

Infrared spectra of heterocumulenes. II. Infrared spectral data of some ketenimines*

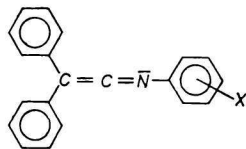
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Infrared spectral data of seven aromatic diphenylketene-*N*-phenylimine derivatives are reported. Integrated absorption intensities of $\nu_{\text{as}}(\text{CCN})$ of ketenimines with $\nu_{\text{as}}(\text{XYZ})$ of typical heterocumulenes are compared and correlated with σ -substituent constants. It has been found that the CCN group of ketenimines studied is electron-releasing.

Although *N*-analogs of ketenes, ketenimines, have been known for more than 50 years [1], until recently very little information has been available on this class of compounds. Only in the last few years the synthesis and the physical and chemical properties of these compounds have been studied more thoroughly [2–8]. Not very much is known about the characteristics of infrared bands of ketenimines. *Stevens* and *French* reported the synthesis and u.v. and i.r. spectra of diphenyl-*N*-4-tolylimine [5] and of four aliphatic ketenimines [6]. These authors assigned strong absorption bands in the range of 2000–2050 cm^{-1} in the spectra of ketenimines to the asymmetric stretching vibration of the $>\text{C}=\text{C}=\text{N}$ group. In this work we report characteristic data of the $\nu_{\text{as}}(\text{CCN})$ bands of seven ketenimines (Scheme 1).



	<i>I</i>	<i>II</i>	<i>III</i>	<i>IV</i>	<i>V</i>	<i>VI</i>	<i>VII</i>
X =	4-OCH ₃	4-CH ₃	H	4-Cl	4-Br	4-NO ₂	3-CH ₃

Scheme 1

Experimental

Compounds (*I–V*) and (*VII*) were prepared by dehydrating the appropriate diphenylacetic acid anilides with triphenylphosphine bromide according to the method of *Bestmann et al.* [3]. Compound (*VI*) was prepared by dechlorination of the respective α -chloroiminochloride with powdered copper according to the method of *Singhal and Smith* [8].

Spectral measurements

Infrared spectra of the compounds studied were recorded for solutions in CCl_4 with a UR-20 (Zeiss, Jena) instrument operating under the conditions described previously [9, 10].

Integrated absorption intensities were determined by a method described in the previous paper [10]. The range of integration was 160 cm^{-1} (80 cm^{-1} on both sides from the maximum of absorption).

Results and discussion

In the i.r. spectra of all the studied ketenimines characteristic intense absorption bands near 2000 cm^{-1} were observed (Table 1; Fig. 1).

It is known [11, 12] that compounds containing the cumulative system of double bonds ($\text{X}=\text{Y}=\text{Z}$), such as isothiocyanates, allenes, ketenes, *etc.*, absorb in the range

Table 1

 Infrared spectral data of substituted diphenylketene-*N*-phenylimines

No.	$\bar{\nu}_1$	ϵ	$\bar{\nu}_{\text{max}}$	ϵ	$\bar{\nu}_2$	ϵ	$\Delta\nu_{1/2}$	$A \cdot 10^{-4}$
<i>I</i>	—		1998	893	1980	112	23	5.5
<i>II</i>	—		2002	883	1980	87	22	5.9
<i>III</i>	—		2003	875	1980	151	23	6.8
<i>IV</i>	2016	236	2001	695	1986	272	31	6.5
<i>V</i>	2012	536	1999	606	1986	245	38	6.9
<i>VI</i>	2012	397	1997	605	—	—	42	8.7
<i>VII</i>	—		2003		1986		25	—

$\bar{\nu}$ and $\Delta\nu_{1/2}$ in cm^{-1} ; A in $\text{l mol}^{-1} \text{ cm}^{-2}$; ϵ in $\text{l mol}^{-1} \text{ cm}^{-1}$.

of $1900\text{--}2100 \text{ cm}^{-1}$. Therefore the absorption bands at $\sim 2000 \text{ cm}^{-1}$ observed in the spectra of ketenimines can be assigned to the asymmetrical stretching vibration of the >C=C=N group.

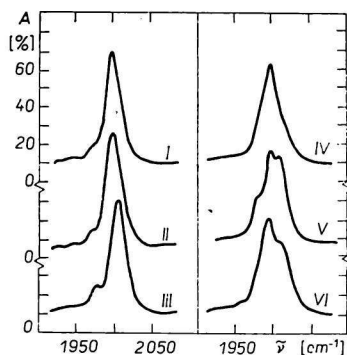


Fig. 1. Infrared spectra of ketenimines in the range of $1900\text{--}2100 \text{ cm}^{-1}$.

From the data listed in Table 1 it can be seen that the studied ketenimines display the absorption band of $\nu_{\text{as}}(\text{CCN})$ split into a doublet (in the case of chloro and bromo derivatives into a triplet), whilst the maximum of absorption corresponds to the band at 2000 cm^{-1} . The wavenumber of this band is only slightly influenced by substituents. However, the intensity of this band is relatively high ($\epsilon = 605 \rightarrow 893 \text{ l mol}^{-1} \text{ cm}^{-1}$) and it decreases with the increasing electron-withdrawing power of the substituent.

The second component of this band of complex shape is observed at wavenumbers ($1980\text{--}1986 \text{ cm}^{-1}$) lower than those of the previous band. Its wavenumber is almost substituent independent. The intensity of this band is relatively low ($\epsilon = 87 \rightarrow 272 \text{ l mol}^{-1} \text{ cm}^{-1}$) and it is not observed in the spectrum of nitro derivative (VI). In the spectra of compounds (IV), (V), and (VI) an additional third relatively intense band ($\epsilon = 230\text{--}530 \text{ l mol}^{-1} \text{ cm}^{-1}$) in the range of $2012\text{--}2016 \text{ cm}^{-1}$ has been observed.

The complex structure of these absorption bands can be explained analogously as in the case of carbodiimides and other heterocumulenes [9] absorbing in this region. Therefore it can be assumed that the complex structure of absorption bands is due to the Fermi resonance interaction between one fundamental vibration of the CCN group and some overtones or combination tones (Fig. 2).

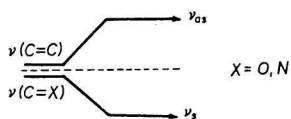


Fig. 2. Interaction of the vibration of C=C and C=X bonds (the origin of $\nu_{\text{s}}(\text{C}=\text{C}=\text{X})$ and $\nu_{\text{as}}(\text{C}=\text{C}=\text{X})$).

It is known that ketenes [13] absorb at higher wavenumbers (by $\sim 130 \text{ cm}^{-1}$) than ketenimines (e.g. diphenylketene absorbs at 2130 cm^{-1}) and the absorption band is split into a doublet. In the case of cumulative systems $\text{C}=\text{C}=\text{X}$, where $\text{X} = \text{O}, \text{N}$, no characteristic vibrations of the $\text{C}=\text{C}$ and $\text{C}=\text{X}$ bonds appear; but strong interactions occur giving two bands more closely corresponding to triple and single bond wavenumbers. The wavenumber of the $\nu_{\text{as}}(\text{C}=\text{C}=\text{X})$ band depends, besides other factors mainly on the force constant (k) of the $\text{C}=\text{X}$ bond: (k) values for the $\text{C}=\text{C}$, $\text{C}=\text{N}$, and $\text{C}=\text{O}$ bonds are approximately 9.5×10^5 , 12.1×10^5 , and $15.5 \times 10^5 \text{ dyn cm}^{-1}$, respectively.

By comparing the force constants of $\text{C}=\text{C}$, $\text{C}=\text{N}$, and $\text{C}=\text{O}$ bonds it can be seen that the wavenumbers of the $\nu_{\text{as}}(\text{CCO})$ band increase with the increasing force constant, which is in agreement with the experimental data.

Half-band widths of these complex bands are in the range of $22\text{--}42 \text{ cm}^{-1}$ and increase with the increasing electron-withdrawing power of the substituent.

Integrated absorption intensities (A) of ketenimines studied are in the range of $5.5 \times 10^4\text{--}8.7 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-2}$. As seen from Table 1, integrated absorption intensities are more sensitive to the influence of substituents as compared with the wavenumbers of the bands and they increase with the increasing electron-withdrawing power of substituents.

We have found a linear relationship between $\log A$ and σ_p and σ_p^+ constants, respectively ($r = 0.958$, $\rho = 0.175$; $r = 0.970$, $\rho^+ = 0.128$) suggesting the possibility of direct relation between the electrical properties of the substituents and the intensity of absorption in these systems. A positive slope ρ of this dependence points out that with the increasing electron-withdrawing power of the substituents the greater change of the dipole moment of the bands during the vibration appears resulting in higher values of integrated absorption intensities of the $\nu_{\text{as}}(\text{CCN})$ bands.

Table 2

Infrared spectral characteristics of C-heterocumulenes

R-X=Y-Z	Type of compounds	$\nu_{\text{as}}(\text{XYZ})$ $\bar{\nu}$ [cm ⁻¹]	A · 10 ⁻⁴	Ref.
R-N=C=O	Isocyanates	2280—2220	12—17	[12]
R-N=C=S	Isothiocyanates	2140—1910	13—18	[16]
R-N=C=Se	Isoselenocyanates	2130—2100	15—20	[17]
R-N=C=N-R	Carbodiimides	2180—2100	12—26	[15]
(R) ₂ C=C=N-R	Ketenimines	2050—1990	6—9	[6, 7]

A in l mol⁻¹ cm⁻².

The slope ρ is for ketenimines half that for carbodiimides [10] pointing to the lower sensitivity of this group to electron effects of the substituents.

A positive slope ρ suggests that the CCN group is electron-releasing similarly as OH, NH₂, and other electron-releasing groups [14]. From the infrared spectral data of similar compounds (Table 2) it follows that integrated absorption intensities of ketenimines are lower by about half than those with other C-heterocumulenes. From the comparison of these compounds it is seen that, with the exception of ketenimines, no other heterocumulenes possess the central atom identical with any of the remaining two atoms of the cumulative system. Therefore the polarity of the bonds as well as the change of the dipole moment during the vibration of the CCN group might be expected to be lower than those with other heterocumulenes which would explain the decrease in integrated absorption intensities of $\nu_{\text{as}}(\text{CCN})$ bands.

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