

IR SPECTRAL CHARACTERISTICS OF NONCYCLIC DIACYLIMIDES*

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Open chain diacylimides have N—H frequencies higher than cyclic diacylimides. The occurrence of several weak bands in the region 3300–3100 cm^{-1} along with a regular N—H band may be considered as characteristic of noncyclic diacylimides. By contrast the two carbonyl bands of cyclic diacylimides, appear as one strong band at 1735–1720 cm^{-1} in the noncyclic compounds with a weak shoulder at 1690–1680 cm^{-1} .

To study the pharmacology and IR spectral characteristics of the cyclobutane ring system, we have synthesized 65 new imides and amides of several cyclobutane carboxylic acids.¹ We have earlier reported frequencies characteristic of the cyclobutane ring system.² A survey of the relevant literature showed that the paucity of IR spectroscopic information on the —CONHCO— group derives from studies on cyclic diacylimides i.e. hydantoin, succinimides, the purines and related products.³ In this communication we wish to supplement the small body of information on frequencies due to the —CONHCO— grouping in noncyclic diacylimides. Further, we wish to discuss some features of the carbonyl absorption and N—H stretching vibrations in cyclobutane compounds other than diacylimides i.e. amides, ureides and hydrazides.

Experimental

All spectra were determined in either dilute chloroform solution or potassium chloride pellets and recorded in the region between 4000–625 cm^{-1} using a Perkin-Elmer Model 237 grating type IR spectrophotometer. The machine used in this work recorded frequency linearly. Accuracy of the measurements is estimated to be $\pm 2 \text{ cm}^{-1}$. The scan speed was 24 min per drum revolution.

Discussion

The —CONHCO—group does not commonly occur in noncyclic compounds, it is found, however, in many cyclic materials such as hydantoin, succinimides and purines. To better differentiate cyclic and noncyclic diacylimides we compared the N—H stretching and carbonyl absorption frequencies in 34 new noncyclic diacylimides i.e.

imides of certain cyclobutane carboxylic acids, with those of cyclic diacylimides.

N—H Stretching Absorption.—Bellamy³ has reported cyclic diacylimides like hydantoin and succinimides in the solid state show a single, bonded amide NH absorption in the 3200 cm^{-1} region. Randall *et al.*⁴ have reported that since solid and solution spectra of cyclic diacylimides are similar, there must be little hydrogen bonding in the solid state. However, it is difficult to reconcile this point of view with the low frequencies reported for the N—H stretching band in both solid state and dilute solution spectra. In our studies most of the imide and diimide solid state spectra show a sharp band at 3265–3250 cm^{-1} plus several weak bands at 3300–3100 cm^{-1} attributable to N—H stretching vibrations, instead of a single, bonded amide NH absorption in the 3200 cm^{-1} region. The strongest of the 3300–3100 cm^{-1} bands is recorded in Table 1. In dilute chloroform solution, most of the noncyclic diacylimides show a shift of the 3265–3250 cm^{-1} band to 3400 cm^{-1} (Table 1). The 3300–3100 cm^{-1} bands are unaffected. The low frequency bands appear to be due to hydrogen bonding. The major difference in the N—H frequencies for noncyclic and cyclic diacylimides appears to be that the noncyclic compounds have N—H bands at higher frequencies. Further, while no band due to hydrogen bonding appears in the cyclic diacylimide spectra, the noncyclic compounds have several weak intensity bands. This suggests, that several weak bands in the region 3300–3100 cm^{-1} may be characteristic of the noncyclic diacylimides.

Carbonyl Absorption.—In the solid state cyclic diacylimides show two widely separated carbonyl bands³ in the region 1790–1720 and 1710–1670 cm^{-1} . Solid state spectra of the noncyclic diacylimides show a single band at 1735–1720 cm^{-1} with a shoulder at 1690–1680 cm^{-1} (Table 1). The 1690–1680 cm^{-1} band is generally so weak that it is undetectable. However, in dilute chloroform

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TABLE I.—IR FREQUENCIES OF CERTAIN NONCYCLIC DIACYLIMIDES.

Acyl group		1800–1600 cm ⁻¹	3450–3100 cm ⁻¹	Acyl group		1800–1600 cm ⁻¹	3450–3100 cm ⁻¹
N-Acylcyclobutanecarboxamides				Crotonyl	S	1730	3250, 3150
Formyl ⁶	S ^a	1745, 1675	3260, 3190	4-Hydroxybutyryl	C	1725, 1690	3400, 3250
	C ^b	1745, 1685	3400, 3250		S	1730	3355, 3190
Acetyl ⁶	S	1725	3255, 3170	C	1725, 1680	3395, 3250	
	C	1740, 1685	3395, 3255	Phenylacetyl	S	1725, 1690	3260, 3170
Propionyl ⁶	S	1725, 1690	3256, 3160	C	1730, 1690	3395, 3255	
	C	1735, 1690	3395, 3255	Chloroacetyl	S	1745, 1700	3260, 3180
Butyryl ⁶	S	1730	3265, 3190	C	1725, 1700	3350, 3240	
	C	1735, 1690	3395, 3255	Dichloroacetyl	S	1745, 1700	3260, 3175
Valeryl ⁶	S	1730, 1690	3250, 3155	C	1775, 1740	3370	
	C	1735, 1690	3400, 3255	3, 5-Dimethoxybenzoyl	S	1710, 1680	3290
Hexanoyl ⁶	S	1730	3255, 3175	C	1720, 1690	3400, 3255	
	C	1730, 1690	3395, 3255	3-Methoxybenzoyl	S	1735, 1680	3340
Heptanoyl	S	1725, 1655	3255, 3155	C	1745, 1685	3340, 3155	
	C	1730, 1690	3400, 3250	2-Methoxybenzoyl	S	1700, 1670	3295
Octanoyl	S	1735	3260, 3180	C	1720, 1690	3400, 3255	
	C	1730, 1690	3400, 3255	Benzoyl	S	1720, 1675	3250, 3145
Nonanoyl	S	1730, 1690	3245, 3155	C	1720, 1690	3400, 3250	
	C	1730, 1690	3395, 3250	2-Furoyl	S	1710, 1670	3240, 3110
Lauroyl ⁶	S	1735	3240, 3145	C	1710, 1690	3395	
	C	1735, 1690	3395, 3250	3,4,5-Trimethoxybenzoyl	S	1705, 1670	3270
Cyclopentanepropionyl	S	1725, 1690	3255, 3160	C	1710, 1690	3395, 3255	
	C	1730, 1690	3400, 3250	4-Methoxybenzoyl	S	1705, 1675	3280, 3155
Isovaleryl ⁶	S	1725	3260, 3170	C	1720, 1690	3400, 3255	
	C	1745, 1690	3395, 3255	N,N'-Diacylcyclobutane-1,1-dicarboxamides			
Isobutyryl ⁶	S	1730, 1690	3250, 3160	Acetyl	S	1725, 1685	3255, 3175
	C	1730, 1690	3395, 3250	C	<u> </u> ^c	<u> </u>	
Pivaloyl ⁶	S	1735, 1695	3290, 3170	Propionyl	S	1735, 1700	3260, 3175
	C	1720, 1685	3400, 3250	C	<u> </u>	<u> </u>	
Cyclohexanecarbonyl	S	1725, 1680	3260, 3160	Hexanoyl	S	1735, 1720	3290, 3205
	C	1720, 1690	3400, 3250	C	1725, 1700	3400, 3260	
1-Adamantanecarbonyl	S	1730	3250, 3150	Cyclobutanecarbonyl	S	1725, 1690	3270, 3190
	C	1725, 1690	3400, 3250	C	<u> </u>	<u> </u>	
Methacryloyl	S	1725, 1680	3260, 3160	Pivaloyl	S	1730, 1680	3325
	C	1720, 1690	3400, 3250	C	<u> </u>	<u> </u>	

S^a=solid state, C^b=chloroform solution, ^c, insoluble in chloroform.

solution the compounds show two widely separated bands at 1745–1725 and 1700–1670 cm⁻¹ (Table I). The major difference in the carbonyl absorption region in cyclic and noncyclic diacylimides appears to be that in the latter case one of the two normal carbonyl bands is much attenuated and appears as a shoulder to the other band. Furthermore, the carbonyl frequency range in the noncyclic compounds is narrowed and there is no apparent influence of structure on these bands.

Most of the 27 secondary amides (i.e. *N*-substituted cyclobutanecarboxamides and cyclobutane-1,

1-dicarboxamides), in dilute chloroform solution show two bands at 3450–3430 and 3320–3300 cm⁻¹, typical of free and hydrogen bonded N—H stretch modes.^{3,5} All have sharp amide I and II bands at 1680–1650 and 1525–1510 cm⁻¹. Additionally, the *N*-substituted diamides show an amide III band at 1285–1275 cm⁻¹. In the *N*-substituted cyclobutanecarboxamides, however, this band is either very weak or absent. Their solid state spectra show a principal N—H band at 3300–3270 cm⁻¹. The amide II band is shifted towards slightly higher frequencies and the amide

I band is unaffected. There is no influence of structure on the amide I, II, III and N—H frequencies.⁵ Exceptions to this generalization are *N*-2-carboxyphenylcyclobutanecarboxamide and its methyl and ethyl esters. In dilute chloroform solution these compounds showed indistinguishable broad, weak bands in the N—H region. However, in concentrated chloroform solution they show a broad N—H band at 3500 cm^{-1} instead of the two normal bands.⁵

The substituted urea derivatives of cyclobutanecarboxylic acid show two amide I bands instead of one corresponding to two CONH groups.⁵ The bands fall at $1685\text{--}1670$ and $1720\text{--}1695\text{ cm}^{-1}$. As the solid and solution spectra of these compounds are clearly similar,⁵ there is little hydrogen bonding in the solid state.

The solid state spectra of the substituted hydrazides derived from cyclobutanecarboxylic acid differ slightly from those of secondary amides. The N—H stretch in the hydrazides falls near 3200 cm^{-1} . In 1,2-dicyclobutanecarbonyl hydrazine, the amide I and II bands fall at frequencies lower than in secondary amides but in chloroform solution its spectrum is similar to those of the secondary amides.⁵

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