

266. *The Infrared Spectra of Some Diacylamines in the 6 μ Region.*

By R. A. ABRAMOVITCH.

Diacetylamino-compounds show more than one amide carbonyl stretching band in the 6 μ region, but in dilute solution and with a slit schedule of 1.5 mm. only one band is observed; this is resolvable into its component bands at narrower slit schedules. Dilution experiments show the absence of molecular association. The multiplicity of bands is attributed to vibrational coupling of the C=O groups.

DURING a study of the 1 : 2 : 3 : 4-tetrahydro-1-oxo- β -carbolines it was observed¹ that a 2-acetyl derivative exhibited two bands, attributed to amide carbonyl stretching vibrations, in the 6 μ infrared region. Similar observations had been made² on compounds containing the group -CO-NH-CO- in a cyclic structure, *e.g.*, succinimides; the two bands found, one between 5.6 μ and 5.8 μ and the other between 5.85 μ and 6.00 μ , were assigned one to each of the cyclic carbonyl groups. Spectra of solutions and solid were reported to be very similar and the absence of hydrogen bonding was demonstrated by the fact that *N*-pentylsuccinimide also had both bands. On the other hand, *N*-bromosuccinimide has only one band³ at 1732 cm.⁻¹ in solution (1710 cm.⁻¹ in the solid state). Molecules containing the group -CO-NR-CO- not as part of a ring have not been investigated systematically. In some cases one band is reported for diacylamino-compounds, in others two. Grove, Jeffs, and Rustidge⁴ and Witkop and Patrick⁵ have reported the spectra of a number of substituted *NN*-diacetylanilines, as summarised in Table 1. Their data seem to indicate that if the diacylamine is symmetrically substituted only one carbonyl band is observed in the 6 μ region, whereas if it is unsymmetrically substituted, two bands are observed. This is not in accord with the results obtained with the succinimides, for instance, where symmetrical ring compounds show two carbonyl bands.² A single band at 1694 cm.⁻¹ is reported by Orr, Sims, and Manson⁶ for an unsymmetrically

¹ Abramovitch, *J.*, 1956, 4593.

² Randall, Fowler, Fuson, and Dargl, "Infrared Determination of Organic Structures," Van Nostrand, New York, 1949, p. 14.

³ Gierer, *Z. Naturforsch.*, 1953, 8b, 654.

⁴ Grove, Jeffs, and Rustidge, *J.*, 1956, 1956.

⁵ Witkop and Patrick, *J. Amer. Chem. Soc.*, 1952, 74, 3861.

⁶ Orr, Sims, and Manson, *J.*, 1956, 1337.

substituted dibenzoylamino-compound, whereas diacetylamine itself is stated to exhibit a single carbonyl peak at 1708 cm^{-1} (in chloroform). Simple *NN*-diacetylanilines have now been examined to see whether there is any justification in the apparent pattern: symmetrical, one band; unsymmetrical, two bands. The compounds studied include

TABLE 1.

Compound	Ref.	ν (cm^{-1})
2 : 6-Diacetoxy- <i>NN</i> -diacetyl-4-methoxyaniline	4	1717 *
<i>NN</i> -Diacetyl-2 : 6-dibenzoyloxy-4-methoxyaniline	4	1710 *
2 : 4-Diacetoxy- <i>NN</i> -diacetyl-6-methoxyaniline	4	1730, 1705 *
<i>NN</i> -Diacetyl-2-benzoyloxy-4 : 6-dimethoxyaniline	4	1716, 1696 *
2-Acetoxy- <i>NN</i> -diacetyl-4 : 6-dimethoxyaniline	4	1719, 1706 *
4-Acetoxy- <i>NN</i> -diacetyl-2 : 6-dimethoxyaniline	4	1715 *
<i>NN</i> -Diacetyl-2-benzoyloxyaniline	5	1724, 1712 ^b
2-Acetoxy- <i>NN</i> -diacetylaniline	5	1730, 1709 ^b
<i>NN</i> -Diacetyl-2-methoxyaniline	5	1718, 1706 ^b

* Nujol mull. ^b Chloroform solution.

symmetrically and unsymmetrically monosubstituted diacetylanilines, diacetylbenzylamine, and diacetylnaphthylamines. A number of mixed diacylamines (acyl groups not identical) were also examined, and succinimide and *N*-bromosuccinimide re-examined.

EXPERIMENTAL

Most of the diacetylanilines were prepared by Sudborough's general method.⁷ *NN*-Diacetyl-*o*-anisidine was prepared as described by Witkop and Patrick,⁶ and *NN*-diacetylbenzylamine as described by Holmes and Ingold.⁸

NN-Diacetyl-*m*-toluidine had b. p. 164—168°/16 mm. (Found: C, 68.8; H, 7.1. $\text{C}_{11}\text{H}_{13}\text{O}_2\text{N}$ requires C, 69.1; H, 6.8%).

NN-Diacetyl-*p*-anisidine formed needles, m. p. 60° [from light petroleum (b. p. 40—60°)] (Found: C, 63.5; H, 6.5. $\text{C}_{11}\text{H}_{13}\text{O}_2\text{N}$ requires C, 63.8; H, 6.3%).

N-Acetyloxindole was prepared as described by Suida.⁹ 2-Acetyl-1 : 2 : 3 : 4-tetrahydro-1-oxo- β -carboline has already been described.¹

2-Acetyl-1 : 2 : 3 : 4-tetrahydro-9-methyl-1-oxo- β -carboline.—1 : 2 : 3 : 4-Tetrahydro-9-methyl-1-oxo- β -carboline¹ was refluxed for 2 hr. with an excess of acetic anhydride and a few drops of acetic acid, and the solution poured into water. The product crystallised from methanol in colourless rods, m. p. 108—109° (Found: C, 69.4; H, 7.2. $\text{C}_{14}\text{H}_{14}\text{O}_2\text{N}_2$ requires C, 69.4; H, 7.3%).

TABLE 2. Amide carbonyl frequencies (cm^{-1}) of diacetylamino-compounds as liquid films or Nujol mulls.

<i>NN</i> -Diacetyl-	ν (cm^{-1})	<i>NN</i> -Diacetyl-	ν (cm^{-1})
Benzylamine *	1727 (sh), 1718, 1701	<i>m</i> -Toluidine *	1730 1715 1706 (sh)
1-Naphthylamine ^b ...	1727, 1706		(broad)(broad)
2-Naphthylamine ^b ...	1727 (sh), ^c 1712 (broad)	<i>p</i> -Toluidine *	1727, 1720, 1706 (sh)
Aniline *	1724 (sh), 1712, 1701 (sh) *	<i>o</i> -Anisidine *	1728, 1720, 1704 (sh)
Aniline *	1724 (sh), 1709 (sh), 1701	<i>p</i> -Anisidine *	1728, 1718, 1709 (sh) *
<i>o</i> -Toluidine *	1733, 1720, 1689 (sh)m	<i>p</i> -Anisidine ^b	1730, 1712

All the extinction coefficients are high. Slit schedule 1.5 mm. (except for diacetylaniline). * Liquid film. ^b Nujol mull. ^c Slit schedule 1 mm. ^d Slit schedule 0.5 mm. ^e Not very well defined shoulder.

2-Acetyl-1 : 2 : 3 : 4-tetrahydro-7-methoxy-9-methyl-1-oxo- β -carboline.—Prepared as above from the oxocarboline,¹ the acetyl derivative formed colourless rods, m. p. 162° (Found: C, 65.8; H, 6.1. $\text{C}_{15}\text{H}_{16}\text{O}_3\text{N}_2$ requires C, 66.2; H, 5.9%), from alcohol.

2-Acetyl-1 : 2 : 3 : 4-tetrahydro-8-methyl-1-oxo- β -carboline, m. p. 146—147°, was similarly

⁷ Sudborough, *J.*, 1901, **79**, 533.

⁸ Holmes and Ingold, *J.*, 1925, **127**, 1800.

⁹ Suida, *Ber.*, 1879, **12**, 1327.

obtained as pale yellow needles from alcohol (Found : C, 68.9; H, 5.8. $C_{14}H_{14}O_2N_2$ requires C, 69.4; H, 5.8%).

Infrared Spectra.—A Grubb-Parsons double-beam spectrometer, type S4, with a sodium chloride prism was used. The frequency scale was calibrated by ammonia vapour bands (accuracy ± 5 cm^{-1} in the 6 μ region). "AnalaR" chloroform was used. The measurements on mulls and liquid films were carried out with a slit schedule of 1.5 mm. (except for diacetyl-aniline, when measurements were carried out at slit schedules of 1 mm. and 0.5 mm.).

TABLE 3. Carbonyl frequencies (cm^{-1}) of chloroform solutions of diacylamines. Effect of altering slit schedule and concentration (constant cell thickness of 0.01 in.).

	Slit schedule 1.5 mm.		Slit schedule 0.5 mm.		
	50 mg./c.c.	10 mg./c.c.	50 mg./c.c.	10 mg./c.c.	10 mg./c.c.
<i>NN</i> -Diacetyl-Benzylamine ...	1718 s, 1701 s	1709 s	1727 (sh)m, 1709 (sh)s, 1689 s	1727 (sh)w, 1712 (sh)ms, 1698 s, 1686 (sh)m	
1-Naphthylamine	1739 (sh)s, 1727 s	1724 s	1727 (sh)s, 1706 (sh)s, 1698 s	1727 (sh)m, 1709 s, 1701 (sh)m	
2-Naphthylamine	1730 (sh)s, 1718 s	1721 s	1730 (sh)m, 1709 (sh)s, 1701 s	1727 (sh)m, 1709 s, 1701 (sh)s	
Aniline	1721 (sh)s, 1709 s (broad)	1718 s	1727 (sh)ms, 1706 (sh)s, 1695 s	1724 (sh)m, 1704 s, 1698 (sh)s	
<i>o</i> -Toluidine	1727 s, 1712 s (broad)	1718 s	1727 (sh)m, 1706 (sh)s, 1701 s	1727 (sh)m, 1709 s, 1701 (sh)s	
<i>m</i> -Toluidine	1733 s, 1718 s (broad)	1718 s	1727 (sh)s, 1709 (sh)s, 1695 s	1727 (sh)m, 1709 s, 1701 (sh)s	
<i>p</i> -Toluidine	1727 (sh)s, 1709 s (broad)	1718 s	1724 (sh)m, 1704 (sh)s, 1692 s	1727 (sh)w, 1706 s, 1701 (sh)s	
<i>o</i> -Anisidine	1727 (sh)s, 1718 s (broad)	1718 s	1727 (sh)ms, 1709 (sh)s, 1701 s	1727 (sh)m, 1709 s, 1701 (sh)s	
<i>p</i> -Anisidine	1727 (sh)s, 1715 s (broad)	1718 s	1727 (sh)ms, 1706 (sh)s, 1698 s	1727 (sh)m, 1706 s, 1701 (sh)s	

TABLE 4. Amide carbonyl frequencies (cm^{-1}) of chloroform solutions of some diacylamines. Effect of dilution (variable cell thickness).

Compound	Slit schedule (mm.)	Concn. (mg./c.c.)	Cell thickness (in.)	ν
<i>NN</i> -Diacetyl-1-naphthylamine	0.5	100	0.0025	1724 (sh)m 1698 s
	0.5	50	0.005	1686 (sh)s 1724 (sh)m 1701 s
	0.5	10	0.025	1692 (sh)s 1724 (sh)m 1701 s
	1.5	100	0.0025	1692 (sh)s 1724 (sh)s 1715 s
	1.5	50	0.005	1724 (sh)s 1712 s
	1.5	10	0.025	1715 s
<i>NN</i> -Diacetyl- <i>p</i> -anisidine	0.5	50	0.005	1724 (sh)m 1701 s
	0.5	10	0.025	1692 (sh)s 1724 (sh)m 1701 s
	1.5	50	0.005	1686 (sh)s 1715 s
	1.5	10	0.025	1715 s

Chloroform solution spectra were measured at slit schedules of both 1.5 mm. and 0.5 mm. to obtain better resolution. A variable-path cell was used to study the effect of dilution, *e.g.*, when the concentration of the solution was halved the cell-thickness was doubled.

The results are summarised in Tables 2, 3, 4, and 5; abbreviations have their usual meanings (sh = shoulder).

TABLE 5. *Amide carbonyl frequencies (cm.⁻¹) of miscellaneous diacylamino-compounds. (Slit schedule 1.5 mm.)*

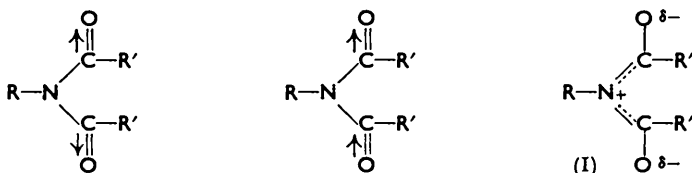
Compound	ν	Compound	ν
<i>N</i> -Acetyloxindole •	1770 s	Succinimide •	1786 s
	1689 s		1727 (sh)s
<i>N</i> -Acetyloxindole †	1770 s		1715 s broad
	1689 s	Succinimide †	1786 mw
2-Acetyl-1 : 2 : 3 : 4-tetrahydro-1-oxo- β -carboline •	1701 s		1764 m
	1672 s		1730 s
2-Acetyl-1 : 2 : 3 : 4-tetrahydro-9-methyl-1-oxo- β -carboline •	1701 (sh)s •	<i>N</i> -Bromosuccinimide •	1783 m
	1686 s		1727 (sh)
2-Acetyl-1 : 2 : 3 : 4-tetrahydro-7-methoxy-9-methyl-1-oxo- β -carboline •	1686 s broad		1709 s broad
	1672 (sh)s	<i>N</i> -Bromosuccinimide †	1783 (sh) vw
	1695 s		1733 s
2-Acetyl-1 : 2 : 3 : 4-tetrahydro-8-methyl-1-oxo- β -carboline •	1675 s	<i>N</i> -Bromosuccinimide †, ‡	1730 (sh)m
			1721 s
			1715 (sh)s
			1698 (sh)m

• Nujol mull. † Dilute chloroform solution. • Not very well defined shoulder. ‡ Slit schedule 0.5 mm.

DISCUSSION

In all the compounds examined at least two bands appear in the 6 μ region, both of which can be attributed to amide carbonyl stretching vibrations. In many cases some of the bands only appear as shoulders and these may not be very well defined. Also, as can be seen from Table 3 (column 2) when very dilute chloroform solutions are used, with slit schedules of 1.5 mm., the diacetylanilines exhibit a single strong sharp peak at 1718 cm.⁻¹, though this can be resolved into its component bands by using narrower slit schedules, as the data in the last column of Table 3 show. The possible symmetry effect, mentioned in connection with the data in Table 1, does not, in fact, exist and it seems probable that all *NN*-diacylamino-compounds exhibit doublets for the amide absorption if examined at sufficiently slow chart speeds and narrow enough slit schedules. Thus, contrary to report,³ *N*-bromosuccinimide shows more than one carbonyl band in the region (Table 5).

The measurements in chloroform solution rule out the possibility that the multiplicity of bands could be due to association in the condensed state. This is even better illustrated in the dilution experiments carried out with *NN*-diacetyl-1-naphthylamine and diacetyl-*p*-anisidine (these compounds were chosen because of the very well-defined bands they show in the solid state) and by varying the path length in inverse ratio to the dilution (Table 4), when no change, in either position or apparent intensity of the bands, is observed. This is in agreement with the results obtained by Hunter and Reynolds¹⁰ who showed, by cryoscopic measurements on various diacylamines, that when no imido-hydrogen is present molecular association is completely suppressed.



There seems to be no reason to attribute either of the bands to a specific carbonyl group, as has been done³ in the cases of the succinimides, for instance. It appears more likely that this multiplicity of bands is a further example of the more general case of vibrational coupling between carbonyl groups¹¹ of which diacyl and diaroxy peroxides and acid anhydrides are others. The main bands observed could, for instance, be attributed

¹⁰ Hunter and Reynolds, *J.*, 1950, 2857.

¹¹ Jones and Sandorfy, "Technique of Organic Chemistry. Vol. IX. Chemical Applications of Spectroscopy." Interscience, London, 1956, p. 495.

to symmetrical and unsymmetrical vibrational coupling of the two carbonyl groups. In the symmetrical acid anhydrides the bands may be separated by 65 cm.^{-1} compared with $20\text{--}30\text{ cm.}^{-1}$ in symmetrical peroxides.¹¹ In the mixed diacylamines there is more justification for attributing the separate bands to the individual amide carbonyl groups, since the difference in the fundamental stretching frequency of the two carbonyl groups will make coupling between these groups less likely.

As has already been noted,⁴⁻⁶ the C=O absorption in *NN*-diacetyl derivatives is at higher frequencies than the C=O absorption in the corresponding monoacetyl compound. This is in agreement with the effect of the presence of electrophilic groups on the nitrogen atom¹² which increase the double-bond character of the carbonyl group and also with the fact that the effect of the positive charge on the nitrogen atom in the dipolar form is shared between the two acetyl groups (I), with the same result. The appearance of a doublet in this region, together with the absence of NH bands in the $3\ \mu$ region, can then be used to distinguish between diacetyl- and monoacetyl-amino-derivatives, as suggested by Grove, Jeffs, and Rustidge.⁴

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KING'S COLLEGE (UNIVERSITY OF LONDON),
STRAND, LONDON, W.C.2.

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¹² Richards and Thompson, *J.*, 1947, 1248.
