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INFRARED SPECTRA AND SUBSTITUENT EFFECTS IN 3-ARYLMETHYLENE-4,7-DITHIA-4,5,6,7-TETRAHYDROPHTHALIDES

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The infrared spectra in the region of the C=O and C=C stretching vibrations of substituted *trans*-3-phenylmethylene-4,7-dithia-4,5,6,7-tetrahydrophthalides, *trans*-3-(1-naphthyl)methylene-4,7-dithia-4,5,6,7-tetrahydrophthalides and *trans*-3-(1-naphthyl)methylenephthalides were studied. In all the series the C=O stretching frequencies were linearly dependent on substituent constants σ. With substituted 3-phenylmethylene-4,7-dithia-4,5,6,7-tetrahydrophthalides their hydrogen bonds with ethanol were also studied. It was found that $\Delta\nu(OH)$ values correlate well with σ. Comparison of the obtained linear dependences with analogous correlations for substituted 3-phenylmethylenephthalides revealed that electronic effects are better transmitted in substituted 3-phenylmethylene-4,7-dithia-4,5,6,7-tetrahydrophthalides than in substituted 3-phenylmethylenephthalides. The transmission of substituent effects in the series of 4-substituted naphthalene derivatives is comparable with that in the corresponding series of 3- and 4-substituted benzene derivatives. The linear dependence of $\nu(C=O)$ on σ for 3-phenylmethylene-4,7-dithia-4,5,6,7-tetrahydrophthalides was used to calculate σ_α constants for 1-naphthyl and 2-naphthyl groups.

In the works[1−4] we have studied electronic effects and their transmission in 3-arylmethylenephthalides and similar systems, using infrared and [1]H—NMR spectroscopy. The infrared spectra of 3-arylmethylene-4,7-dithia-4,5,6,7-tetrahydrophthalides in organic solvents have not so far been reported. In the work[5], dealing with synthesis of these compounds, solid-phase spectra (parafin oil) were measured. A systematic study of the infrared spectra of substituted 3-(1-naphthyl)methylenephthalides has not yet been undertaken.

Continuing our previous works, in the present communication we have studied the infrared spectra in the region of the C=O and C=C stretching vibrations of series of substituted *trans*-3-phenylmethylene-4,7-dithia-4,5,6,7-tetrahydrophthalides (*I*), *trans*-3-(1-naphthyl)methylene-4,7-dithia-4,5,6,7-tetrahydrophthalides (*II*), and, for purposes of comparison, the spectra of substituted *trans*-3-phenylmethylenephthalides (*III*) (ref.[1]) and *trans*-3-(1-naphthyl)methylenephthalides (*IV*). With the use of linear relationships between the C=O stretching frequencies and substituent σ constants the transmission of substituent effects in the above systems has been studied.

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EXPERIMENTAL

Preparation of the dithiatetrahydrophthalides *I* and *II* was already reported[5]. The substituted 3-(1-naphthyl)methylenephthalides (*IV*) were prepared by the known procedures[6,7]. The compounds were purified prior to application by repeated crystallization or by chromatography. The melting points of all the compounds agreed well with literature data[5-7].
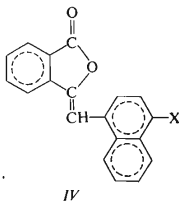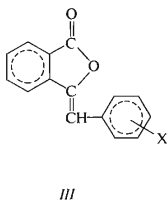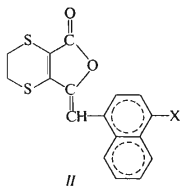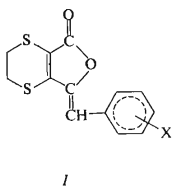
The infrared spectra of the compounds of type *I*, *II* and *IV* were measured on a Zeiss UR 20 spectrophotometer, in the region of 2000—1500 cm^{-1}. The wavenumber scale of the instrument was calibrated by the standard spectrum of an indene–cyclohexane–camphor ternary system. The measurements in the 2000—1600 cm^{-1} region were made with 8 . 10^{-3}M solutions of the compounds in chloroform, using 0·1 cm thick cells. The spectra in the 1600—1500 cm^{-1} region were measured with 8 . 10^{-2}M solutions in chloroform in cells thick 0·01 cm. The frequencies in the region of the C=O and C=C stretching vibrations were read with the accuracy of ±1 cm^{-1}. In the study of hydrogen bonds between the compounds of type *I* and ethanol, the spectra were measured in the region of 3800—3200 cm^{-1}. The measurements were carried out with tetrachloromethane solutions in which the concentration of the studied compound was 3 . 10^{-2}—4 . 10^{-2}M and that of ethanol was 2 . 10^{-2}M. The cells were c. 0·5 cm thick. The frequencies of the absorption bands corresponding to associated O—H groups were read with the accuracy of ±2 cm^{-1}. The ethanol used in the measurements was anhydrous. Carbon tetrachloride and chloroform were purified and dried in the usual way.

The spectral data were correlated with σ constants reported by McDaniel and Brown[8]. The linear correlations were statistically analysed[9] on a Gier digital computer. The energies of hydrogen bonds of the compounds of type *I* with ethanol were calculated according to the work[10], using the relation $-\Delta H = 0·016\ \Delta\nu(OH) + 0·63$.

RESULTS AND DISCUSSION

As shown[1-3] the infrared spectra of cyclic compounds containing the

$$\begin{matrix} & & \text{O} \\ & & \parallel \\ -\text{C}-\text{Z}-\text{C}=\text{CH}- \end{matrix}$$

grouping (Z=O, S, NH) show complex C=O stretching bands. The origin of these complex absorption bands and their applicability to correlations with structure were discussed in previous communications[2,3]. Quite in harmony with expectation, the complex character is also displayed by the absorption bands corresponding to the C=O stretching vibrations in all the compounds under study.

The spectral data for dithiatetrahydrophthalides *I* are summarized in Table I. The strong C=O stretching bands of these compounds are located in the 1 777 to 1 757 cm^{-1} region. The C=O stretching bands of 3-phenylmethylenephthalides *III* occur[1] in the 1 792−1 775 cm^{-1} region. The shift of the C=O stretching frequencies to the lower-frequency region observed for the former compounds can be explained by stronger conjugation between the carbonyl group and the system of C=C bonds, as well as by electron-donor action of the two sulphur atoms. As the result of the stronger conjugation also medium absorption bands corresponding to the C=C stretching vibration of the central double bond are located in the lower-frequency region (1 658 − 1 625 cm^{-1}) than are the corresponding bands in the 3-phenylmethyl-enephthalides *III* (1 671 − 1 668 cm^{-1}).

The assignment of the absorption bands to the stretching vibration of the C=C bond in 4,7-di-thia-4,5,6,7-tetrahydrophthalide skeleton was based on comparison of the spectra of the compounds of type *I* with the spectrum of 3,6-dithia-3,4,5,6-tetrahydrophthalanhydride. The spectrum of the latter compound exhibits the absorption band at 1 560 cm^{-1} which, can be attributed[11] to the C=C stretching vibration. In the spectra of the studied tetrahydrophthalides *I* these weak to medium bands occur in the 1 541 − 1 537 cm^{-1} region. The frequency shift to the lower-frequency region, relative to the C=C stretching frequency in 3,6-dithia-3,4,5,6-tetrahydro-phthalanhydride, is caused again by stronger conjugation in the system of double bonds.

The C=O stretching frequencies of dithiatetrahydrophthalides *II* (Table II) do not differ much from those of corresponding benzene analogues *I*. The absorption bands of the stretching vibrations of both C=C bonds in the compounds of type *II* are slightly shifted to the lower-frequency region, relative to the corresponding bands of their benzene analogues *I*.

In Table III are presented spectral data obtained for 3-(1-naphthyl)methylene-phthalides (*IV*). The frequencies of the C=O stretching vibration of these compounds (1 790 − 1 774 cm^{-1}) are close to the frequencies of the C=O stretching vibration of corresponding benzene analogues (*III*) and are higher than the frequencies found for dithiatetrahydrophthalides *II*. The absorption bands corresponding to the stretch-ing vibration of the central C=C bond lie in the case of the compounds of type *IV* in the lower-frequency region than the bands of their benzene analogues *III*.

Under conditions specified in Experimental, dithiatetrahydrophthalides *I* form weak intermolecular hydrogen bonds with ethanol, which are of the type >C=O... ...H—O—. In Table I are given characteristic data for these hydrogen bonds, Δν(OH),

TABLE I

IR Data and Energies of Hydrogen Bonds with Ethanol, of 3-Phenylmethylene-4,7-dithia-4,5,6,7-tetrahydrophthalides (*I*)

Compound	X	ν(C=O), cm^{-1}	ν(C=C), cm^{-1} in		$\Delta\nu$(OH), cm^{-1}	$-\Delta H$ kcal mol^{-1}
			>C=CH—	—S—C=C—S—		
1	4-NH$_2$	1 757	1 653	1 541	^{a}	^{a}
2	4-OCH$_3$	1 760	1 653	1 541	108	2·36
3	4-CH$_3$	1 762	1 653	1 537	103	2·28
4	3-CH$_3$	1 764	1 654	1 538	99	2·21
5	H	1 765	1 653	1 540	98	2·20
6	4-F	1 766	1 658	1 537	96	2·17
7	3-OCH$_3$	1 767	1 654	1 540	100	2·23
8	4-I	1 769	1 653	1 540	95	2·15
9	4-Cl	1 768	1 653	1 540	93	2·12
10	3-F	1 770	1 656	1 539	89	2·05
11	3-I	1 770	1 653	1 540	^{a}	^{a}
12	3-Cl	1 771	1 655	1 540	87	2·01
13	4-NO$_2$	1 777	1 652	1 538	^{a}	^{a}

^{a} The spectra were not recorded because of low solubility of the compounds in tetrachloromethane.

TABLE II

IR Data for Substituted 3-(1-Naphthyl)methylene-4,7-dithia-4,5,6,7-tetrahydrophthalides (*II*)

Compound	X	ν(C=O), cm^{-1}	ν(C=C), cm^{-1} in	
			>C=CH—	—S—C=C—S—
14	NH$_2$	1 754	1 647	—^{a}
15	OCH$_3$	1 759	1 648	1 535
16	CH$_3$	1 762	1 648	1 537
17	H	1 764	1 650	1 537
18	NHCOCH$_3$	1 766	1 650	1 539
19	Cl	1 767	1 649	1 538
20	Br	1 767	1 649	1 538
21	NO$_2$	1 782	1 647	—^{a}

^{a} The absorption bands could not be measured because of low solubility of the compounds in chloroform.

i.e. the differences between the frequencies of free OH and associated OH stretching vibrations. As follows from comparison with hydrogen bonds studied under identical experimental condition[1] the compounds of type *I* form in average of about 0·5 kcal mol^{-1} stronger hydrogen bonds with ethanol than do 3-phenylmethylenephthalides *III*. This fact can again be explained by stronger conjugation between the C=O group and the system of C=C bonds as well as by the effect of sulphur atoms in the compounds of type *I*, compared to 3-phenylmethylenephthalides *III*. In the series of compounds of types *II* and *IV* hydrogen bonds with ethanol could not be studied because of very poor solubility of these compounds in tetrachloromethane.

TABLE III

Infrared Spectral Data for Substituted 3-(1-Naphthyl)-methylenephthalides (*IV*)

Compound	X	ν(C=O), cm^{-1}	ν(C=C), cm^{-1} in >C=CH—
22	NH$_2$	1 774	1 659
23	OCH$_3$	1 778	1 659
24	CH$_3$	1 780	1 660
25	H	1 781	1 661
26	NHCOCH$_3$	1 782	1 662
27	I	1 783	1 660
28	Cl	1 784	1 662
29	Br	1 784	1 661
30	NO$_2$	1 790	1 661

TABLE IV

Statistical Parameters of Linear Dependences of Type $y = \varrho\sigma + q$ for 3-Arylmethylene-4,7-dithia-4,5,6,7-tetrahydrophthalides *I* and *II* and 3-Arylmethylenephthalides *III* and *IV*

Meaning of symbols: ϱ slope of the dependence; s_p the error in ϱ; q the intercept; s_q the error in q; s standard deviation; r correlation coefficient; n the number of experimental data used in the correlation.

Series	y	$\varrho \pm s_p$	$q \pm s_q$	s	r	n
I	ν(C=O)	14·54 ± 0·62	1 765·2 ± 0·2	0·8	0·990	13
II	ν(C=O)	15·13 ± 1·38	1 764·1 ± 0·3	1·1	0·978	7
III	ν(C=O)	12·02 ± 0·66	1 782·2 ± 0·2	0·8	0·985	13
IV	ν(C=O)	11·09 ± 0·35	1 781·4 ± 0·0	0·4	0·997	9
I + ethanol	$\Delta\nu$(OH)	−28·92 ± 1·99	98·6 ± 0·4	1·3	−0·984	9

TABLE V

Calculated σ_α Constants for 1- and 2-Naphthyl Groups

Phthalide	ν(C=O), cm^{-1}	σ_α	
		1-Naphthyl	2-Naphthyl
17	1 764	-0.08 ± 0.02	—
3-(2-Naphthyl)methylene-4,7-dithia-4,5,6,7-tetrahydro	1 763	—	-0.15 ± 0.02
25	1 781	-0.10 ± 0.02^a	—
3-(2-Naphthyl)methylene	1 780	—	-0.18 ± 0.03^a

^{a} The data taken from ref.[1].

Similarly[1] as in 3-phenylmethylenephthalides *III* also in the compounds of types *I*, *II* and *IV* studied in the present work good linear correlations exist between the frequencies of the C=O stretching vibration and substituent constants σ (Table IV). In the case of the compounds of type *I* also $\Delta\nu$(OH), characterizing hydrogen bonds with ethanol, can be correlated with σ (Table IV). In correlating the C=O stretching frequencies for series *II* with σ we have omitted the value for the nitro derivative (compound 21) which seriously deviated from the calculated line. A similar deviation has also been observed for the 3-methoxy derivative (compound 7) in the case of the correlation of $\Delta\nu$(OH) with σ for the compounds of type *I*. Statistical parameters of the calculated linear dependences for the series *I*, *II* and *IV* are summarized in Table IV, along with the data reported in work[1] for the series *III* which are presented here for purposes of comparison. As follows from the comparison of the slopes of the linear dependence of ν(C=O) on σ for the series *I* and *III* the slope in the former case is greater $\left(\varrho = 14.54 \pm 0.62\right)$ than in the latter $\left(\varrho = 12.02 \pm 0.66\right)$. This indicates that electronic effects are transmitted on the C=O group better in 3-phenylmethylene-4,7-dithia-4,5,6,7-tetrahydrophalides *(I)* than in 3-phenylmethylenephthalides *(III)*. In the case of 3-phenylmethylenephthalides *III* we have observed[1,3] that electronic effects are transmitted mainly through *p*-electrons of the oxygen of the lactone ring. In accordance with this assumption, and the difference between the slopes of the dependence of ν(C=O) on σ for the series *I* and *III* one can conclude that (in contradistinction to the compounds of type *III*) in the compounds of type *I* the transmission of electronic effects on the C=O group proceeds mainly through the system of conjugated C=C bonds. This assumption agrees well also with the observation that in the compounds of type *I* the conjugation between the reaction center, the C=O group, and the system of conjugated double bonds is stronger than in the compounds *III*. This makes the transmission of substituent effects *via* C=C bond more efficient. As follows from comparison of the slopes substituent effects are better trans-

mitted through the conjugated $C=C$ bond of the compounds of type I than through the oxygen of lactons ring of the compounds of type III.

From comparison of slopes of the $v(C=O)$ vs σ plots (Table IV) it can be seen that the slopes for the series I and II are identical, taking into account the calculated errors in ϱ in both cases. Similarly, also the slopes for the series III and IV are nearly identical. From the foregoing it follows that substituent effects are transmitted in 4-substituted naphthalene derivatives II and IV to similar extent as in analogous 3- and 4-substituted benzene derivatives I and III. Similar results have also been obtained by Wells and Adcock[12].

The linear dependence of $v(C=O)$ on σ for the compounds of type I, which of all the correlations given in Table IV, is statistically most significant, can be used to calculate σ_α constants of 1-naphthyl and 2-naphthyl groups. The obtained σ_α constants are given in Table V, along with the values of σ_α constants determined from the dependence for the series III in the work[1]. From the given values it can be concluded that a weak electron-donor effect of 1-naphthyl group is comparable with the effect of 3-methyl-phenyl group and the effect of 2-naphthyl group is very close in magnitude to that of 4-methylphenyl group.

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