

The infrared spectra and the structure of some homophthalimides*

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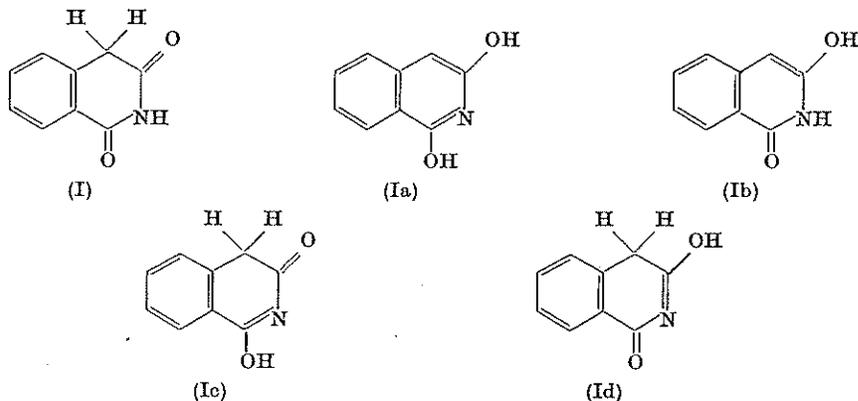
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Abstract—The spectra of NH and NCH₃ homophthalimides in the solid and solution phase have been observed and the various absorption bands have been correlated with functional groupings in the compounds. In the solid state and in concentrated solution, the NH homophthalimides are associated by intermolecular hydrogen bonds between the 1-carbonyl and imide groups. The assignment of a di-keto configuration to the structure of homophthalimides is most consistent with the observed spectra.

Introduction

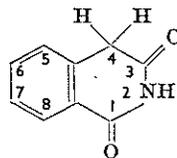
The infrared absorption spectra of homophthalimides† as a group have not been treated previously, although some references to the spectra of certain homophthalimides have been made [1, 2, 3]. The homophthalimides present an interesting problem because of the various tautomers which can exist, e.g. (I)–(Id).



Previous investigations have not arrived at an unambiguous structural assignment [1, 2, 4, 5, 6].

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† According to I.U.C. nomenclature, homophthalimides are named as 1:3-dioxo-2:4:4-trihydroisoquinolines. In this report they are named as substituted homophthalimides and the ring atoms are numbered as follows:



The problem of elucidating structure where a number of tautomers is possible is common also to other compounds containing the —CONHCO— group, e.g. phthalimides, succinimides, uracils, hydroxyprimidines and related compounds. Infrared absorption studies on some of these compounds have enabled structural assignments to be made [7, 8].

The present work describes the spectra of seven homophthalimides. The changes observed when comparing spectra obtained in the solid phase and in solution are useful in the elucidation of the structure of this group of compounds.

Experimental

The infrared spectra were determined on a Beckman Infrared Spectrophotometer, Model IR-3, equipped with lithium fluoride or sodium chloride optics and on a Baird, Model A, spectrometer. A polystyrene film was used to calibrate the instruments. Samples were measured either as solid dispersions in pressed potassium bromide pellets against a pure potassium bromide pellet or as solutions

Table 1. Infrared spectra of some homophthalimides (cm^{-1}). Pressed KBr dispersions

(I) Homophthalimide	(II) 7:8-Dimethoxyhomophthalimide	(III) 4-(3':4'-Methylenedioxyphenylethyl)-7:8-dimethoxyhomophthalimide	(IV) 4:4-Dimethylhomophthalimide	(V) 2-Methylhomophthalimide	(VI) 2-Methyl-7:8-dimethoxyhomophthalimide	(VII) 2:4:4-Tri-methylhomophthalimide
3175	3194	3175	3215	2882	2950	2949
3077	3086	3086	3096	1718 s	2849	2915
2950	2950	2941	2985	1667 s	1712 s	2857
2857	2841	2849	2941	1610	1675 s	1712 s
1706 s	1704 s	1704 s	2865	1590	1603	1667
1684 s	1684 s,sh	1678 s	1709 s	1495	1585	1608
1610	1605	1603	1692 s	1473	1497 s	1493
1490	1587	1580	1605	1427	1456	1471
1466	1493	1504	1471	1385	1433	1466
1445	1445	1493 s	1458	1368	1408	1456
1370	1420	1453	1385	1346	1391	1422
1339	1351	1429	1368	1309	1353 s	1389
1287 s	1326	1351	1353	1297	1338	1362 s
1189 w	1293	1333	1294	1247	1314	1307 s
1139	1271	1299	1266	1195	1279 s	1290 s
1031 w	1218	1266 s	1247	1126	1239	1259
922 w	1195	1236	1174	1086	1205	1248
879	1168	1174	1145	1003	1124	1215
806	1149	1151	1038	928	1080	1179
759	1062	1064 sh	969 w	804	1062	1159
740	1050	1052	925	742	1007	1092
682	958	1034	842	686	966	1058
	935 w	1020 sh	820		934	1038
	922 w	985	799		931	990
	876	932	769		832	969
	829	857	756		803	879 w
	801	836	707		792	869 w
	770 w	818	680		738 w	802
	739	792	667		690	771 s
	703	699				700
						679

s = strong; w = weak; sh = shoulder

against the pure solvent as a reference. Harshaw Chemical Co. powdered potassium bromide, infrared quality, was used for the preparation of pressed pellets. Eastman Kodak "Spectro Grade" solvents were used for preparing solutions for infrared examination.

The compounds were obtained from the Chemical Laboratories of Boston University.* Purity was established by comparison of the melting points with reported values from the literature and/or by elementary analyses.

Results and discussion

In Table 1 the frequencies of the absorption bands for the series of compounds are listed. Significant differences can be seen in that compounds (I)–(IV) each show two absorption bands at c. 3077 and 3175 cm^{-1} , whereas compounds (V)–(VII) lack these absorption bands. Thus, if we assume the di-keto structure, e.g. (I), it is convenient to divide the homophthalimides into two groups, based upon the substituent on the 2 (the nitrogen) atom. One group then contains the NH compounds and the other group contains the NCH_3 compounds.

Table 2. NH and C=O stretching frequencies of homophthalimides (cm^{-1})

Compound No.	NH frequencies		C=O frequencies			
	Solid	Solution [†]	Solid		Solution [‡]	
			1C=O	3C=O	1C=O	3C=O
(I)	3077,* 3175*	3378	1684*	1706	1704	1721
(II)	3086,* 3195*	3378	1684*	1704	1704	1715
(III)	3086,* 3175*	3378	1678*	1704	1704	1715
(IV)	3096,* 3215*	3390	1692*	1709	1709	1718
(V)		3086,* [†] 3215,* [†] 3390 [†]			1698,* [†] 1709, [†] 1718 [†]	
(VI)			1667	1718	1681	1727
(VII)			1675	1712	1684	1727
			1667	1712	1678	1721

* These frequencies are perturbed by intermolecular hydrogen bonding.

[†] Concentrated solution.

[‡] Compounds (I)–(III) were studied in CHCl_3 solutions; compounds (IV)–(VII) in CCl_4 solutions.

NH *homophthalimides*. In Table 2 the pertinent absorption frequencies in solid and solution phase are compared. The solutions are dilute enough so that there is no intermolecular hydrogen bonding. The absorption bands in the 3070–3390 cm^{-1} region are assigned to NH stretching modes. The one absorption band at about 3390 cm^{-1} in the spectra of dilute solutions is due to NH stretching in unassociated molecules. The possibility that this band is due to an OH stretching vibration is highly unlikely, as the lower limit for free OH stretching has been generally defined at 3509 cm^{-1} , and 3610 cm^{-1} is the usual assignment for unbonded enolic OH [9, 10]. Figure 1 demonstrates the shifts which occur in the 3070–3400 cm^{-1} region for 4:4-dimethylhomophthalimide when comparing the spectrum of the compound in the solid phase to spectra of solutions of decreasing concentration. The appearance of two broader bands at lower frequencies (c.

* The samples were kindly provided by Professor W. J. GENSLER and Mrs. N. WANG.

3077 cm^{-1} , 3175 cm^{-1}) which are found in the solid phase and the concentrated solution spectra are characteristic of hydrogen bonded NH groups in secondary amides [11]. In a study of peptide linkages DARMON and SUTHERLAND [12] and DARMON [13] have observed two absorption bands at 3058 and 3175 cm^{-1} . The band at 3175 cm^{-1} was attributed to associated NH in the *cis*-form of $-\text{CONH}-$. In the non-cyclic amides the 3175 cm^{-1} band is replaced by an absorption at

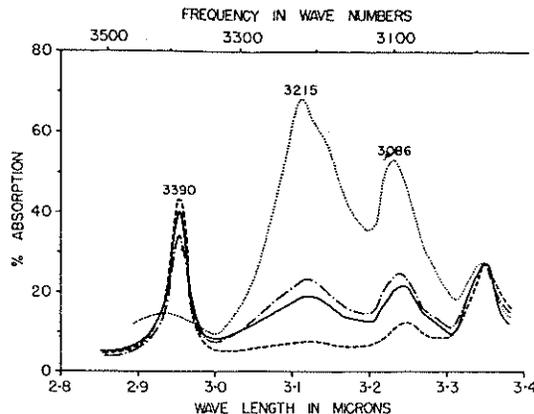


Fig. 1.

3279 cm^{-1} , which has been attributed to associated NH in the *trans*-configuration [12, 13, 14]. The appearance of a bonded NH vibration at 3155–3215 cm^{-1} in the homophthalimides in which the $-\text{CONH}-$ configuration must be *cis*, is in agreement with the above reports.

On dilution, the hydrogen bonds are broken as indicated by the disappearance of the absorptions at 3077 and 3175 cm^{-1} , and the appearance of only one absorption at 3378 cm^{-1} . From the band shifts observed in the 1667–1754 cm^{-1} region it is apparent that a carbonyl group is taking part in this association. Assuming a di-keto configuration, the 1- and 3-carbonyl positions are not equivalent and as pointed out later, non-coplanar. Therefore, two absorptions little affected by coupling would be expected. In the homophthalimides, two very intense bands are found in this region. Since the 1-carbonyl position is conjugated with the phenyl ring, the absorption band at the lower frequency (c. 1706 cm^{-1} for dilute solutions) can be assigned to that group. The band at c. 1721 cm^{-1} may be assigned to the absorption of the carbonyl in the 3-position.

Comparison of the carbonyl group band shifts in Table 2 indicates that only the 1-carbonyl group of the NH homophthalimides is involved in the intermolecular bonding. In the NCH_3 compounds, which are not involved in any bonding (discussed further on), the band shifts of the 1- and 3-carbonyl groups on going from the solid to solution phase are from 9–15 cm^{-1} (mean value is 11 cm^{-1}). These shifts are attributed to phase change. MIYAZAWA, SHIMANOCHI and MIZUSHIMA [15] have recently reported that the carbonyl absorption band in amides shifts to lower frequencies on passing from solution to the crystalline state. In the NH homophthalimides the shifts for the 3-carbonyl absorption band are

about the same as found in the NCH_3 compounds. However, the 1-carbonyl group bands shift to a lower frequency by larger amounts (mean value is 21 cm^{-1}). This shift is attributed to the change in phase plus the effect of intermolecular hydrogen bonding. It is expected that the 1-carbonyl group which is made more electronegative by the conjugative effect of the aromatic nucleus, would be involved almost exclusively (over the 3-carbonyl position) in hydrogen bonding.

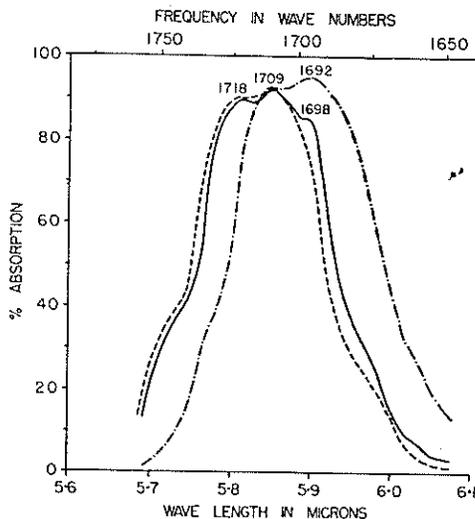
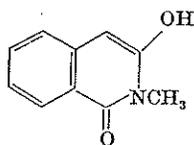


Fig. 2.

This interpretation is substantiated by the data from the studies on 4:4-dimethyl homophthalimide, (IV) (see Table 2 and Fig. 2). The spectrum of a dilute solution shows two bands at 1709 and 1718 cm^{-1} which are assigned to the unassociated carbonyl groups at the 1- and 3-positions respectively. In a concentrated solution some of the molecules are in the associated form and the appearance of the band at 1698 cm^{-1} , since there is no phase change, can be due only to hydrogen bonding involving the 1-carbonyl group.

NCH_3 homophthalimides. Interpretation of the infrared spectra of the NCH_3 homophthalimides is simplified by the absence of any absorption bands in the 3070 – 3390 cm^{-1} region. The presence of an OH group and, therefore, tautomers such as (Va) are eliminated. Compound (VII) is uncomplicated since it cannot



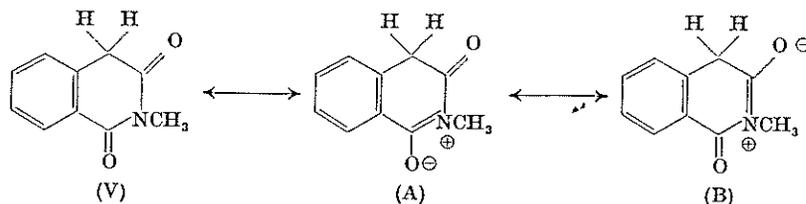
(Va)



(VII)

exist in any other tautomeric form as there are no hydrogen atoms available. There is no possibility of intermolecular association by hydrogen bonding in the NCH_3 homophthalimides. Two bands, which arise from carbonyl stretching

vibrations, are found in the 1667–1718 cm^{-1} region. The bands are sharper than those observed in the case of the NH homophthalimides and are insensitive to concentration changes. The 1-carbonyl group absorptions are found at slightly lower frequencies than in the case of the 1-carbonyl groups in unassociated NH homophthalimides. The lowering of the frequency is probably due to the effect of the N-methyl group on the resonance configurations of the molecule. Resonance form (A) would tend to make the 1-carbonyl oxygen more electronegative. Resonance form (B) would also tend to shift the 3-carbonyl group absorption to a lower



frequency. However, this is not observed and probably indicates that resonance form (B) makes no significant contribution. This is further suggested by the observation that the 3-carbonyl group is non-coplanar with the remainder of the molecule, as demonstrated by molecular models.

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