THE C=O STRETCHING VIBRATION OF 1,3-BENZ[*f*]INDANEDIONE DERIVATIVES

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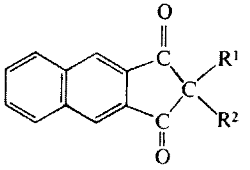
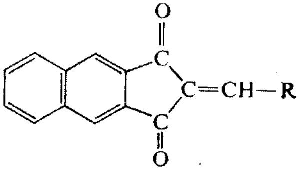
Carbonyl stretching vibrations of twenty seven 1,3-benz[*f*]indanedione derivatives have been measured in tetrachloromethane and chloroform. An empirical linear relationship including 50 experimental points was found between the wavenumbers of symmetric and asymmetric C=O stretching vibration bands. With 2-benzylidene derivatives, the arithmetic means of the wavenumbers of symmetric and asymmetric C=O stretching vibration bands correlate satisfactorily with σ^+ substituent constants. Spectral measurements and the linear correlation were compared with those of other 1,3-indanediones. The influence of the structure molecular geometry, and electronic state on the C=O stretching vibration is discussed. The preparation of some new 1,3-benz[*f*]indanediones is also descirbed.

Infrared spectra measured in solid state have been used previously[1,2] to determine the structure of some 1,3-benz[*f*]-indanediones. However, the C=O stretching vibration of this compound has not yet been measured in organic solvents. In a series of papers[3-10] we have systematically studied the C=O stretching vibration in various series of 1,3-indanediones, 4,7-dithia-4,5,6,7-tetrahydro-1,3-indanediones and 5,7-dioxo-6,7-dihydro-5*H*-dibenzo[*a*,*c*]cycloheptenes.

Continuing our investigation of infrared spectra of cyclic 1,3-diketones, we have measured in tetrachloromethane and in chloroform the carbonyl stretching vibration of a series of 1,3-benz[*f*]indanediones. The investigated compounds can be formally divided into two structural types: compounds containing a $C_{(2)}$ atom in sp^3-hybrid state (*I*) and compounds containing a $C_{(2)}$ atom in sp^2-hybrid state (*II*).



I



II

EXPERIMENTAL

Syntheses, purification and some physico-chemical constants of compounds *I* with the exception of 2-bromo-2-(3-bromophenyl)-1,3-benz[*f*]indanedione were described in papers[2,11–14].

2-*Bromo*-2-(3-*bromophenyl*)-1,3-*benz*[*f*]*indanedione*: 0·32 g of 2-(3-bromophenyl)-1,3-benz[*f*]-indanedione was dissolved in 5 ml of acetic acid and a solution of bromine (0·08 ml) in acetic acid (1 ml) was added. The mixture was heated for a few minutes. After cooling the precipitate was filtered off; m.p. 174–175°C (acetic acid): For $C_{19}H_{10}Br_2O_2$ (430·1), calculated: 37·16% Br; found 37·15% Br.

Compounds II were prepared from the condensation product of naphthalene-2,3-dicarboxylic anhydride and ethylacetoacetate, by treatment with substituted benzaldehyde, furfural or cinnamaldehyde in acetic acid according to[1]. The products were crystallized from acetic acid. Analytical data and melting points of new compounds are given in Table I.

Methods: The spectra were measured in tetrachloromethane and in chloroform on a Zeiss UR20 spectrophotometer by the reported technique[4]. The linear ν_s *vs* ν_{as} and $\bar{\nu}$ *vs* σ^+ correlations were processed by means of statistic relations using a Regnecentralen Gier digital computer. In Hammett correlations σ^+ substituent constants collected in paper[15] were used.

TABLE I

1,3-Benz[*f*]indanediones *II*

R	Formula (m.w.)	Calculated/Found				M.p., °C[a]
		% C	% H	% N	% Hal.	
4-ClC_6H_4	$C_{20}H_{11}ClO_2$ (318·8)	75·36 74·34	3·48 3·40	—	11·12 11·34	258–260
3-BrC_6H_4	$C_{20}H_{11}BrO_2$ (363·2)	66·14 65·95	3·05 3·08	—	22·00 22·13	260–262
3-IC_6H_4	$C_{20}H_{11}IO_2$ (410·2)	58·56 57·92	2·70 2·63	—	30·94 31·09	243–245
3-$CH_3OC_6H_4$	$C_{21}H_{14}O_3$ (314·3)	80·24 80·79	4·49 4·42	—	—	163–164
3-$NO_2C_6H_4$	$C_{20}H_{11}NO_4$ (329·3)	72·95 72·60	3·37 3·23	4·25 3·81	—	310–315 (dec.)
4-$CH_3CONHC_6H_4$	$C_{22}H_{15}NO_3$ (341·4)	77·41 77·82	4·43 4·33	4·10 3·72	—	302–305 (dec.)
$C_6H_5CH{=}CH$	$C_{22}H_{14}O_2$ (310·4)	85·14 83·97	4·55 4·44	—	—	228–230
2-C_4H_3O[b]	$C_{18}H_{10}O_3$ (274·3)	78·83 78·03	3·67 3·60	—	—	240–242

Melting points were determined in a Thiele apparatus and were not corrected; [b] furyl.

RESULTS AND DISCUSSION

Wavenumbers of the C=O stretching vibration bands measured in tetrachloromethane and chloroform for 1,3-benz[*f*]indanediones *I* and *II* are listed in Tables II and III, respectively. All compounds *I* and *II*, analogously to other 1,3-indanedione derivatives[3-10] exist in the organic solvents mainly in the diketo form and display doubled carbonyl bands corresponding to the symmetric (ν_s) and asymmetric (ν_{as}) stretching mode of 1,3-dicarbonyl system. The wavenumbers of bands of 1,3-benz-[*f*]indanediones are c. 5 cm^{-1} lower than those of the corresponding 1,3-indanediones[3-6]. This can be explained by stronger electron-donating effect of naphthalene ring in comparison with that of benzene ring.

It is known[16] that the wavenumber separation: $\Delta\nu = \nu_s - \nu_{as}$ can be used as a measure of the degree of mechanical coupling in vibrating 1,3-dicarbonyl system. The $\Delta\nu$ values observed with 1,3-benz[*f*]indanediones *I* and *II* are 26–33 cm^{-1} and 28–42 cm^{-1}, respectively and are only a little lower than those found in corresponding 1,3-indanediones[3-10], *i.e.* 31–40 cm^{-1} and 36–49 cm^{-1}, respectively. From the mentioned it follows that the vibration coupling in 1,3-benz[*f*]indanediones is somewhat weaker than in the case of 1,3-indanediones. This can be probably caused by little decrease in the angle between the two vibrating C=O groups. It can be mentioned that a more significant variation in the degree of vibration coupling has

TABLE II

Wavenumbers (cm^{-1}) of the Carbonyl Stretching Vibration Bands of 1,3-Benz[*f*]indanedione *I* Containing a $C_{(2)}$ Atom in sp^3-Hybrid State

Compound	R^1	R^2	In CCl_4		In $CHCl_3$	
			ν_{as}	ν_s	ν_{as}	ν_s
1	H	H	1 720	1 748	1 716	1 745
2	H	C_6H_5	1 720	1 750	1 717	1 749
3	H	4-$CH_3C_6H_4$	1 720	1 751	1 718	1 749
4	H	3-BrC_6H_4	1 719	1 749	1 717	1 748
5	H	4-$CH_3CONHC_6H_5$	[b]	[b]	1 718	1 748
6	H	3,4-$(OCH_3)_2C_6H_3$	1 720	1 751	1 718	1 749
7	H	1-$C_{10}H_7$[a]	1 720	1 751	1 717	1 750
8	H	2-$C_{10}H_7$[a]	1 720	1 751	1 718	1 748
9	C_6H_5	$CH_2C_6H_5$	1 716	1 749	1 714	1 745
10	C_6H_5	$CH_2CH=CH_2$	1 716	1 749	1 714	1 746
11	Br	C_6H_5	1 728	1 756	1 724	1 751
12	Br	3-BrC_6H_4	1 729	1 754	1 725	1 751

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[a] Naphthyl; [b] low solubility in CCl_4.

been found on the bases of $\Delta\nu$ values in the series of 4,7-dithia-4,5,6,7-tetrahydro-1,3-indanediones[9] and 5,7-dioxo-6,7-dihydro-5*H*-dibenzo[*a*,*c*]cycloheptenes[10] in comparison with 1,3-indanediones and 1,3-benz[*f*]indanediones. This may be explained by the larger change in the angle between the two vibrating C=O groups. The degree of vibration coupling changes also significantly passing from the series *I* to series *II*, which may be accounted for the electronic effect of substituted benzylidene moiety conjugated directly with both carbonyl groups. The electron-withdrawing substituents cause a decrease and the electron-donating substituents cause an increase in $\Delta\nu$ values as well as in the degree of the mechanical coupling of C=O stretching vibrations.

Similarly as in other series of 1,3-dicarbonyl compounds[5,9,10,17,18] also in 1,3-benz[*f*]indanediones studied here a significant linear correlations exist between wavenumbers of the symmetric and asymmetric C=O stretching vibration bands measured in both solvents. As the slopes of regression lines for ν_s *vs* ν_{as} correlations for data measured in both solvents CCl_4 and $CHCl_3$ are practically identical, we can express the ν_s *vs* ν_{as} correlation as a common relationship for all data measured in

TABLE III

Wavenumbers of the Carbonyl Stretching Vibration Bands of 1,3-Benz[*f*]indanediones *II* Containing a $C_{(2)}$ Atom in sp^2-Hybrid State

Compound	R	In CCl_4			In $CHCl_3$		
		ν_{as}	ν_s	$\bar{\nu}$	ν_{as}	ν_s	$\bar{\nu}$
13	4-$(CH_3)_2NC_6H_4$	1 680	1 720	1 700·0	1 671	1 712	1 691·5
14	4-$CH_3OC_6H_4$	1 691	1 726	1 708·5	1 683	1 723	1 703·0
15	4-$CH_3CONHC_6H_4$	[c]	[c]	—	1 688	1 725	1 706·5
16	C_6H_5	1 695	1 731	1 713·0	1 690	1 727	1 708·5
17	3-$CH_3OC_6H_4$	1 695	1 731	1 713·0	1 690	1 728	1 709·0
18	4-ClC_6H_4	1 696	1 733	1 714·5	1 693	1 730	1 711·5
19	4-BrC_6H_4	1 696	1 732	1 714·0	1 692	1 728	1 710·0
20	3-IC_6H_4	1 698	1 735	1 716·5	1 696	1 731	1 713·5
21	3-BrC_6H_4	1 697	1 734	1 713·5	1 695	1 731	1 713·0
22	4-$NO_2C_6H_4$	1 699	1 735	1 717·0	1 698	1 733	1 715·5
23	3-$NO_2C_6H_4$	[c]	[c]	—	1 704	1 737	1 720·5
24	4-$(C_2H_5)_2NC_6H_4$	1 679	1 718	1 698·5	1 670	1 711	1 690·5
25	2-C_4H_3O[a]	1 693	1 729	1 711·0	1 685	1 725	1 705·0
26	3-C_8H_6N[b]	[c]	[c]	—	1 674	1 716	1 695·0
27	$CH{=}CHC_6H_5$	1 694	1 728	1 711·0	1 686	1 724	1 705·0

[a] Furyl; [b] indolyl; [c] low solubility in CCl_4.

both solvents (Fig. 1)

$$\nu_s = 0{\cdot}756\nu_{as} + 448{\cdot}9\,, \quad r = 0{\cdot}995\,, \quad s_\varrho = 0{\cdot}011\,, \quad s = 1{\cdot}3\,,$$

where r is correlation coefficient, s_ϱ is the standard deviation of ϱ and s is the standard deviation of correlation. For the sake of comparison we have calculated from the data measured in CCl_4, $CHCl_3$ and CH_3CN and from those published earlier[4] an analogous relationship for 406 experimental points of 1,3-indanediones:

$$\nu_s = 0{\cdot}781\nu_{as} + 412{\cdot}8\,, \quad r = 0{\cdot}993\,, \quad s_\varrho = 0{\cdot}005\,, \quad s = 1{\cdot}6\,.$$

It was shown by Fayat and Faucaud[17,18] that in cyclic imides and anhydrides in most cases the ν_{as} is more sensitive to the solvent than the ν_s which causes that the slopes of ν_s *vs* ν_{as} correlations are always lower than 1. In the case of diketo form of 1,3-cyclopentanedines and 1,3-cyclohexanediones[17], in which mesomeric interaction between the vibrating C=O groups is absent, the slopes of ν_s *vs* ν_{as} correlations are nearly 1, *i.e.* the wavenumbers of symmetric and asymmetric C=O stretching vibration bands are equally influenced by solvents. In 1,3-indanediones[4], where the π-electrons of benzene ring contribute to the mesomeric interaction in the five-membered 1,3-dicarbonyl system, the value of the slope of ν_s *vs* ν_{as} relationship (0·781) indicates a significant asymmetry in the sensitivity of the symmetric and asymmetric C=O

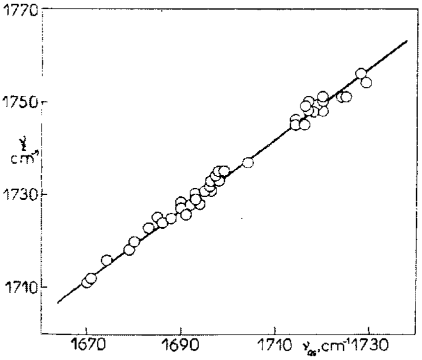

FIG. 1

The Correlation of the Wavenumbers of Symmetric and Asymmetric C=O Stretching Vibration Bands of 1,3-Benz[*f*]indanediones *I* and *II* in Tetrachloromethane and in Chloroform

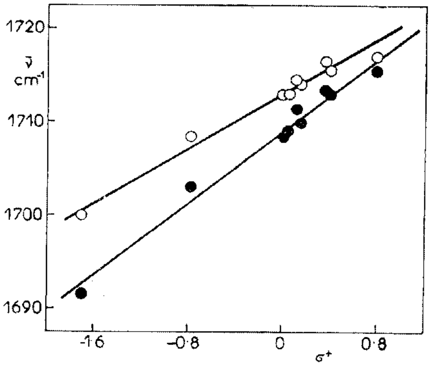

FIG. 2

Plot of the Arithmetic Means $\bar{\nu}$ of the Wavenumbers of Symmetric and Asymmetric C=O Stretching Vibration Bands *vs* σ^+ Substituent Constant for Substituted 2-Benzylidene-1,3-benz[*f*]indanediones (*II*)
○ In tetrachloromethane, ● in chloroform.

stretching frequencies to the structure variation. This effect becomes somewhat more extensive in the case of 1,3-benz[*f*]indanediones (the slope of ν_s *vs* ν_{as} relationship is 0·756) due to the higher electron-donating ability of naphthalene ring in comparison with benzene ring. In the case of 4,7-dithia-4,5,6,7-tetrahydro-1,3-indanediones[9], where only two π-electrons contribute to the mesomeric interaction between the carbonyl groups, the slope of ν_s *vs* ν_{as} relationship is 0·825 and the above mentioned effect of asymmetry is weaker in comparison with 1,3-indanediones.

As in the case of 2-benzylidene derivatives of other 1,3-indanediones[3,5-8], also in the series of substituted 2-benzylidene-1,3-benz[*f*]indanediones we found the validity of Hammett correlations between the arithmetic means of wavenumbers of the symmetric and asymmetric C=O stretching ($\bar{\nu}$) and σ^+ substituent constants. The regression parameters of straight lines are (see Fig. 2), for 9 experimental points from data measured in CCl_4

$$\bar{\nu} = 7{\cdot}04\sigma^+ + 1712{\cdot}9\,, \quad r = 0{\cdot}986\,, \quad s_\varrho = 0{\cdot}45\,, \quad s = 0{\cdot}9$$

and for 9 experimental points from data measured in $CHCl_3$

$$\bar{\nu} = 9{\cdot}72\sigma^+ + 1709{\cdot}1\,, \quad r = 0{\cdot}990\,, \quad s_\varrho = 0{\cdot}53\,, \quad s = 1{\cdot}1\,.$$

The comparison of the slopes (ϱ) of $\bar{\nu}$ *vs* σ^+ correlation in series of 2-benzylidene-4,7-dithia-4,5,6,7-tetrahydro-1,3-indanediones[7] ($\varrho = 4{\cdot}14\ \text{cm}^{-1}$ in CCl_4 and $\varrho = 5{\cdot}40\ \text{cm}^{-1}$ in $CHCl_3$), 2-benzylidene-1,3-indanediones ($\varrho = 6{\cdot}20\ \text{cm}^{-1}$ in CCl_4 and $8{\cdot}92\ \text{cm}^{-1}$ in $CHCl_3$) and 2-benzylidene-1,3-benz[*f*]indanediones ($\varrho = 7{\cdot}04\ \text{cm}^{-1}$ in CCl_4 and $\varrho = 9{\cdot}72\ \text{cm}^{-1}$ in $CHCl_3$) shows that the sensitivity of substituent effects to the C=O groups increases in the same order as the mesomeric interaction between the carbonyl groups and the asymmetry of structure sensitivity of the symmetric and asymmetric C=O stretching vibrations increase. It seems that the $\varrho(\nu_s\ vs\ \nu_{as})$ values are nearly linearly dependent on the corresponding $\varrho(\bar{\nu}\ vs\ \sigma^+)$ values.

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