

ON PHTHALIDES AND INDANDIONES. XXXIX.\*  
INFRARED SPECTRA AND SUBSTITUENT EFFECTS  
IN 3-AROXYMETHYLENEPHTHALIDES  
AND 3-ARYLTHIOMETHYLENEPHTHALIDES

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Received April 7th, 1970

Infrared spectra of 31 derivatives of *trans*- and *cis*-3-phenoxyethylenephthalides and *trans*-3-phenylthiomethylenephthalide in the region of the C=O and C=C stretching vibrations were studied. In three series of the compounds investigated linear correlations of the C=O stretching frequencies with  $\sigma$  constants of substituents were observed. It was found that the introduction of oxygen or sulphur bridges into the structure of *trans*-3-arylmethylenephthalides reduces transmission of electronic effects of substituents, sulphur being more efficient than oxygen. On the basis of the above correlations, the coefficients  $\pi$  for transmission of electronic effects through sulphur and oxygen atoms in this system were calculated. The effect of geometric isomerism upon the transmission of electronic effects in 3-aroxyethylenephthalides is discussed.

Solid-phase infrared spectra of some *trans*- and *cis*-3-phenoxyethylenephthalide, 3-( $\alpha$ -naphthoxy)- and 3-( $\beta$ -naphthoxy)-methylenephthalide were reported<sup>1,2</sup>. The infrared spectra of substituted 3-phenylthiomethylenephthalides have not yet been studied. In a previous communication<sup>3</sup> we dealt with substituent effects and their transmission in *trans*-3-arylmethylenephthalides and *trans*-3-arylmethylenecinchomeronides.

In the present work we studied the transmission of electronic effects in a series of substituted *trans*-3-phenoxy-(*I*), *cis*-3-phenoxy-methylenephthalides(*II*), and *trans*-3-phenylthiomethylenephthalides(*III*) by means of infrared spectra in the region of the C=O stretching vibrations.

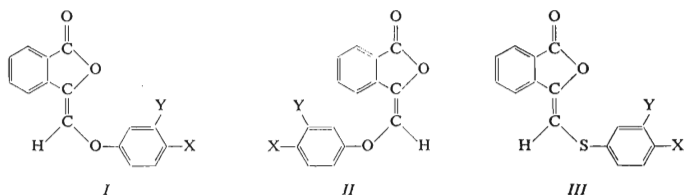
#### EXPERIMENTAL

*Compounds studied.* *trans*- and *cis*-3-Aroxyethylenephthalides (*I* and *II*) were prepared according to refs.<sup>1,4</sup>. Their melting points agreed well with those reported. The synthesis, analytical data and melting points of the new *trans*-3-arylthiomethylenephthalides<sup>5</sup>(*III*) will be reported in the subsequent paper. All the compounds studied were purified by repeated crystallization prior to their application.

\* Part XXXVIII: This Journal 36, 1843 (1971).

*Spectral measurements.* IR spectra in the  $1900\text{--}1600\text{ cm}^{-1}$  region were recorded on a Zeiss UR 20 double beam spectrophotometer. The wavenumber scale of the instrument was calibrated by means of the spectrum of the standard indene-cyclohexanone-camphor mixture after Jones<sup>6</sup>. NaCl cells (c. 0.1 and 0.01 cm thickness) and  $8 \cdot 10^{-3}$  and  $8 \cdot 10^{-2}\text{ M}$  solutions of the compounds in chloroform were used in the measurements. Absorption bands were read with the accuracy of  $\pm 1\text{ cm}^{-1}$ . Chloroform of analytical purity grade, dried and purified in the usual way were used in the measurements. Some *trans*- and *cis*-aroxymethylenephthalides (*I* and *II*) were measured as nujol mulls (about 0.002 cm thickness).

*Treatment of data.* In spectral data-structure correlations (Figs 1–3)  $\sigma$  constants reported by McDaniel and Brown<sup>7</sup> were used. The parameters of linear correlations were computed on a Gier digital computer using statistical relations given in ref.<sup>8</sup>. The C=O and C=C stretching frequencies for the compounds studied as well as  $\sigma$  substituent constants used are summarized in Tables I–III.



## RESULTS AND DISCUSSION

The infrared spectra of all the 3-aroxymethylenephthalides (*I* and *II*) and 3-aryltiomethylenephthalides (*III*) studied exhibit strong absorption band in the  $1794\text{--}1777\text{ cm}^{-1}$  region due to the C=O stretching vibration. In a previous work<sup>3</sup> we observed a splitting of this band to doublets in the case of 3-arylmethylenephthalides, the separation of the maxima being  $15\text{--}20\text{ cm}^{-1}$  and the ratio of their intensities being approximately one. This splitting was supposed<sup>3</sup> to be the result of vibrational coupling or of Fermi resonance. The half-bandwidths of C=O stretching bands of aroxymethylenephthalides (*I* and *II*) and arylthiomethylenephthalides (*III*) are about  $35\text{--}40\text{ cm}^{-1}$ , which indicates that also here we deal with complex bands. As the frequencies of the resolved absorption bands, similarly as in the case of 3-arylmethylenephthalides<sup>3</sup>, are not accessible without analysis of such a complex band, data given in Tables I–III are the observed frequencies of complex bands.

The C=O stretching frequencies of *trans*-3-arylmethylenephthalides<sup>3</sup>, when compared with these for compounds *I* and *III*, are shifted by  $6\text{--}8\text{ cm}^{-1}$  to lower values. This shift indicates a reduction in the C=O bond polarity in compounds *I* and *III*, relative to *trans*-3-phenylmethylenephthalides, which is a consequence of a worse transmission of electronic effects of substituent through the sulphur or oxygen atoms. The C=O stretching frequencies of *cis*-3-phenoxy-methylenephthalide

lides (II) are by  $5-8\text{ cm}^{-1}$  lower than those found for the corresponding *trans*-isomers. This finding is in contradistinction with the results of earlier studies<sup>1,2</sup> which showed that *cis*-3-phenoxy-methylenephthalide and *cis*-3-naphthoxy-methylenephthalides (measured as nujol mulls) absorb in the region of the C=O stretching vibrations at higher frequencies than do the corresponding *trans*-isomers. To clear up this problem, we measured the solid-phase infrared spectra of some couples of the *cis*-, *trans*-isomers of 3-aroxy-methylenephthalides (as nujol mulls). We have found that the C=O stretching bands in these spectra substantially differ from those observed with chloroform solutions. The *trans*-isomers show a broad absorption band which splits into a doublet, the separation of its maxima being as much as  $20-25\text{ cm}^{-1}$ .

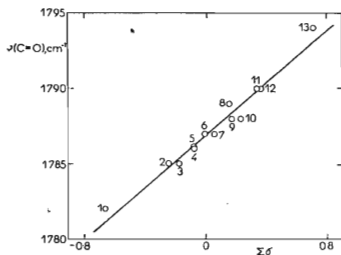


FIG. 1

The Plot of  $\nu(\text{C}=\text{O})$  versus  $\Sigma\sigma$  for *trans*-3-Aroxy-methylenephthalides (I)

For numbering of compounds see Table I.

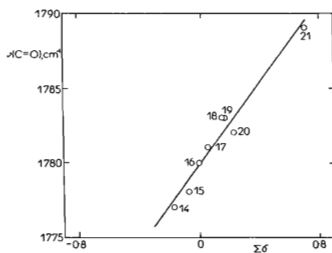


FIG. 2

The Plot of  $\nu(\text{C}=\text{O})$  versus  $\Sigma\sigma$  for *cis*-3-Aroxy-methylenephthalides (II)

For numbering of compounds see Table II.

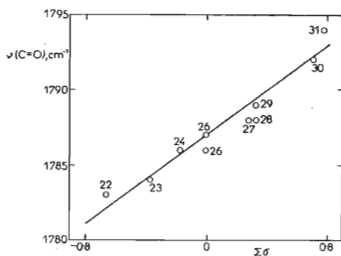


FIG. 3

The Plot of  $\nu(\text{C}=\text{O})$  versus  $\Sigma\sigma$  for *trans*-3-Arylthiomethylenephthalides (III)

For numbering of compounds see Table III.

The *cis*-isomers exhibit a broad absorption band markedly shifted to lower frequencies, compared with the more intense absorption maximum in the doublets of the *trans*-isomers. We believe these discrepancies might be caused either by intermolecular interactions of the compounds in solid phase or by the equilibrium formation of conformes arising from a restricted rotation of the aroxy group around the C—O bond.

TABLE I  
Spectral Data and  $\sum\sigma$  Constants for Substituted *trans*-3-Phenoxy-methylenephthalides (I)

Compound No	X	Y	$\sum\sigma$	$\nu(\text{C}=\text{O})$ $\text{cm}^{-1}$	$\nu(\text{C}=\text{C})$ $\text{cm}^{-1}$
1	NH <sub>2</sub>	H	-0.66	1 782	1 705
2	CH <sub>3</sub>	CH <sub>3</sub>	-0.24	1 785	1 706
3	CH <sub>3</sub>	H	-0.17	1 785	1 706
4	H	CH <sub>3</sub>	-0.07	1 786	1 706
5	H	C <sub>2</sub> H <sub>5</sub>	-0.07	1 786	1 706
6	H	H	0.00	1 787	1 707
7	F	H	0.06	1 787	1 707
8	Cl	CH <sub>3</sub>	0.16	1 789	1 708
9	I	H	0.18	1 788	1 707
10	Cl	H	0.23	1 788	1 707
11	H	F	0.34	1 790	1 708
12	H	Cl	0.37	1 790	1 706
13	H	NO <sub>2</sub>	0.71	1 794	1 708

TABLE II  
Spectral Data and  $\sum\sigma$  Constants for Substituted *cis*-3-Phenoxy-methylenephthalides (II)

Compound No	X	Y	$\sum\sigma$	$\nu(\text{C}=\text{O})$ $\text{cm}^{-1}$	$\nu(\text{C}=\text{C})$ $\text{cm}^{-1}$
14	CH <sub>3</sub>	H	-0.17	1 777	1 696
15	H	CH <sub>3</sub>	-0.07	1 778	1 698
16	H	H	0.00	1 780	1 698
17	F	H	0.06	1 781	1 698
18	Cl	CH <sub>3</sub>	0.16	1 783	1 700
19	I	H	0.18	1 783	1 699
20	Cl	H	0.23	1 782	1 699
21	H	NO <sub>2</sub>	0.71	1 789	1 700

The observed C=O stretching frequencies for all the types of the compounds studied correlate well with  $\sum\sigma$  constants of substituents ( $r$  is the correlation coefficient and  $s$  is the standard deviation): *trans*-3-phenoxyethylenephthalides (I) (Fig. 1)

$$\nu(\text{C}=\text{O}) = 8.68(\pm 0.50) \sum\sigma + 1786.9(\pm 0.1); \quad r = 0.982, \quad s = \pm 0.6, \quad (1)$$

*cis*-3-phenoxyethylenephthalides (II) (Fig. 2)

$$\nu(\text{C}=\text{O}) = 13.55(\pm 1.1) \sum\sigma + 1779.8(\pm 0.4); \quad r = 0.978, \quad s = \pm 0.8, \quad (2)$$

*trans*-3-phenylthiomethylenephthalides (III) (Fig. 3)

$$\nu(\text{C}=\text{O}) = 7.45(\pm 0.54) \sum\sigma + 1787.0(\pm 0.2); \quad r = 0.979, \quad s = \pm 0.7. \quad (3)$$

For the sake of comparison we give here also the analogical correlation found<sup>3</sup> for substituted *trans*-3-phenylmethylenephthalides:

$$\nu(\text{C}=\text{O}) = 12.02(\pm 0.66) \sum\sigma + 1782.2 (\pm 0.2); \quad r = 0.985, \quad s = \pm 0.8. \quad (4)$$

The slopes of the correlations for *trans*-3-aryloxyethylenephthalides (I) and *trans*-3-arylthiomethylenephthalides (III) have lower values than those obtained for the *trans*-3-arylmethylenephthalides. These results indicate that the introduction of oxygen or sulphur bridges into the structure of 3-arylmethylenephthalides makes the transmission of electronic effects from the substituted phenyl group to the carbonyl group more difficult. From the slopes of Eqs. (1) and (3) and that of Eq. (4) the transmission coefficients of electronic effects of substituents through the heteroatom bridges  $\pi(\text{—O—})$  and  $\pi(\text{—S—})$  can be calculated:  $\pi(\text{—O—}) = \rho_1/\rho_4 = 0.72$  and  $\pi(\text{—S—}) = \rho_3/\rho_4 = 0.62$ , where  $\rho_1$ ,  $\rho_3$ , and  $\rho_4$  are the slopes of the above correlations.

From the comparison of the calculated coefficients it follows that in the system under study electronic effects are better transmitted by oxygen atom than by sulphur atom. The transmission of electronic effects through oxygen or sulphur atoms became the subject of a number of studies in which various methods and compounds were used. Some studies<sup>9-12</sup> show that electronic effects of substituents are better transmitted by sulphur than by oxygen atoms. However, the reverse situation was also observed in some cases<sup>13,14</sup>. A general scheme was proposed by Marcus and co-workers<sup>14</sup>. On the basis of their NMR studies and a survey of the results of other authors, Marcus and coworkers concluded that in a conjugative role as an acceptor or an acceptor-donor of negative charge, the sulphur atom is a better transmitter than the oxygen atom. However, when only conjugative electron-donating properties of bridge heteroatoms play role, the reverse situation is observed.

TABLE III  
Spectral Data and  $\sum\sigma$  Constants for Substituted *trans*-3-Phenylthiomethylenephthalides (III)

Compound No	X	Y	$\sum\sigma$	$\nu(\text{C}=\text{O})$ $\text{cm}^{-1}$	$\nu(\text{C}=\text{C})$ $\text{cm}^{-1}$
22	NH <sub>2</sub>	H	-0.66	1 783	1 638
23	OH	H	-0.37	1 784	1 639
24	CH <sub>3</sub>	H	-0.17	1 786	1 639
25	NHCOCH <sub>3</sub>	H	0.00	1 786	1 639
26	H	H	0.00	1 787	1 640
27	I	H	0.18	1 788	1 640
28	Cl	H	0.23	1 788	1 640
29	Br	H	0.23	1 789	1 640
30	H	NO <sub>2</sub>	0.71	1 792	1 641
31	NO <sub>2</sub>	H	0.78	1 794	1 641

From the above discussion it follows that, consistently with the conclusions of Marcus and coworkers<sup>14</sup>, in the case studied here, a better transmission of electronic effects through oxygen than through sulphur atoms indicates that these atoms in a conjugated system play predominantly a role of electron donors, the oxygen atom being a better electron donor than the sulphur atom. In contrast, in other systems like *e.g.* substituted diphenyloxides and diphenylsulphides<sup>12</sup> the bridge atoms display acceptor-donor properties and therefore the sulphur atom by virtue of their ability to 3- $d_{\pi}$  acceptor-conjugation, becomes a better transmitter of electronic effects than the oxygen atom.

The higher value of the slope of the  $\nu(\text{C}=\text{O}) - \sigma$  dependence for *cis*-aroxymethylenephthalides (*I*) (Eq. (1)) as compared with that for the *trans*-isomers (*II*) (Eq. (2)), speaks for a better transmission of electronic effects in the *cis*- than in the corresponding *trans*-isomers.

The absorption bands with weak or medium intensity belonging to the C=C stretching vibration of the central >C=CH-group in the *trans*- and *cis*-3-aroxymethylenephthalides occur in the higher frequency region (1708–1696  $\text{cm}^{-1}$ ), compared with analogical bands of 3-arylmethylenephthalides<sup>3</sup> (1668–1660  $\text{cm}^{-1}$ ). This increase in the C=C stretching frequencies of compounds *I* and *II* may be accounted for by the effect of two oxygen atoms in the vicinity of the C=C bond, in accordance with the analogical cases reported in literature<sup>15</sup>. The C=C stretching bands of *trans*-3-aroxymethylenephthalides (*I*) (1708–1705  $\text{cm}^{-1}$ ) are shifted to higher frequencies, compared with the *cis*-isomers (*II*) (1700–1696  $\text{cm}^{-1}$ ). Therefore, in addition to the C=O stretching vibration, the C=C stretching vibration, too,

can be used in distinguishing different geometric isomers of 3-methylenephthalide derivatives. The C=C stretching bands of *trans*-3-arylthiomethylenephthalides (*III*) occur in the 1641–1638 cm<sup>-1</sup> region. The lower frequencies of the C=C stretching bands of these compounds, in comparison with both the 3-methylenephthalides (*I* and *II*) and 3-arylmethylenephthalides (*III*), may be accounted for by the effect of the sulphur atom adjacent to the C=C bond, consistently with the analogical cases reported<sup>16</sup>. The C=C stretching frequencies for all the compounds studied (*I–III*) are not markedly influenced by change of solvent polarity as well as by electronic effects of substituents.

*We wish to thank doc. Dr Š. Toma and doc. Dr P. Hrnčiar for valuable comment and stimulating discussions.*

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Translated by J. Hetflejš.