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THE C=O STRETCHING BANDS OF 1,3-INDANDIONE DERIVATIVES

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Abstract—IR spectra of one hundred and fifty-four 1,3-indandione derivatives representing various structural types have been measured in the C=O stretching region. Linear relationships were found in three solvents between the symmetrical and asymmetrical C=O stretching frequencies. The degree of vibrational coupling in the 1,3-indandione derivatives being compared with that in acyclic β-diketones. The influence of the structure of the compounds studied on the positions of the C=O stretching bands as well as the validity of linear relationships between the symmetrical and asymmetrical C=O stretching frequencies is discussed.

A NUMBER OF PAPERS have been published on the IR spectra of 1,3-indandione derivatives. Most of these papers[1–3] deal with the study of spectra of 1,3-indandione derivatives recorded in the solid state. However. the C=O stretching frequencies of 1,3-indandione derivatives in organic solvents have not been systematically studied. It is known. that some dicarbonyl compounds display doubled absorption bands in the C=O region, assigned to the symmetrical and asymmetrical stretching mode of the carbonyl groups.[4] However, the relation between the symmetrical and asymmetrical stretching frequencies of the C=O groups has not yet been studied in cyclic β-diketones. Similar linear relations between the symmetrical and asymmetrical stretching vibrational modes have been reported by Fayat and Foucaud in some cyclic imides[5] and anhydrides.[6]

This paper deals with the study of IR spectra of solutions of a great number of 1,3-indandione derivatives in the region of asymmetrical and symmetrical C=O stretching frequencies and with the influence of structure on these frequencies.

RESULTS AND DISCUSSION

The frequencies of absorption bands between 1650 cm^{-1} and 1800 cm^{-1} in $CHCl_3$, MeCN and CCl_4 solutions of the investigated 1,3-indandione derivatives are listed in Tables 1 and 2. The 1,3-indandione derivatives studied exist in these solvents mainly in the diketo form. On the other hand in strong proton acceptor solvents compounds with a hydrogen atom in position 2 undergo tautomeric changes[7] and in the solid state they form intermolecularly hydrogen-bonded associates.[8] As it can be seen from Tables 1 and 2. all investigated compounds show a doubled absorption band in the C=O region. The lower frequency band is always of higher intensity than that of the higher frequency. The difference between the two frequencies lie in the range 30–50 cm^{-1} in most compounds. This doubling is generally attributed to mechanical coupling between the in-phase and the out-of-phase vibration of two C=O groups, as it is the case in acyclic β-diketones.[9] In accordance with Kaneti *et al.*[10] we assigned the band with lower frequency to the asymmetrical and that with

TABLE 1. THE C=O STRETCHING BANDS OF 1,3-INDANDIONE DERIVATIVES (DATA IN cm^{-1})

Compound	Substituents on 1.3-indandione skeleton	CHCl$_3$		MeCN		CCl$_4$	
		ν_{as}	ν_s	ν_{as}	ν_s	ν_{as}	ν_s
1	2-(3.4-dimethylphenoxy)	1729	1765	1732	1769	1732	1767
2	2-(3-methyl-4-chlorophenoxy)	1731	1767	1731	1768	1734	1770
3	2-(3-nitrophenoxy)	1729	1765	—	—	1733	1768
4	2-(2-naphtoxy)	1730	1766	1731	1766	1732	1768
5	2-(1-naphtoxy)	1729	1766	1727	1760	—	—
6	2.2-dihydroxy	1729	1761	1734	1769	1737	1771
7	2-phenyl-5-aza*	1727	1762	—	—	—	—
8	2-(4-iodophenyl)-5-aza*	1728	1736	—	—	—	—
9	2-(4-fluorophenyl)-5-aza*	1726	1762	—	—	—	—
10	2-(3-methylphenyl)-5-aza*	1727	1763	—	—	—	—
11	2-(4-methylphenyl)-5-aza*	1727	1762	—	—	—	—
12	2-bromo-2-phenyl	1725	1760	1725	1760	1724	1760
13	2-chloro-2-phenyl	1731	1765	1731	1765	1734	1767
14	2-bromo-2-(3-chlorophenyl)	1727	1764	1726	1759	1734	1767
15	2-bromo-2-(3-bromophenyl)	1725	1760	1725	1761	1725	1762
16	2-bromo-2-(4-bromo-1-naphtyl)	1727	1762	1726	1763	1732	1768
17	2-thiocyanato-2-(3-iodophenyl)	1727	1761	1726	1760	1724	1761
18	2-thiocyanato-2-(4-bromophenyl)	1730	1762	1733	1766	1739	1765
19	2-thiocyanato-2-phenyl	1725	1759	1726	1760	1729	1762
20	2-phenylthio	1720	1753	1722	1755	1724	1756
21	2-(2.5-dichlorophenylthio)	1721	1754	1723	1756	1724	1756
22	2-(2-chlorophenylthio)	1719	1753	1721	1754	1724	1757
23	2-(2-methylphenylthio)	1719	1753	1718	1753	1724	1756
24	2-(perchlorophenylthio)	1718	1752	1721	1754	1723	1754
25	2-(5-nitro-2-benzothiazolythio)	1725	1762	—	—	1722	1753
26	2-(2-benzothiazolylthio)	1724	1761	1720	1755	1723	1761
27	unsubstituted	1718	1752	1721	1753	1724	1757
28	2-phenyl	1718	1754	1717	1752	1723	1756
29	2-(4-iodophenyl)	1719	1755	1718	1753	1723	1757
30	2-(3-chlorophenyl)	1719	1755	1718	1753	1723	1757
31	2-(3-bromophenyl)	1719	1755	1719	1754	1723	1757
32	2-(4-fluorophenyl)	1722	1757	1722	1755	1724	1757
33	2-(3-nitrophenyl)	1721	1756	1721	1755	1725	1757
34	2-(4-nitrophenyl)	1719	1755	1721	1755	1725	1757
35	2-(4-chlorophenyl)	1718	1754	1719	1755	1722	1756
36	2-(4-methoxyphenyl)	1717	1753	1717	1753	1720	1755
37	2-(4-bromophenyl)	1719	1755	1718	1753	1723	1756
38	2-(4-methylphenyl)	1717	1753	1718	1754	1724	1758
39	2-(4-acetaminophenyl)	1718	1754	1720	1755	1724	1758
40	2-(4-aminophenyl)	1717	1753	1716	1750	1724	1757
41	2-(2-iodophenyl)	1720	1756	1724	1758	1724	1758
42	2-(2-chlorophenyl)	1720	1758	1724	1758	1725	1760
43	2-(1-naphtyl)	1720	1754	1720	1754	1723	1757
44	2-(4-methyl-1-naphtyl)	1721	1756	1720	1756	1724	1758
45	2-(4-bromo-1-naphtyl)	1719	1755	1718	1751	1724	1757
46	2-(4-chloro-1-naphtyl)	1720	1756	1720	1753	1724	1757
47	2-(4-nitro-1-naphtyl)	1719	1757	1720	1754	1724	1758
48	2-(4-acetamino-1-naphthyl)	1718	1755	1719	1754	1722	1756
49	2-(4-amino-1-naphtyl)	1718	1754	1718	1753	1722	1754
50	2-(2-naphtyl)	1717	1754	1718	1755	1721	1755
51	2-(1-nitro-2-naphtyl)	1724	1759	1723	1758	1725	1760

TABLE 1—*continued*

Compound	Substituents on 1.3-indandione skeleton	$CHCl_3$		MeCN		CCl_4	
		ν_{as}	ν_s	ν_{as}	ν_s	ν_{as}	ν_s
52	2-(1-bromo-2-naphtyl)	1720	1756	1723	1759	1723	1757
53	2-(5-methyl-4-kumarinyl)	1720	1755	1726	1760	—	—
54	2-(6-methyl-4-kumarinyl)	1720	1755	1723	1756	1723	1756
55	2-(7-hydroxy-4-kumarinyl)	1721	1754	1723	1756	1724	1756
56	2-(5.7-dimethyl-4-kumarinyl)	1718	1754	1723	1756	1724	1756
57	2-(6.7-dimethyl-4-kumarinyl)	1720	1755	1723	1756	1724	1758
58	2-(4-benzo[h]kumarinyl)	1722	1754	1723	1756	1724	1756
59	2-(3-kumarinyl)	1721	1756	1723	1756	1723	1755
60	2-ferrocenyl	1715	1750	—	—	1722	1755
61	2-(5.6.7.8-tetrahydro-1-naphtyl)	1717	1753	1716	1753	1723	1756
62	2-(5.6.7.8-tetrahydro-2-naphtyl)	1717	1753	1717	1753	1723	1756
63	2-methyl-2-(4-iodophenyl)	1716	1751	1715	1751	1719	1752
64	2-methyl-2-(4-nitrophenyl)	1716	1752	1715	1752	1718	1753
65	2-benzyl-2-(2-bromophenyl)	1714	1748	1713	1749	1717	1750
66	2-benzyl-2-(2-iodophenyl)	1712	1748	1711	1748	1716	1751
67	2-alyl-2-(2-chlorophenyl)	1716	1753	1716	1755	1720	1756
68	2-benzyl-2-phenyl	1713	1749	1713	1749	1715	1750
69	2-methyl-2-(2-bromophenyl)	1719	1755	1718	1755	1724	1758
70	2-benzyl-2-(2-chlorophenyl)	1719	1755	1719	1755	1724	1756
71	2-ethyl-2-(2-chlorophenyl)	1715	1753	1715	1754	1718	1755
72	2-alyl-2-(2-bromophenyl)	1717	1754	1716	1755	1720	1757
73	2-methyl-2-(2-chlorophenyl)	1718	1756	1719	1755	1724	1758
74	2-ethyl-2-(2-bromophenyl)	1714	1753	1715	1754	1716	1754
75	2-ethyl-2-phenyl	1709	1747	1709	1749	1711	1751
76	2-isopropyl-2-phenyl	1718	1754	1717	1754	1722	1758
77	2-methyl-2-(4-chlorophenyl)	1714	1751	1716	1752	1718	1753
78	2-methyl-2-(2-iodophenyl)	1717	1753	1718	1754	1722	1756
79	2-phenyl-2-(ethoxycarbonyl-chloromethyl)	1717	1751	1720	1756	1722	1755
80	2-methyl-2-phenyl	1713	1751	1716	1752	1718	1754
81	2-methyl-2-(1-nitro-2-naphtyl)	1719	1755	1720	1756	1722	1757
82	2-methyl-2-(1-chloro-2-naphtyl)	1718	1755	1718	1755	1722	1757
83	2-methyl-2-(1-bromo-2-naphtyl)	1717	1754	1718	1754	1721	1756
84	2-methyl-2-(2-naphtyl)	1714	1751	1716	1752	1716	1751
85	2-isopropyl-2-(1-nitro-2-naphtyl)	1713	1749	1714	1753	1715	1750
86	2-alyl-2-(1-chloro-2-naphtyl)	1715	1752	1717	1754	1717	1753
87	2-benzyl-2-(2-naphtyl)	1711	1748	1712	1749	1713	1748
88	2-alyl-2-(1-bromo-2-naphtyl)	1715	1752	1716	1752	1718	1753
89	2-alyl-2-(1-nitro-2-naphtyl)	1717	1753	1717	1753	1718	1754
90	2-ethyl-2-(2-naphtyl)	1711	1748	1712	1750	1712	1749
91	2-benzyl-2-(1-nitro-2-naphtyl)	1714	1751	1716	1753	1715	1752
92	2-alyl-2-(2-naphtyl)	1712	1749	1712	1750	1714	1750
93	2-benzyl-2-(1-chloro-2-naphtyl)	1713	1750	1714	1752	1716	1753
94	2-benzyl-2-(1-bromo-2-naphtyl)	1712	1750	1714	1751	1715	1752
95	5-amino-2-phenyl	1703	1742	1704	1742	1709	1748
96	5-bromo-2-phenyl	1723	1757	1723	1758	1725	1758
97	5-chloro-2-phenyl	1722	1756	1723	1756	1725	1757
98	5-nitro-2-phenyl	1728	1763	1727	1762	1731	1764
99	5-bromo-2-(4-bromophenyl)	1723	1757	1723	1758	1724	1758
100	5-chloro-2-(4-nitrophenyl)	1723	1756	1725	1758	1725	1757
101	5-amino-2-(1-naphtyl)	1715	1750	1716	1750	1720	1755

TABLE 1—*continued*

Compound	Substituents on 1.3-indandione skeleton	CHCl$_3$		MeCN		CCl$_4$	
		ν_{as}	ν_s	ν_{as}	ν_s	ν_{as}	ν_s
102	5-nitro-2-(1-naphtyl)	1727	1763	1726	1761	1730	1766
103	5-chloro-2-(4-nitro-1-naphtyl)	1724	1758	1723	1757	1724	1758
104	5-bromo-2-(4-nitro-1-naphtyl)	1724	1758	1723	1757	1725	1759
105	4-nitro-2-phenyl	1728	1762	1729	1763	1731	1764
106	4-amino-2-phenyl	1692	1740	1693	1741	1698	1745
107	4-amino-2-(1-naphtyl)	1695	1741	1694	1740	1698	1745
108	2-phenylmethylene	1690	1733	1695	1736	1694	1735
109	2-(4-methoxyphenylmethylene)	1684	1726	1689	1731	1691	1733
110	2-(4-nitrophenylmethylene)	1696	1739	1702	1741	1699	1741
111	2-(4-dimethylaminophenylmethylene)	1670	1717	1680	1725	1681	1725
112	2-(3.4-methylenedioxyphenylmethylene)	1685	1728	1695	1732	1691	1731
113	2-(4-aminophenylmethylene)	1678	1722	1683	1725	1689	1728
114	2-(3-chlorophenylmethylene)	1692	1734	1696	1737	1696	1737
115	2-(3-nitrophenylmethylene)	1695	1736	1700	1738	1696	1737
116	2-(4-chlorophenylmethylene)	1691	1734	1696	1738	1695	1739
117	2-(4-methylphenylmethylene)	1689	1729	1695	1735	1695	1735
118	2-(3-hydroxyphenylmethylene)	1690	1732	1699	1735	1699	1737
119	2-(4-cyanophenylmethylene)	1696	1740	1700	1741	1699	1741
120	2-(2-chlorophenylmethylene)	1696	1738	1698	1740	1698	1740
121	2-(2-methoxyphenylmethylene)	1689	1732	1691	1733	1693	1736
122	2-(2-hydroxyphenylmethylene)	1681	1725	1691	1732	1679	1725
123	2-(3-phenylpropenylidene)	1686	1726	1690	1728	1691	1730
124	2-(2-furylmethylene)	1688	1730	1691	1732	1693	1734
125	2-(2-thienylmethylene)	1686	1729	1690	1731	1691	1733
126	2-(3-pyridylmethylene)	1694	1737	1696	1739	1698	1741
127	2-ferrocenylmethylene	1681	1724	1683	1725	1688	1728
128	2-(1′-methoxyferrocenylmethylene)	1675	1720	1679	1721	1684	1725
129	2-(1′-ethylferrocenylmethylene)	1677	1722	1682	1724	1685	1726
130	2-(1′-chloroferrocenylmethylene)	1681	1724	1685	1726	1689	1729
131	2-(2-chloroferrocenylmethylene)	1682	1724	1687	1728	1690	1730
132	2-phenylazo	1672	1721	1680	1723	1674	1728
133	2-(3-nitrophenylazo)	1682	1728	—	—	1681	1724
134	2-(4-hydroxyphenylazo)	1668	1716	1670	1718	—	—
135	2-(4-methylphenylazo)	1670	1718	1676	1722	1670	1727
136	2-(2-nitrophenylazo)	1688	1732	1689	1734	1691	1735
137	2-(4-carboxyphenylazo)	1680	1726	—	—	—	—
138	2-(4-sulfophenylazo)	1676	1723	—	—	1680	1723
139	2-(4-bromophenylazo)	1677	1725	—	—	1680	1733
140	2-(4-dimethylaminophenylazo)	1661	1709	1667	1713	1663	1718
141	2-(4-diethylaminophenylazo)	1659	1707	—	—	1662	1717
142	2-(4-phenylaminophenylazo)	1664	1713	1670	1717	1667	1724
143	2-[4-(ethyl-2-chloroethylamino)phenylazo]	1660	1709	1665	1713	—	—
144	2-[4-(ethyl-2-hydroxyethylamino)phenylazo]	1661	1710	1664	1712	1663	1720
145	2-(2-carboxyphenylazo)	1684	1725	1689	1730	—	—
146	2-(3-hydroxyphenylazo)	1672	1718	1677	1722	—	—
147	2-(3-sulfo-4-methylphenylazo)	1686	1732	—	—	—	—

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* The number 5 denotes the position of the nitrogen heteroatom in 1.3-indandione skeleton. For some compounds in this Table data were not available because of low solubility in the respective solvents.

higher frequency to the symmetrical stretching mode of two C=O groups (Scheme 1 for 1,3-indandione). If comparing the difference between the symmetrical and assymetrical frequency $\Delta\nu = \nu_s - \nu_{as}$ in a series of 1,3-indandione derivatives, we find that in compounds where the C_2 atom is not bound by a double bond, the $\Delta\nu$ values are in the range 31–40 cm^{-1}. In compounds in which the C_2 atom is doubled-bonded to CH group or a nitrogen atom, the $\Delta\nu$ values lie in the range 36–49 cm^{-1}.

SCHEME 1

From the above mentioned results we can conclude that in the compounds of the latter type the mechanical coupling will be more favoured than in compounds of the former type. This phenomenon can be explained by the change of the tetrahedral C_2 atom into sp^2-hybrid state which leads to a deformation of bond angles in the 1 3-indandione skeleton and to a more planar orientation of the two C=O groups. According to the work of Bellamy *et al.*[4] in systems where the vibrating groups are coplanar the mechanical coupling is more favoured than in systems where coplanarity is disturbed. Mecke and Funck[9] investigated the spectra of acetylacetone derivatives and found that the $\Delta\nu$ values of these lie in the range 20–25 cm^{-1}. The degree of vibrational coupling determined on the basis of $\Delta\nu$ values has been observed to be higher with 1,3-indandione derivatives than with acyclic β-diketones. The explanation is analogous to the previous case: the C=O groups in the 1,3-indandione skeleton are more planar than those in acyclic β-diketones. In some 1,3-indandione derivatives studied the $\Delta\nu$ values do not lie in the mentioned ranges, these anomalies are due to intramolecular interactions which will be discussed later.

The symmetrical and asymmetrical C=O frequencies (Tables 1 and 2) measured in all three solvents can be interrelated by the following linear expression (Figs 1–3). In $CHCl_3$ from 147 experimental values:

$$\nu_s = 0{\cdot}778\nu_{as} + 417{\cdot}3$$

$$r = 0{\cdot}995 \qquad s\rho = 0{\cdot}006 \qquad s = 1{\cdot}4$$

where r is correlation coefficient, $s\rho$ is the error of the slope and s the standard deviation.

In MeCN from 132 experimental values:

$$\nu_s = 0{\cdot}791\nu_{as} + 395{\cdot}5$$

$$r = 0{\cdot}993 \qquad s\rho = 0{\cdot}008 \qquad s = 1{\cdot}5$$

In CCl_4 from 127 experimental values:

$$\nu_s = 0{\cdot}784\nu_{as} + 407{\cdot}0$$

$$r = 0{\cdot}988 \qquad s\rho = 0{\cdot}011 \qquad s = 1{\cdot}7$$

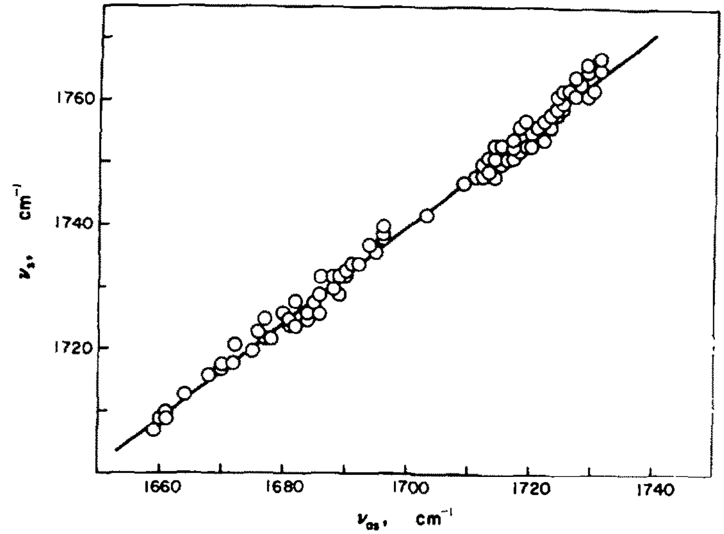

FIG 1. The relationship between the symmetrical and asymmetrical C=O stretching frequencies of 1,3-indandione derivatives in $CHCl_3$.

If we compare the differences between the values of slopes in the above relations we find that these are comparable with the values of errors of the slopes ($s\rho$). It is evident that in all three solvents nearly the same relationship is generally valid between the symmetrical and asymmetrical C=O stretching frequencies in 1,3-indandione derivatives. The linear relation includes experimental data from various structural types of 1,3-indandione derivatives. Substituents vary in all possible positions of the

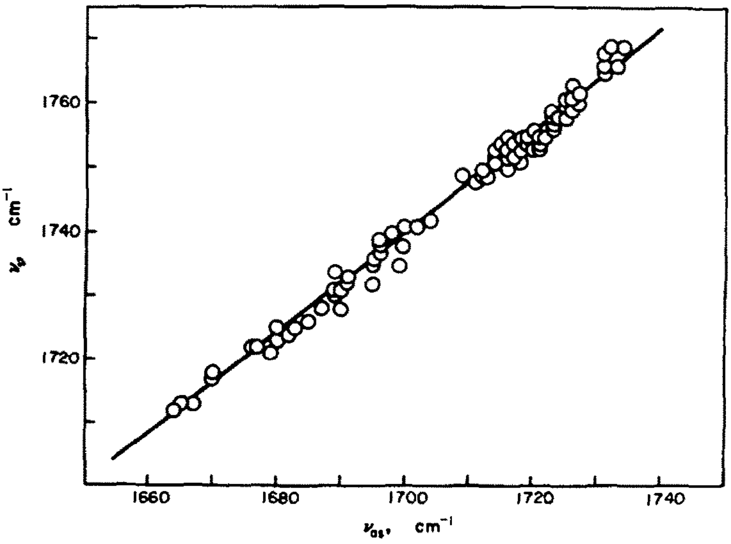

FIG 2. The relationship between the symmetrical and asymmetrical C=O stretching frequencies of 1,3-indandione derivatives in MeCN.

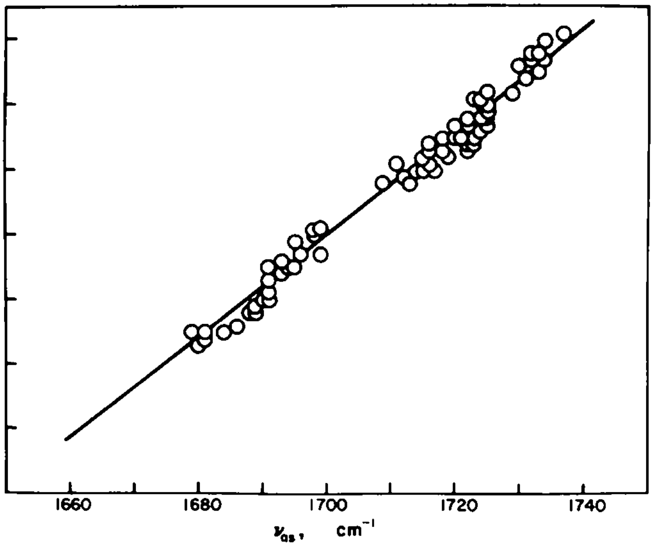

FIG 3. The relationship between the symmetrical and asymmetrical C═O stretching frequencies of 1,3-indandione derivatives in CCl_4.

1,3-indandione skeleton. The relationship is obeyed also by such compounds, the C_2 atoms of which change from sp^3-hybrids to sp^2-hybrids and by compounds with a heteroatom in the aromatic ring of the 1,3-indandione skeleton. From the above results a linear relationship between the symmetrical and asymmetrical C═O stretching frequencies in 1,3-indandiones seems to have a more general validity than other similar relations, *e.g.* in aliphatic nitrocompounds[11] where different relations between $\nu_s(NO_2)$ and $\nu_{as}(NO_2)$ have been found for primary and secondary derivatives.

The studied 1,3-indandione derivatives listed in Table 1 can be divided according to the influence of the structure on the position of C═O stretching bands into ten basic

TABLE 2. THE C═O STRETCHING BANDS OF 1,3-INDANDIONE DERIVATIVES (DATA IN cm^{1-})

Compound	Compound	$CHCl_3$		MeCN		CCl_4	
		ν_{as}	ν_s	ν_{as}	ν_s	ν_{as}	ν_s
148	bis[4-(1,3-indandione-2-yl)-1-naphtyl]mercury	1718	1753	1720	1755	1724	1757
149	bis-(1,3-indandione-2-yl)-sulfide	1718	1752	1721	1753	1722	1753
150	2,2′-bis-[2-(1-naphtyl)-1,3-indandione]	1712	1742	1715	1743	1715	1746
151	2,2′-bis-[2-(2-naphtyl)-1,3-indandione]	1712	1742	1716	1745	1715	1746
152	2,2′-bis-(2-phenoxy-1,3-indandione)	1732	1765 1750	1717 1723	1751	1737	1776
153	2,2′-bis-[2-(3-methylphenoxy)-1,3-indandione]	1733	1765 1750	1716 1732	1754	1737	1770
154	2,2′-bis-[2-(4-methylphenoxy)-1,3-indandione]	1733	1765 1751	1716 1732	1755	1736	1776

structural types (Fig 4). From Fig 4 it can be seen that substituents in position 2 of 1,3-indandione skeleton influence substantially the positions of the C=O stretching bands by their inductive effect. Generally speaking, 2-alkyl-2-aryl-1,3-indandiones (VII) (derivatives with substituents with + I – effect) absorb at lower frequencies than corresponding 2-aryl-1,3-indandiones (VI). On the other hand 2-halogen- and 2-thiocyanato-2-aryl-1,3-indandiones (III) (derivatives with substituents with – I – effect) exhibit the C=O stretching bands at higher frequencies in comparison with the respective 2-aryl-1,3-indandiones (VI). A similar increase of C=O frequencies relatively to the 1,3-indandione (V) and 2-aryl-1,3-indandiones (VI) was observed for 2-aroxy-1,3-indandiones (I) (derivatives with substituents with a strong – I – effect). The 2,2-dihydroxy-1,3-indandione (compound 6, Table 1) can also be included in this group. The 2-arylthio-1,3-indandiones (IV) with regard to the weaker – I – effect of the arylthio group absorb in the region slightly shifted to higher frequencies relatively to the 1,3-indandione (V). All the above mentioned types of 1,3-indandione derivatives obey the ν_s/ν_{as} relation.

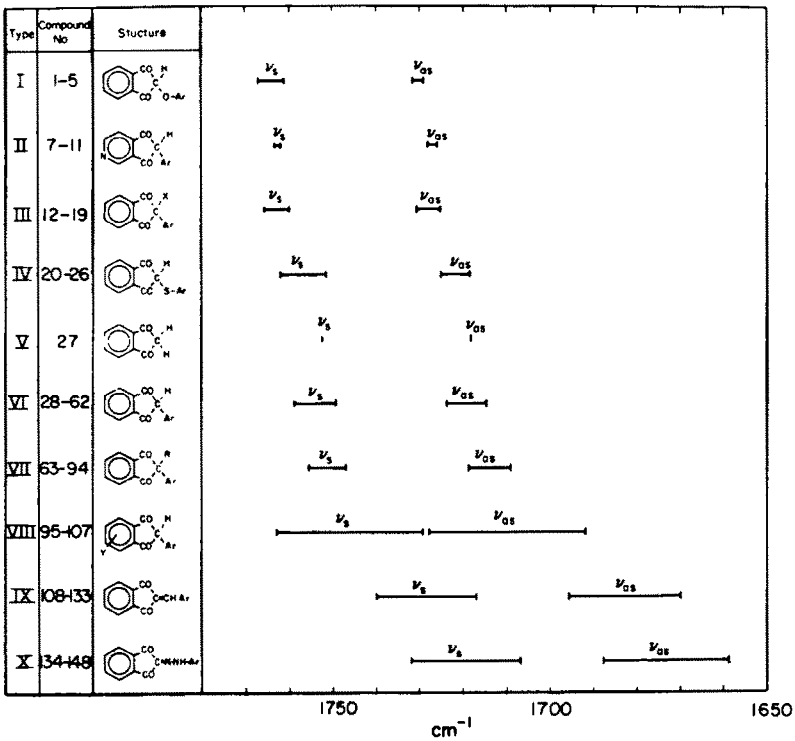

Fig 4. The influence of the structure on the position of C=O stretching bands of 1,3-indandione derivatives in CHCl$_3$.

The C=O stretching frequencies of 2-aryl-5-aza-1,3-indandiones (II) were approximately 10 cm^{-1} higher than those of the corresponding 2-aryl-1,3-indandiones (VI) and is due to the strong electron-withdrawing effect of the nitrogen atom. It is remarkable that the same shift (*i.e.* approximately 10 cm^{-1}) was also found in 3-arylmethylenecinchomeronides[12] in comparison with their carbocyclic analogues, *i.e.* 3-arylmethylenephtalides, although, the structure of these as well as the nature of C=O stretching bands belonging to these compounds are quite different from those the 1,3-indandione derivatives. The symmetrical and the asymmetrical C=O stretching frequencies of 2-phenyl-5-aza-1,3-indandione (compound 7, Table 1) are in a very good agreement with the frequencies measured for 5-nitro-2-phenyl-1,3-indandione (compound 98, Table 1). This observation shows that the effect of the nitrogen heteroatom in position 5 on the 1,3-indandione skeleton is comparable with the electron-withdrawing effect of the nitro substituent on the C_5 atom. The results are also in agreement with those obtained by comparing the C=O stretching frequencies in 3-phenylmethylenecinchomeronide and 4- or 5-nitro-3-phenylmethylenephtalides.[12] In spite of the asymmetric position of the nitrogen heteroatom relative to two C=O groups in the 1,3-indandione skeleton all compounds of type II obey the ν_s/ν_{as} relation. This phenomenon results from the above mentioned fact that the nitrogen heteroatom has the same influence on both C=O bonds of 1,3-indandione skeleton as electron-withdrawing substituents bonded on the benzene ring.

As can be seen from Fig 4 the C=O stretching bands of 4- and 5- substituted 2-aryl-1,3-indandiones (VIII) are observed in a wider range of frequencies than those of the previous types of compounds, which indicates a pronounced transfer of the substituent effects from the benzene ring to the carbonyl groups. In 5-substituted 2-phenyl-1,3-indandiones the symmetrical and asymmetrical C=O stretching frequencies or their arithmetic means correlate with σ^+ constants of substituents.[13] All compounds of the type VIII except 4-aminoderivatives (compounds 106 and 107, Table 1) obey the ν_s/ν_{as} relation. The anomalous behaviour of 4-aminoderivatives is probably a result of intramolecular hydrogen bonding between the C=O and NH_2 groups. Similar deviations from the relation between the symmetrical and asymmetrical stretching frequencies were found[14] in some *ortho*-substituted anilines. It is necessary to mention that 4-nitro-2-phenyl-1,3-indandione (compound 105, Table 1) exists in the solvents employed partly in enol form, stabilized by the intramolecular hydrogen bond. However, the frequencies of the absorption bands of the diketo form which are present together with the bands of the enol form in the spectrum obey the ν_s/ν_{as} relationship well.

The C=O stretching bands of 2-arylmethylene-1,3-indandiones (IX) generally lie at lower frequencies than those of all previous compounds as a result of conjugation of both C=O groups with the arylmethylene group. In our previous work[15] a linear correlation was found between the arithmetic means of the symmetrical and asymmetrical C=O stretching frequencies and σ^+ constants of the substituents for 3- and 4-substituted 2-phenylmethylene-1,3-indandiones. All compounds of the type IX obey the ν_s/ν_{as} relation.

The C=O stretching frequencies of 2-arylazo-1,3-indandiones (X) are shifted to lower values relatively to those observed in previous compounds. This can be explained only by the fact that in the solvents employed these compounds exist in the hydrazone form (Fig 4). Our assumption is also supported by the influence of both carbonyl frequencies of compounds X with substituents on the benzene ring. On the contrary 2-phenyl-2-arylazo-1,3-indandiones[16] existing only in an azo form exhibit the C=O stretching bands in the 1752–1738 cm^{-1} and 1718–1706 cm^{-1} regions, respectively. The arithmetic means of the symmetrical and asymmetrical C=O stretching frequencies of 3- and 4-substituted 2-phenylazo-1,3-indandiones also correlate well with Hammett σ constants.[13] In $CHCl_3$ and MeCN all compounds studied of type X obey the ν_s/ν_{as} relationship. However, in CCl_4 this relation holds only for compounds having strong electron-withdrawing substituents on the benzene ring. The derivatives with electron-donating and weak electron-withdrawing substituents display the symmetrical C=O stretching frequencies anomalously shifted to higher values on passing from CCl_4 to $CHCl_3$ or MeCN. This causes greater deviations from the calculated relation between the symmetrical and asymmetrical C=O stretching frequencies.

A special group of compounds studied are derivatives containing two 1,3-indandione skeletons in one molecule (Table 2). According to the ν_s/ν_{as} relation they can be divided into two types: compounds having two 1,3-indandione skeletons in position 2 bonded through one atom, or a group of atoms (compounds 148 and 149, Table 2) and compounds having these skeletons in position 2 bonded directly (compounds 150–154. Table 2). Compounds of the first type obey the ν_s/ν_{as} relation well. In compounds of the second type the measured symmetrical C=O stretching frequencies are approximately 10 cm^{-1} lower than those calculated from the relationship. Some compounds of the latter type show in the C=O region complex absorption bands, the frequencies of which do not obey the ν_s/ν_{as} relationship. According to the influence of the structure on the position of C=O stretching bands the compounds with two 1,3-indandione skeletons can be easily encountered among the structural types in Fig 4. The frequencies of C=O stretching bands of the compound 149 lie in the range of frequencies of 2-arylthio-1,3-indandiones (IV). Compound 148 absorbs in the range of frequencies for 2-aryl-1,3-indandiones (VI). The region of the absorption of compounds 152–154 is overlapped by frequencies of 2-aroxy-1,3-indandiones (I). Compounds 150 and 151 absorb in a slightly lower region than 2-aryl-1,3-indandiones (VI).

Finally, it was observed that 2-acyl-1,3-indandiones[17] do not obey the linear relationship between the symmetrical and asymmetrical C=O stretching frequencies. These compounds exist in $CHCl_3$ and CCl_4 only in the enol form which is stabilized by a strong chelated intramolecular hydrogen bond between one carbonyl group and the OH group of the enol. as reported previously.[17] It can generally be supposed that other 1,3-indandione derivatives which exist in the enol form, *e.g.* 2-nitro-1,3-indandione and 2-carbalcoxy-1.3-indandiones[8] are stabilized by intramolecular hydrogen bonds and will not obey the ν_s/ν_{as} relationship.

EXPERIMENTAL

The majority of compunds studied have been prepared by the standard literature methods.[18–27] Some of the compounds have been prepared for this purpose and their synthesis will be published later. In the case of 2,2-dihydroxy-1,3-indandione a commercial product of analytical purity (made by Lachema) was used. All compounds investigated have been purified by crystallization or chromatography.

IR spectra were recorded on a Zeiss UR 20 spectrophotometer in the 1600–1800 cm^{-1} region. For the calibration of the wave-number scale a standard spectrum of the mixture indene, camphor and cyclohexanone was used. The absorption bands were read with an accuracy of ± 1 cm^{-1}. The solvents: $CHCl_3$, MeCN and CCl_4, all of analytical purity were purified and dried in the usual manner. In the measurements NaCl cells with a path length 0·01 0·06, 0·25, 2·00 and 3·00 cm were used. Concentrations of solutions were chosen to give absorption of 70–75%.

The linear relationships between the symmetrical and asymmetrical C=O stretching frequencies were evaluated according to the non-approximated statistical relations[28] using a Regnezentralen Gier digital computer.

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