

C=O STRETCHING VIBRATIONS OF 5,6-DIHYDRO-4,7-DITHIA-1,3-INDANEDIONE DERIVATIVES

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The wavenumbers of C=O stretching vibrations of 72 5,6-dihydro-4,7-dithia-1,3-indanedione derivatives were measured in chloroform, acetonitrile and tetrachloromethane. For 187 experimental points a statistically significant linear empirical relationship was found between the wavenumbers of symmetric and asymmetric C=O stretching vibrations. The effect of structure and geometry on C=O stretching vibrations, on the degree of the vibrational coupling in 1,3-dicarbonyl system, as well as on different sensitivity of the C=O symmetric and asymmetric vibration to structural and solvent changes was investigated.

In the previous papers^{1,2} we investigated the transmission of electronic substituent effects in some 5,6-dihydro-4,7-dithia-1,3-indanedione derivatives using C=O stretching vibrations. In the 1,3-indanedione³ and 1,3-benz[*f*]indanedione⁴ series we found statistically significant linear relationships between the wavenumbers of symmetric and asymmetric C=O stretching vibrations.

Recently we turned our attention to the study of the infrared spectra of 5,6-dihydro-4,7-dithia-1,3-indanedione derivatives in order to examine the linear relationships between the wavenumbers of symmetric and asymmetric C=O stretching vibration as well as the relations between structure, position of the bands and degree of the vibrational coupling in the 1,3-dicarbonyl system.

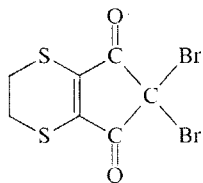
EXPERIMENTAL

The synthesis, properties and purification of the studied derivatives of 5,6-dihydro-4,7-dithia-1,3-indanedione were already described^{1,2,5,6}. The C=O stretching vibrations were determined in chloroform, acetonitrile and tetrachloromethane according to ref.³. The wavenumbers of symmetric and asymmetric C=O stretching vibrations were correlated using a standard linear regression program. The calculations were carried out on a Hewlett-Packard 9100 B computer.

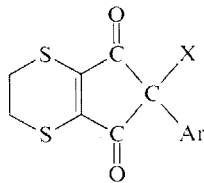
RESULTS AND DISCUSSION

The wavenumbers of the C=O stretching vibrations of 5,6-dihydro-4,7-dithia-1,3-indanediones, measured in chloroform, acetonitrile and tetrachloromethane,

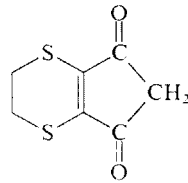
are listed in Table I. All the 5,6-dihydro-4,7-dithia-1,3-indanediones, similarly as other 1,3-indanedione derivatives^{3,4,7,8}, exist in organic solvents preponderantly in the diketo form and, as a result of vibrational coupling, their spectra exhibit bands due to symmetric and asymmetric C=O stretching vibrations:



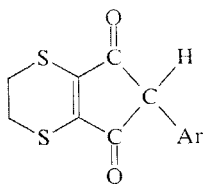
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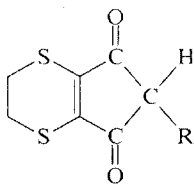
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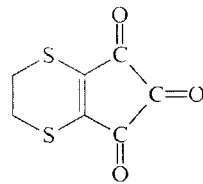
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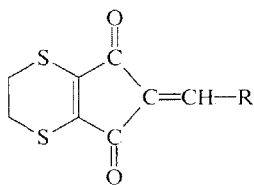
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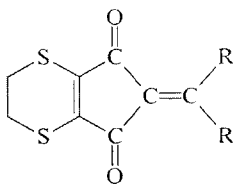
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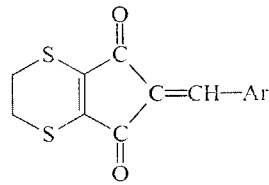
VI



VII



VIII



IX

Compounds, containing an sp^2 hybridised $C_{(2)}$ atom (measured in acetonitrile) are an exception. Their spectra exhibit an anomalously broad and intense absorption band at about 1650 cm^{-1} which often overlaps with bands of symmetric and asymmetric C=O stretching vibration.

The studied compounds can be divided into several groups, according to the effect of their structure on the position of the C=O absorption bands (Fig. 1). It is seen from the Figure that the substituents on the 5,6-dihydro-4,7-dithia-1,3-indanedione skeleton have a marked effect on the symmetric as well as asymmetric vibrations. 2,2-Dihalo derivatives I and 2-halo-2-aryl derivatives II, *i.e.* compounds with electron-accepting substituent, absorb at higher wavenumbers than the unsubstituted compound III. Thanks to the +I-effect of the alkyl group the absorption bands

TABLE I

Wavenumbers of C=O Stretching Vibrations, ν_{as} and ν_s (cm^{-1}), in the Spectra of Substituted 5,6-Dihydro-4,7-dithia-1,3-indanediones

Com- pound	Substituent	CHCl_3^a		CH_3CN^a		CCl_4^a	
		ν_{as}	ν_s	ν_{as}	ν_s	ν_{as}	ν_s
1	2,2-dibromo	1 711	1 751	1 711	1 751	—	—
2	2-bromo-2-phenyl	1 702	1 743	1 700	1 743	1 708	1 748
3	2-chloro-2-phenyl	1 706	1 748	1 706	1 748	1 712	1 752
4	unsubstituted	1 699	1 740	1 701	1 741	1 707	1 744
5	2-phenyl	1 697	1 741	1 697	1 740	1 705	1 744
6	2-(4-methoxyphenyl)	1 697	1 741	1 698	1 741	1 704	1 745
7	2-(3-methoxyphenyl)	1 698	1 741	1 697	1 741	1 705	1 744
8	2-(3-fluorophenyl)	1 698	1 742	1 697	1 741	1 705	1 744
9	2-(3-chlorophenyl)	1 699	1 743	1 697	1 742	1 705	1 746
10	2-(4-methylphenyl)	1 697	1 741	1 696	1 741	1 705	1 745
11	2-(1-naphthyl)	1 697	1 741	1 697	1 741	1 705	1 745
12	2-methyl	1 696	1 741	1 698	1 742	1 705	1 744
13	2-ethyl	1 694	1 737	1 695	1 736	1 701	1 742
14	2-hydroxymethyl	1 696	1 740	1 702	1 741	1 707	1 743
15	2-carboxy	1 695	1 739	1 698	1 741	—	—
16	2-oxy	1 698	1 738	1 698	1 737	—	—
17	2-(1-methylethylidene)	1 674	1 724	1 676	1 723	1 678	1 724
18	2-(2-hydroxyethylidene)	1 695	1 737	1 697	1 737	1 693	1 732
19	2-(1-methylpropylidene)	1 674	1 721	1 674	1 720	1 683	1 724
20	2-cinnamylidene	1 675	1 720	1 678	1 721	1 680	1 722
21	2-cyclohexylidene	1 677	1 718	1 676	1 719	1 680	1 721
22	2-cyclopentylidene	1 679	1 724	1 681	1 724	1 684	1 725
23	2-phenylmethylene	1 676	1 722	1 676	1 722	1 681	1 724
24	2-(4-dimethylaminophenylmethylene)	1 664	1 712	1 663	1 710	1 671	1 717
25	2-(4-aminophenylmethylene)	1 669	1 715	1 670	1 715	—	—
26	2-(4-hydroxyphenylmethylene)	1 671	1 717	1 675	1 718	1 677	1 723
27	2-(3-methoxy-4-hydroxyphenylmethylene)	1 669	1 717	1 670	1 717	1 675	1 723
28	2-(3,4-methylenedioxyphenylmethylene)	1 672	1 717	1 675	1 718	—	—
29	2-(4-methoxyphenylmethylene)	1 671	1 717	1 675	1 718	1 678	1 722
30	2-(3-methylphenylmethylene)	1 674	1 720	1 677	1 722	1 680	1 722
31	2-(3-methoxyphenylmethylene)	1 676	1 723	1 677	1 722	1 680	1 724
32	2-(4-iodophenylmethylene)	1 677	1 723	—	—	1 682	1 724
33	2-(4-chlorophenylmethylene)	1 677	1 722	1 676	1 722	1 679	1 722
34	2-(3-iodophenylmethylene)	1 677	1 723	1 675	1 723	1 682	1 726
35	2-(3-chlorophenylmethylene)	1 677	1 723	1 677	1 723	1 681	1 726
36	2-(3-bromophenylmethylene)	1 678	1 723	1 678	1 723	1 682	1 726
37	2-(4-cyanophenylmethylene)	1 679	1 724	1 679	1 724	1 683	1 727
38	2-(3-nitrophenylmethylene)	1 679	1 724	1 680	1 725	—	—
39	2-(4-nitrophenylmethylene)	1 680	1 724	1 681	1 725	1 683	1 727

TABLE I
(Continued)

Com- pound	Substituent	CHCl ₃ ^a		CH ₃ CN ^a		CCl ₄ ^a	
		ν_{as}	ν_s	ν_{as}	ν_s	ν_{as}	ν_s
40	2-furfurylidene	1 675	1 723	1 677	1 722	1 681	1 726
41	2-(5-methylthiofurfurylidene)	1 670	1 715	—	—	1 677	1 724
42	2-(5-methylfurfurylidene)	1 671	1 717	1 676	1 720	1 678	1 725
43	2-(5-phenylthiofurfurylidene)	1 673	1 722	—	—	1 679	1 726
44	2-(5-chlorofurfurylidene)	1 675	1 723	1 647	—	1 680	1 727
45	2-(5-iodofurfurylidene)	1 674	1 723	1 648	—	1 681	1 727
46	2-(5-bromofurfurylidene)	1 675	1 724	1 647	—	1 680	1 727
47	2-(5-nitrofurfurylidene)	1 697	1 728	1 700	1 740	1 684	1 732
48	2-(5-phenyl-2-furfurylidene)	1 670	1 716	1 648	—	1 677	1 724
49	2-[5-(4-hydroxyphenyl)-2-furfurylidene]	1 668	1 715	1 671	1 717	1 675	1 721
50	2-[5-(4-methoxyphenyl)-2-furfurylidene]	1 669	1 715	1 670	1 715	1 676	1 722
51	2-[5-(4-methylphenyl)-2-furfurylidene]	1 670	1 715	1 746	—	1 677	1 724
52	2-[5-(4-aminophenyl)-2-furfurylidene]	1 670	1 715	1 671	1 717	—	—
53	2-[5-(3-aminophenyl)-2-furfurylidene]	1 670	1 717	1 652	—	1 676	1 724
54	2-[5-(2-aminophenyl)-2-furfurylidene]	1 670	1 717	1 672	1 718	—	—
55	2-[5-(2-chlorophenyl)-2-furfurylidene]	1 671	1 717	—	—	1 677	1 724
56	2-[5-(2-bromophenyl)-2-furfurylidene]	1 670	1 716	—	—	1 678	1 724
57	2-[5-(2-fluorophenyl)-2-furfurylidene]	1 671	1 715	—	—	—	—
58	2-[5-(3-chlorophenyl)-2-furfurylidene]	1 671	1 717	—	—	1 678	1 725
59	2-[5-(3-bromophenyl)-2-furfurylidene]	1 671	1 717	1 675	1 718	1 679	1 725
60	2-[5-(3-nitrophenyl)-2-furfurylidene]	1 673	1 718	—	—	—	—
61	2-[5-(4-nitrophenyl)-2-furfurylidene]	1 674	1 719	1 672	1 715	—	—
62	2-[5-(2-nitrophenyl)-2-furfurylidene]	1 675	1 720	1 678	1 723	1 679	1 726
63	2-[5-(2-chlorophenyl)-2-furfurylidene]	1 673	1 718	1 677	1 722	1 680	1 726
64	2-(5-phenyl-2-thenylidene)	1 671	1 719	1 675	1 723	1 679	1 725
65	2-[5-(4-aminophenyl)-2-thenylidene]	1 668	1 718	1 670	1 718	1 677	1 723
66	2-[5-(4-methoxyphenyl)-2-thenylidene]	1 670	1 718	1 648	—	1 679	1 723
67	2-[5-(4-methylphenyl)-2-thenylidene]	1 670	1 719	1 648	—	1 678	1 725
68	2-[5-(3-methylphenyl)-2-thenylidene]	1 671	1 719	1 675	1 723	1 679	1 725
69	2-[5-(4-chlorophenyl)-2-thenylidene]	1 672	1 720	1 672	1 721	1 680	1 725
70	2-[5-(4-bromophenyl)-2-thenylidene]	1 672	1 720	1 673	1 723	1 680	1 726
71	2-[5-(3-bromophenyl)-2-thenylidene]	1 671	1 720	1 673	—	1 680	1 726
72	2-[5-(4-nitrophenyl)-2-thenylidene]	1 674	1 721	1 649	—	1 682	1 726

^a Some compounds were sparingly soluble in the given solvents and therefore the corresponding wavenumbers were not measured. Some of the data for compounds 23—72 were taken from ref.¹⁻².

tion including 187 experimental data obtained in these three solvents (Fig. 2):

$$\nu_s = 0.825\nu_{as} + 339.7; \quad r = 0.984. \quad s_\rho = 0.011, \quad s = 1.8,$$

where r is correlation coefficient, s_ρ is standard deviation of ρ and s is standard deviation. The use of such common correlation of ν_s with ν_{as} is justified also by the results of Fayat and Faucaud¹⁰ who correlated the values ν_s with the values ν_{as} found for the same 1,3-dicarbonyl compound in a whole series of solvents. From 406 experimental data published in ref.³ we calculated an analogous common relation-

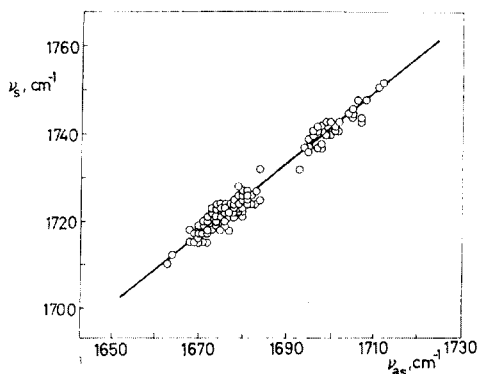


FIG. 1

Plot of Symmetric against Asymmetric C=O Stretching Vibration Wavenumbers for Substituted 5,6-Dihydro-4,7-dithia-1,3-indanediones (in CHCl_3 , CH_3CN and CCl_4)

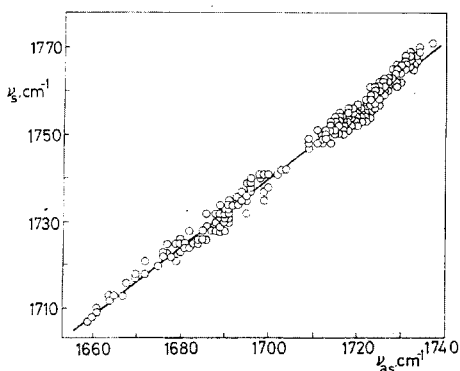
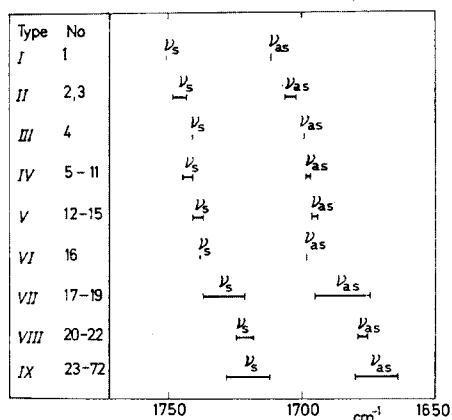


FIG. 2

Plot of Symmetric against Asymmetric C=O Stretching Vibration Wavenumbers for 1,3-Indanediones (in CHCl_3 , CH_3CN and CCl_4)

FIG. 3
Effect of Structure on the Wavenumbers of Symmetric and Asymmetric C=O Stretching Vibrations in 5,6-Dihydro-4,7-dithia-1,3-indanediones (in CHCl_3)



ship also for 1,3-indanedione derivatives (Fig. 3):

$$\nu_s = 0.781\nu_{as} + 412.8; \quad r = 0.993, \quad s_q = 0.005, \quad s = 1.6.$$

The slope of this linear empirical relationship, q , can be regarded as a semiquantitative measure of a different influence of structure and solvent on the wavenumber of the symmetric and asymmetric C=O stretching vibration. For majority of 1,3-dicarbonyl compounds q is smaller than 1: this means that the wavenumber of the asymmetric C=O stretching vibration is more sensitive to structural and solvent effects than the wavenumber of the symmetric vibration. 1,3-Cyclopentanedione and 1,3-cyclohexanedione derivatives¹⁰ represent an exception: for these compounds $q = 1$; this shows an identical effect of the structure and solvent on the wavenumbers ν_s and ν_{as} . From a comparison of the slopes q , found for series of 1,3-indanediones^{3,4} as well as for other 1,3-dicarbonyl compounds⁹⁻¹¹, it follows that the mentioned difference in the effect of structure and solvent on ν_s and ν_{as} will greatly depend on the mesomeric interaction between the vibrating C=O groups. This difference is smaller for 5,6-dihydro-4,7-dithia-1,3-indanediones ($q = 0.825$) than for 1,3-indanediones ($q = 0.781$) since in the former compounds the mesomeric interaction between the C=O groups is mediated only by two π -electrons of the C=C bond.

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