

Infrared Spectroscopic Investigations of some Hydrazides

J. BUUR JENSEN*

Leo Pharmaceutical Products, Copenhagen, Denmark

The infrared spectra of some hydrazides in the solid state and in chloroform solution have been investigated in the $6\ \mu$ region. Characteristic frequencies in the solid state are found at $1\ 630$ – $1\ 660\ \text{cm}^{-1}$, $1\ 620\ \text{cm}^{-1}$ and between $1\ 570$ and $1\ 530\ \text{cm}^{-1}$. Corresponding bands in the solutions are found around $1\ 670$, $1\ 620$ and $1\ 500\ \text{cm}^{-1}$. The assignment of the bands to different group frequencies is discussed. Investigations in the $3\ \mu$ region on phenylacetic acid hydrazide make it evident that hydrogen bonding takes place in the solid state and in concentrated solutions.

Furthermore it is shown, that the spectrum of cinnamic acid hydrazide synthesized by Godtfredsen and Vangedal¹ is in agreement with the spectra of the other hydrazides, while the spectrum of the compound which Muckermann² believed to be cinnamic acid hydrazide shows essential differences.

In a recent publication from this laboratory Godtfredsen and Vangedal¹ have proved, that the compound synthesized by Muckermann² was 3-phenyl-5-pyrazolidone and not, as hitherto believed, cinnamic acid hydrazide. This observation caused the author to investigate the infrared spectra of some hydrazides. The present publication deals mainly with the spectra in the $6\ \mu$ region, but measurements in the $3\ \mu$ region are also reported.

Only few spectra of hydrazides are found in the literature; thus Lenormant³ in a work on amides has recorded the spectrum of acetic acid hydrazide, while Mattu and Pirisi⁴ have recorded that of *isonicotinic* acid hydrazide.

EXPERIMENTAL

All spectra are absorption spectra measured on a Beckman infrared spectrophotometer model IR 2 equipped with rock salt optics and automatic recorder. A computing device, as described by Foreman and Jackson⁵ was used for the purpose of eliminating background absorption. Spectra of solids were recorded in KBr-discs. The KBr employed was prepared as described by Clauson-Kaas *et al.*⁶ The discs contained 0.5 % hydrazide, weighed about 0.2 g and were prepared in a pressing device and under experimental

* Present address: Specialitetsskontrollen, Copenhagen, Denmark.

conditions as described elsewhere⁷. Spectra of chloroform solutions were recorded in rock salt cells. The employed chloroform was Merck a.g.

All the hydrazides were synthesized in this laboratory. With the exception of cinnamic acid hydrazide, which was synthesized by the method of Godtfredsen and Vangedal¹, they were all prepared by the reaction of the corresponding ethyl ester with hydrazine. Melting points agreed with those found in the literature.

RESULTS AND DISCUSSION

Figs. 1 and 2 show, respectively, the spectra of the solid hydrazides and those of the chloroform solutions. In addition the spectrum of 3-phenyl-5-pyrazolidone is given. Among the spectra of the solids acetic acid hydrazide is absent, as it was impossible to prepare a sufficiently transparent disc with this compound, presumably due to its low melting point. However, the spectrum given by Lenormant³ is in comparatively good agreement with those given in Fig. 1.

One observes at once that the transition from the solid state to dilute solution is associated with distinct changes in the spectra. In the solid state the hydrazides absorb strongly between 1 630 and 1 660 cm^{-1} , while this absorption in chloroform solution is shifted to frequencies about 20 cm^{-1} higher. Likewise the hydrazides in the solid state show medium absorption in the region around 1 530—1 570 cm^{-1} . This absorption is found in the solutions at essentially lower frequencies around 1 500 cm^{-1} . The absorption of the phenyl groups can be observed⁸ around 1 500 and 1 600 cm^{-1} , and finally is a medium to strong band found in the neighbourhood of 1 620 cm^{-1} in the spectra of the dissolved hydrazides. In the spectra of the solid hydrazides this absorption may be overlapped by the strong band at 1 630—1 660 cm^{-1} , but the absorption pattern makes it evident, that this band also is present in the spectra of the solid hydrazides.

In the following it is attempted to assign the absorption bands to different groups in the molecule. It should be noted at once that the spectra of the hydrazides resemble those of the N-monosubstituted amides. Considerable contribution to the understanding of the spectra of the amides is offered by among others Richards and Thompson⁹, Lenormant³ and latest by Gierer¹⁰.

The strong absorption of the hydrazides around 1 650 cm^{-1} in the solid state and 1 670 cm^{-1} in chloroform solution in analogy with the N-monosubstituted amides must be ascribed to the carbonyl group. Normally one would expect its absorption at a somewhat higher frequency around 1 710 cm^{-1} . The reason for the low frequency is explained by a weakening of the double bond, due to the following resonance:



In the spectra of the N-monosubstituted amides Richards and Thompson⁹ observed, that the absorption of the carbonyl group is dependant on the state

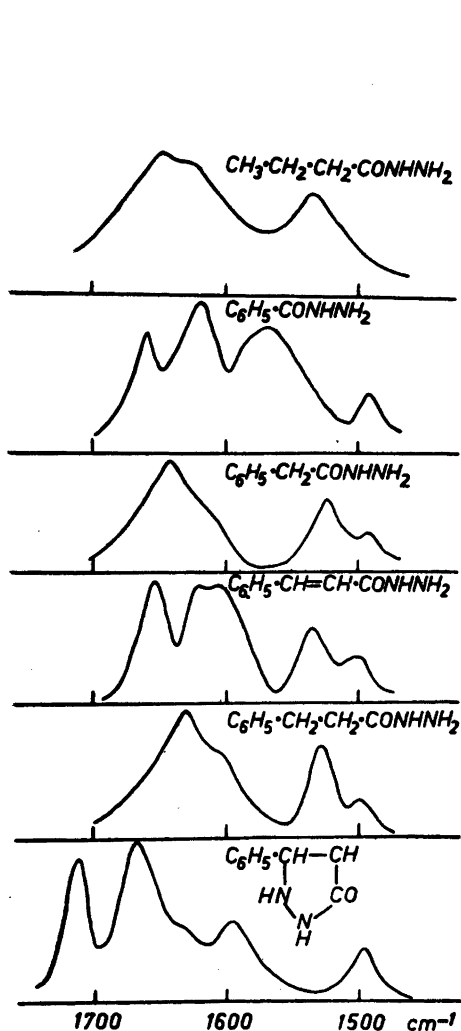


Fig. 1. I.R.-spectra of solid hydrazides (KBr discs containing 0.5 % hydrazide).

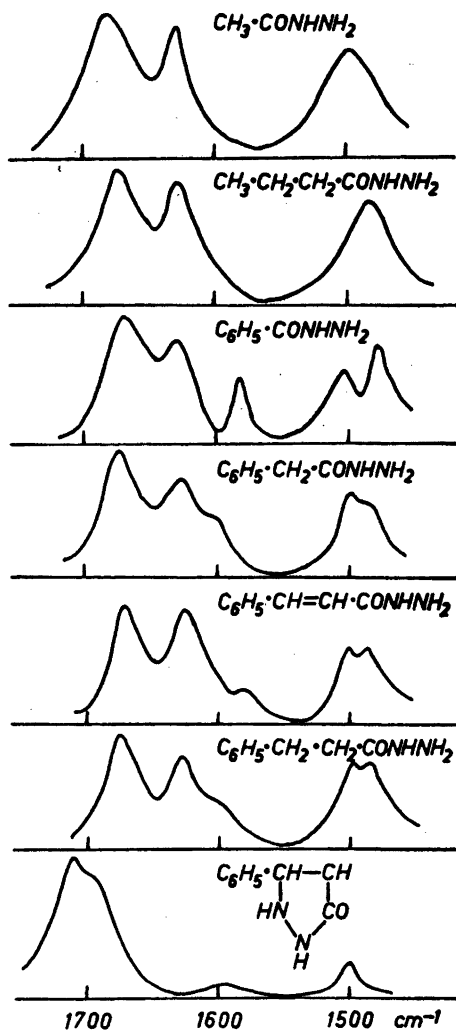


Fig. 2. I.R.-spectra of hydrazides (1 % in CHCl_3)

in the same manner as here observed for the absorption of the carbonyl group in the hydrazides.

The medium band observed between 1530 and 1570 cm^{-1} in the solid hydrazides is also found in the spectra of solid N-monosubstituted amides⁹, and in both cases this absorption is shifted to lower frequencies in the spectra of the solutions⁹. There are yet different opinions on the causes of this absorption. In the N-monosubstituted amides Richards and Thompson assign this absorption to NH deformation frequency, while Lenormant is of the opinion that

the absorption can be attributed to an "ionized" form $\left[\begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C} \\ \diagdown \\ \text{NH} \end{array} \right]^-$.

Finally Gierer assigns the band in N-methylacetamide to a deformation of the group $\begin{array}{c} \text{CH}_3 \\ \diagup \\ \text{---N} \\ \diagdown \\ \text{H} \end{array}$. A final explanation of this problem is still missing, and it

will only be brought to attention, that the spectra of the hydrazides also on this point resemble the N-monosubstituted amides.

Absorption around 1600 cm^{-1} and 1500 cm^{-1} is found in the hydrazides containing a phenyl group, and must be due to this⁸. Only the assignment of the medium or strong band around 1620 cm^{-1} is remaining. Absorption at this frequency is due most often to C=C stretching, C=N stretching or NH₂ deformation⁸. As absorption of the carbon-carbon double bond is most often weak, and as only cinnamic acid hydrazide contains this bond, absorption can not originate here. If the absorption is assigned to a C=N group it must involve a ketone-enol equilibrium in the solid state, which is most unlikely. It is therefore most reasonable to assign the absorption around 1620 cm^{-1} to a NH₂ deformation frequency in conformity with what is observed in primary amines⁸. This assignment may be further evidenced by the fact, that this band is absent in the spectra of the hydrohalides³.

From Figs. 1 and 2 it is seen that the spectrum of cinnamic acid hydrazide synthesized by the method of Godtfredsen and Vangedal¹ is in exact agreement with the spectra of the other hydrazides, while 3-phenyl-5-pyrazolidone, which Muckermann² believed to be cinnamic acid hydrazide, differs in essential degree. This may be regarded as a further proof of the structure determinations of these compounds accomplished by Godtfredsen and Vangedal¹.

The variations mentioned in the spectra on passing from dilute chloroform solution to solids may be ascribed to association of the molecules in the solid state under the formation of hydrogen bonds. A concrete proof of this can be derived from the spectra in the $3\ \mu$ region, as it is well established that free —NH-groups give rise to narrow bands in the region $3500\text{--}3300\text{ cm}^{-1}$ while the bonded groups give rise to broader bands at somewhat lower frequencies⁸. The employed rock salt optics, however, are not suitable for measurements in this region due to low resolution, and the experimental technique in recording the spectra of solids is complicated by scattering.

For this reason, reference is made only to the measurements which are performed on phenylacetic acid hydrazide. Although they cannot be regarded as exhaustive, they form a basis sufficient to verify that association takes place in concentrated solutions and in the solid state.

Figs. 3 and 4 show the spectra of phenylacetic acid hydrazide in the solid state and in chloroform solution, respectively. The spectrum of the chloroform solution shows a narrow band of high intensity at approximately 3450 cm^{-1} , and a weaker broad one at approximately 3340 cm^{-1} . An eventual absorption at lower frequency is difficult to measure due to the background absorption of the chloroform. The spectrum of the solid substance lacks ab-

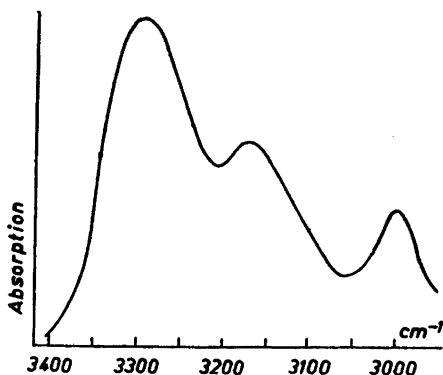


Fig. 3. I.R.-spectrum of phenyl acetic acid hydrazide in the solid state (0.5% in KBr).

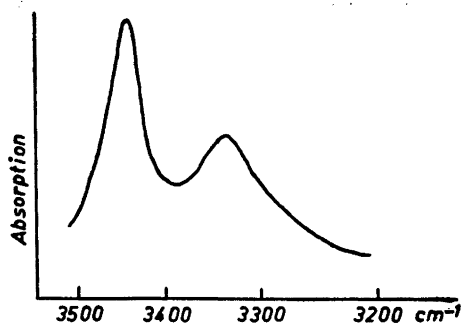


Fig. 4. I.R. spectrum of phenylacetic acid hydrazide (1% in CHCl_3).

sorption at 3450 cm^{-1} , instead an intense band is found centered around 3300 cm^{-1} , a weaker broad band around 3175 cm^{-1} , and furthermore a weak band at approximately 3000 cm^{-1} . There is no doubt that a complete association takes place in the solid state, as the narrow band in the solution must be assigned to a free —NH— group, while the broad band in the spectrum of the solid substance is due to a bonded —NH— group.

The absorption at 3340 cm^{-1} found in the chloroform solution may consist of two bands unresolved by the available spectrograph. However, the absorption at this frequency increases more rapidly at increasing concentrations than the absorption at 3450 cm^{-1} . This fact may be explained by association in concentrated solutions.

On the basis of the measurements carried out here it is, however, difficult to determine in which form association takes place. It may be mentioned that during the time this work was done, a publication by Jensen¹¹ on X-ray crystallographic investigations of isonicotinic acid hydrazide appeared, in which the author claims the existence of hydrogen bonds of the type NH---N . However it seems most unreasonable not to consider hydrogen bonds of the NH---OC type, solely because the frequency of the carbonyl group in the $6\ \mu$ region is displaced significantly to higher frequencies when passing from the solid state to dilute solutions.

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REFERENCES

1. Godtfredsen, W. O. and Vangedal, I. S. *XIVth International Congress of Pure and Applied Chemistry, Zürich 1955, Congress Handbook*, p. 232.
2. Muckermann, E. *Ber.* **42** (1909) 3449.
3. Lenormant, H. *Bull. soc. chim. France* [5] **15** (1948) 33.
4. Mattu, F. and Pirisi, E. *Ann. Chim. Rome* **43** (1953) 580.

5. Foreman, R. W. and Jackson, W. Jr. *Instruments* **22** (1949) 497.
6. Clauson-Kaas, N., Nedenskov, P., Bak, B. and Rastrup-Andersen, J. *Acta Chem. Scand.* **8** (1954) 1088.
7. Jensen, J. B. *Ibid.* **8** (1954) 393.
8. Bellamy, J. L. *The infrared spectra of complex molecules*, Methuen, London 1954.
9. Richards, R. E. and Thompson, H. W. *J. Chem. Soc.* **1947** 1248.
10. Gierer, A. *Z. Naturforsch.* **8 b** (1953) 644.
11. Jensen, L. H. *J. Am. Chem. Soc.* **76** (1954) 4663.

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