration of the *cis* form and the second to that of the *trans* form. As we have already communicated[3)] our previous assignments[2)] of the AV-I ("$\nu_{C=S}$") band were incorrect.

Another characteristic feature of the spectra of enamino thiones, found in all the examples studied is the presence of intense wide band in the region 786—802 cm^{-1}. This is probably an out-of-plane deformation of the NH group since deuteration causes a decrease in the intensity of the band together with the appearance of a new band at 630 cm^{-1}.

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