

THE INFRARED SPECTRA OF SOME SUBSTITUTED 3-PHENYLIMINOXINDOLE DERIVATIVES

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The infrared spectra of ten substituted 3-phenyliminoxindole derivatives were measured and the spectral data were correlated with constants, expressing electronic effects of substituents. On the basis of the obtained results conclusions were drawn about the transfer of electronic effects of substituents to the particular functional groups. It was found that in sufficiently concentrated solutions the studied compounds *I* exist in the form of dimers.

Infrared spectra of oxindole, isatine and their derivatives, substituted on the aromatic nucleus or on the five-membered heterocyclic ring, have been the subject of several papers¹⁻³. We have studied⁴ the electronic absorption spectra of some substituted 3-phenyliminoxindole derivatives in various solvents.

Since the infrared absorption spectra of substituted 3-phenyliminoxindole derivatives *I* have not been hitherto described, we turned our attention to their study. The spectral data, measured in various solvents, were used in the investigation of electronic substituent effects on the functional groups in compounds *I*.

EXPERIMENTAL

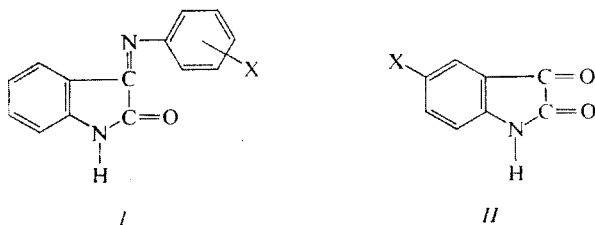
The preparation and physical constants of the substituted 3-phenyliminoxindole derivatives *I* were described previously⁵. The compounds *I* were purified before spectral measurements by subsequent crystallizations from ethanol and chloroform.

The IR-spectra of the compounds *I* were measured on a Zeiss UR-20 spectrophotometer in the regions 1800–1600 cm⁻¹ and 3400–3300 cm⁻¹. The frequency scale of the instrument was calibrated using standard polystyrene and water vapour spectra. The accuracy in the region of C=O and C=N vibrations was ±1 cm⁻¹, measurements in the N—H vibrations region were accurate to ±2 cm⁻¹. The compounds *I* were measured in 0.01–0.5 cm cells in chloroform, pyridine and nitromethane solutions. The concentration was adjusted so that the value of the maximum absorption in the C=O stretching vibrations region was approximately 75%.

The spectral data were correlated with the structure of the compounds *I*, using σ constants published by McDaniel and Brown⁶; σ^* constants were taken from the paper of Brown and Okamoto⁷ and the σ^* constant for 4-OC₂H₅ was taken from ref.⁸. The statistical parameters of the regression analysis were calculated on a digital computer Minsk²¹ using a standard program.

RESULTS AND DISCUSSION

It is known that isatines¹, oxindoles² and similar five-membered heterocyclic compounds, containing adjacent C=O and N—H groups, exist in concentrated solutions in the form of cyclic dimers with hydrogen bonds of the type $>CO \cdots NH<$. These hydrogen bonds manifest themselves in the IR-spectra by splitted absorption bands belonging to C=O and N—H vibrations³, the higher frequency bands corresponding to vibrations of unassociated groups and the bands at lower frequency being due to vibrations of bonded groups.



The C=O, C=N and N—H stretching frequencies which were used in the correlations with the structure of the compounds *I*, were measured in dilute solutions. When the concentration of these solutions is lowered, the dimeric associates of the molecules of the studied compounds *I* are destroyed and the spectra exhibit only single stretching vibration bands of free C=O and N—H groups. The wavenumbers of some characteristic bands of the compounds *I*, measured in chloroform, pyridine and nitromethane, are given in Table I.

As seen from Table I, the spectra exhibit a strong absorption band in the region

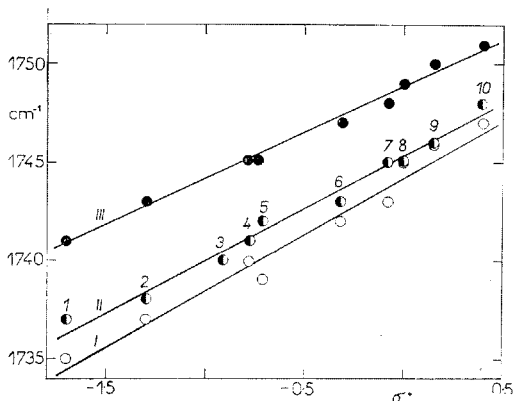


FIG. 1
Plot of the Wavenumbers of the C=O
Stretching Vibrations against σ^* Substituent
Constants for Substituted 3-Phenyliminoxin-
doles *I*

1 $\nu(C=O)$ in chloroform, 2 $\nu(C=O)$
in pyridine, 3 $\nu(C=O)$ in nitromethane.

1751–1735 cm^{-1} due to the C=O stretching vibration. In the spectra of 5-substituted oxindoles² this band is found at 1758–1700 cm^{-1} . The medium or strong band in the region 1665–1650 cm^{-1} belongs to the C=N stretching vibration, and the weak absorption band at 3345–3341 cm^{-1} is due to the N—H stretching vibration. It is evident from Table I that in all solvents, used for the measurements, electron donating substituents in the compounds *I* lower the C=O and C=N stretching frequencies, whereas the electron-accepting substituents have the opposite effect.

The wavenumbers of C=O stretching vibrations, measured in chloroform, pyridine and nitromethane, as well as the wavenumbers of C=N stretching vibrations measured in chloroform, were correlated with σ and σ^* substituent constants. The statistical parameters of the regression analysis are given in Table II.

The correlations of the wavenumbers with σ^* constants are statistically more significant than the correlations with the Hammett σ constants. This indicates strong mesomeric interaction between substituted benzene nucleus and the system —N=C—C=O. For this reason we shall use in further correlations the slopes of the linear relationships based on σ^* constants.

Comparison of the slope of the linear relationship $\nu(\text{C}=\text{N})$ vs σ^* ($\rho = 7.09$) for the data in chloroform with the slope of the relationship $\nu(\text{C}=\text{O})$ vs σ^* ($\rho = 5.82$) shows that the former value is higher. From this it follows that the C=N bond, which in the conjugated system is closer to the substituted benzene ring, is more sensitive to the substituent effects than the C=O bond of the oxindole ring.

TABLE I
Infrared Spectral Data for Substituted 3-Phenyliminoxindole Derivatives *I* (in cm^{-1})

Compound	X	Chloroform			Pyridine	Nitro- methane
		$\nu(\text{C}=\text{O})$	$\nu(\text{C}=\text{N})$	$\nu(\text{N}-\text{H})$	$\nu(\text{C}=\text{O})$	$\nu(\text{C}=\text{O})$
1	4-N(CH ₃) ₂	1 735	1 650	3 345	1 737	1 741
2	4-NH ₂	1 737	^b	3 346	1 738	1 743
3	4-OH	^a	^a	^a	1 740	^a
4	4-OCH ₃	1 740	1 654	3 343	1 741	1 745
5	4-O—C ₂ H ₅	1 739	1 654	3 342	1 742	1 745
6	4-CH ₃	1 742	1 657	3 342	1 743	1 747
7	3-CH ₃	1 743	1 661	3 342	1 745	1 748
8	H	1 745	1 659	3 342	1 745	1 749
9	4-Br	1 746	1 662	3 341	1 746	1 750
10	3-Cl	1 747	1 665	3 341	1 748	1 751

^a The compound is insoluble; ^b overlapping with N—H deformation vibration band.

TABLE II

Statistical Parameters of Linear Correlations of Spectral Data with Substituent Constant for the Substituted 3-Phenyliminoxindole Derivatives *I*

N number of compounds used for correlation, ϱ slope, s_ϱ slope error, q intercept, s_q intercept error, *S* standard deviation, *r* correlation coefficient, *T* value of the correlation significance test.

No	Correlation	Solvent	<i>N</i>	ϱ	s_ϱ	q	s_q	<i>S</i>	<i>r</i>	<i>T</i>
1	$\nu(\text{C}=\text{N})^- \sigma$	chloroform	8	12.72	1.507	1 659.3	0.55	1.55	0.950	7.4
2	$\nu(\text{C}=\text{N})^- \sigma^+$	chloroform	8	7.09	0.673	1 660.4	0.49	1.37	0.961	8.5
3	$\nu(\text{C}=\text{O})^- \sigma$	chloroform	9	10.47	0.761	1 743.5	0.31	0.92	0.975	11.6
4	$\nu(\text{C}=\text{O})^- \sigma^+$	chloroform	9	5.82	0.296	1 744.3	0.24	0.71	0.985	15.1
5	$\nu(\text{C}=\text{O})^- \sigma$	pyridine	10	9.54	0.536	1 744.4	0.22	0.67	0.982	14.9
6	$\nu(\text{C}=\text{O})^- \sigma^+$	pyridine	10	5.25	0.184	1 745.3	0.15	0.47	0.992	21.7
7	$\nu(\text{C}=\text{O})^- \sigma$	nitromethane	9	8.49	0.517	1 748.1	0.21	0.62	0.982	13.9
8	$\nu(\text{C}=\text{O})^- \sigma^+$	nitromethane	9	4.72	0.151	1 748.8	0.12	0.36	0.994	24.2

As seen from the measurements in chloroform, pyridine and nitromethane (Fig. 1), the slopes of the linear relationships $\nu(\text{C}=\text{O})$ vs σ^* decrease with the increasing polarity of the solvent (Table II), *i.e.* the C=O stretching frequencies become less sensitive to the electronic substituent effects with the increasing polarity of the medium.

The fact that in compounds *I* the electronic substituent effects are markedly transmitted to the system $-\text{N}=\text{C}-\text{C}=\text{O}$ leads to the conclusion that the substituted benzene nucleus is coplanar with the azomethine group and thus also with the oxindole ring. Different situation has been found in non-planar benzanilides^{9,10} where the electronic effects of substituents attached to the benzene nucleus of the aniline moiety are practically not transmitted to the C=N bond; in this case the wavenumber $\nu(\text{C}=\text{N})$ is constant and does not depend on the Hammett σ substituent constants.

In order to compare the measured IR-spectral data for the compounds *I* with analogous data for 5-substituted oxindole derivatives *II*, the C=O stretching vibrations were correlated also with σ substituent constants.

Kelie and coworkers² found for 5-substituted oxindole derivatives *II* a linear correlation between wavenumbers of C=O stretching vibrations of the carbonyl in the neighbourhood of NH group and σ substituent constants ($\varrho = 37.5$) and assumed that in these compounds the electronic substituent effects are transmitted through the nitrogen hetero atom. The high value of the slope of this relation ($\varrho = 37.5$) indicates that in 5-substituted oxindole derivatives *II* the electronic substituent effects are transmitted to the C=O group much more efficiently than in the studied 3-phenyliminoxindole derivatives *I* ($\varrho = 10.47-8.49$).

The effect of substituents on the wavenumber of the N—H valence vibration in the oxindole ring is small and it cannot be linearly correlated with substituent constants. Similar effect was observed also in the case of 3-pentylmethylenephthalimides¹¹ where the N—H group is directly conjugated with the substituted benzene ring.

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