

Infrared spectra of heterocumulenes. I.

The influence of substituents on the infrared spectral bands of $\nu_{as}(\text{NCN})$ of some aromatic carbodiimides

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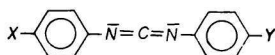
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The influence of substituents on molar absorptivities, integrated absorption intensities and half-band widths of $\nu_{as}(\text{NCN})$ of twelve aromatic carbodiimides has been discussed. A linear relationship between integrated absorption intensities ($\log A$) and Hammett σ and σ^+ substituent constants has been observed ($\rho = 0.449$ and $\rho^+ = 0.247$ respectively). The spectral data suggest that the $-\text{N}=\text{C}=\text{N}-$ group of carbodiimides examined is electron-donating.

Only a limited amount of infrared spectral data is available on carbodiimides. *Khorana* [1] examined some carbodiimides and reported that they absorb at 2150 cm^{-1} . *Meakins* and *Moss* [2] studied the infrared spectra of nine variously substituted carbodiimides in more detail and quoted strong absorption in the range of $2128-2152 \text{ cm}^{-1}$ ($\epsilon = 1300 \rightarrow 1600 \text{ l mol}^{-1} \text{ cm}^{-1}$; $A \sim 10 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-2}$) accompanied in the spectra of three aromatic carbodiimides by a much weaker combination band at lower wavenumbers. The presence of the two absorption bands in this region is assigned by these authors to vibrational interaction between the fundamental vibration and the overtone of some fundamental vibration, both having the same symmetry.

This work reports characteristic spectral data of the bands of $\nu_{as}(\text{NCN})$ of six 4-substituted diphenylcarbodiimides and six 4,4'-disubstituted diphenylcarbodiimides (Scheme 1).



X = Y: $-\text{N}(\text{CH}_3)_2$	I	X = H; Y: $-\text{OCH}_3$	VII
$-\text{OCH}_3$	II	$-\text{CH}_3$	VIII
$-\text{CH}_3$	III	$-\text{H}$	IX
$-\text{Cl}$	IV	$-\text{Cl}$	X
$-\text{Br}$	V	$-\text{Br}$	XI
$-\text{NO}_2$	VI	$-\text{NO}_2$	XII

Scheme 1

Experimental

All carbodiimides studied (except derivatives X and XII; Table 1) were prepared by desulfurization of the corresponding N,N' -disubstituted diphenylthioureas with yellow HgO according to modified procedure [3].

Yellow HgO (21.5 g; 0.1 mole) was slowly added to a refluxing mixture of the appropriate thiourea (0.05 mole) and sulfur (0.1 g) in acetone (500 ml). After 20 min the mixture was cooled and the solid filtered off. The filtrate was evaporated under reduced

Table 1
Infrared spectral data of substituted diphenylcarbodiimides

No.	$\bar{\nu}_1$	ϵ	$\bar{\nu}_2$	ϵ	$\bar{\nu}_3$	ϵ	$A\nu_{1/2}$	$A \cdot 10^{-4}$
<i>I</i>	2140	1438	2115	1438	2040	82	62	14.4
<i>II</i>	2140	1029	2115	943	2085	61	55	14.2
<i>III</i>	2145	963	2115	1212	2045	50	54	15.4
<i>IV</i>	2169	310	2135	1276	2094	207	27	14.6
<i>V</i>	2154	667	2121	930	2078	98	58	12.1
<i>VI</i>	2162	1352	2137	2070	2100	487	63	25.7
<i>VII</i>	2145	972	2115	696	2045	234	57	12.1
<i>VIII</i>	2147	1123	2115	854	2045	75	57	13.8
<i>IX</i>	2147	1306	2115	769	2045	93	58	17.1
<i>X</i>	2147	1568	2115	896	2045	116	56	19.7
<i>XI</i>	2148	2004	2115	1205	2045	117	60	21.1
<i>XII*</i>	2187		2105		2055		—	—

* Not measured. The solubility of the compound in CCl₄ was too low to permit the intensity measurements.

$\bar{\nu}$ and $A\nu_{1/2}$ in cm⁻¹; ϵ in l mol⁻¹ cm⁻¹; A in l mol⁻¹ cm⁻².

pressure to a small volume (50 ml) and light petroleum (50 ml; b.p. 40–60°C) was added. The solid was filtered off and the filtrate evaporated to dryness. The residue was recrystallized from light petroleum (in the case of solid compounds) or redistilled under reduced pressure (in the case of liquids). Only freshly purified carbodiimides can be used in spectral measurements because they polymerize on standing. Compounds *X* and *XII* were prepared according to [4]. B.p. of carbodiimides prepared agreed well with those reported in literature.

Spectral measurements

Infrared spectra of all compounds studied (*I–XII*) were recorded with a UR-20 Zeiss, Jena instrument in the range of 1900–2300 cm⁻¹ using LiF optics. The calibration was checked against the spectrum of polystyrene. The theoretical spectral slit width was 2.2 cm⁻¹. Carbon tetrachloride (spectroscopic grade) was dried over P₂O₅ and redistilled. The concentration of compounds was 10⁻²–10⁻³ M. The cell with a variable thickness (0.02 → 5 mm) was used.

Integrated absorption intensities were determined by a method of absorption areas [5]. The range of integration was 300 cm⁻¹ (150 cm⁻¹ on both sides from the maximum of absorption). Integration was performed by redrawing the absorption band obtained at five different cell thicknesses on tracing paper and by weighing the paper. Extrapolation was carried out by a programme calculator, model Hewlett–Packard 9100 B. No correction was made for the area outside the absorption band.

Results and discussion

From the infrared spectral data of the compounds studied it can be seen (Table 1) that 4-substituted carbodiimides absorb in the region of 2145 to 2180 cm^{-1} , whereas 4,4'-disubstituted derivatives do so in the range 2115–2140 cm^{-1} . In the spectra of both groups of compounds studied the absorption band in the above-mentioned region is split into a triplet (Fig. 1). With monosubstituted diphenylcarbodiimides this triplet can be characterized as follows.

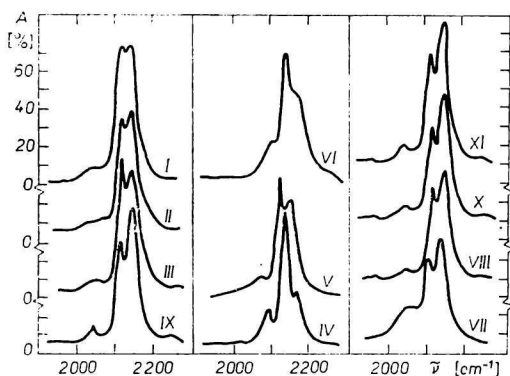


Fig. 1. Infrared spectra of diphenylcarbodiimides.

a) The absorption band at 2145 cm^{-1} corresponding to the maximum of absorption is only little influenced by the nature of the substituents and it can be assigned to the $\nu_{\text{as}}(\text{NCN})$ [1].

b) The absorption band at 2115 cm^{-1} is less intense than the previous one and its wavenumber is independent of the nature of the substituent. From the intensity of the band and also from the analogy of similar systems [6] this band, together with the band at 2145 cm^{-1} , can be interpreted as being Fermi resonance doublet with the average wavenumber at 2130 cm^{-1} .

c) The absorption band at 2045 cm^{-1} is independent of the nature of the substituent. This band might be assigned to the overtone of some fundamental vibration of the aromatic ring.

The absorption bands of disubstituted diphenylcarbodiimides can be characterized as follows.

a) The absorption band at 2115–2135 cm^{-1} (excepting the band of *II*) is the most intense and can be assigned to the $\nu_{\text{as}}(\text{NCN})$. The wavenumber of this band is not influenced by electron-donating substituents but it increases with the increasing electron-withdrawing power of substituents.

b) The absorption band at 2150 cm^{-1} is less intense as compared with the previous one (except the band of *II*). Its wavenumber is not characteristically influenced by substituents, although a shift to higher wavenumbers is observed if the electron-acceptor ability of substituents is increased. Analogously to monosubstituted carbodiimides this as well as the previous band can be also interpreted as being Fermi resonance doublet.

c) The absorption band at 2040–2100 cm^{-1} is not characteristically influenced by substituents; it can be assigned to the overtone of the fundamental vibration of aromatic ring.

As can be seen from Table 1 the absorption bands corresponding to the maximum

of absorption are very intense in both types of compounds studied ($\epsilon = 900 \rightarrow 2000 \text{ l} \cdot \text{mol}^{-1} \text{ cm}^{-1}$). Molar absorptivities of these bands with monosubstituted derivatives increase with the increasing electron-withdrawing power, whereas this dependence is not observed with disubstituted derivatives.

Half-band widths of these bands of complex shape are $55\text{--}63 \text{ cm}^{-1}$, whereas those with monosubstituted derivatives increase with the increasing electron-withdrawing power of the substituents. Integrated absorption intensities A of the bands of compounds studied are $12\text{--}26 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-2}$ and they increase with the increasing power of the substituents, which is significant namely with disubstituted carbodiimides.

An attempt to correlate the integrated absorption intensities of the bands of $\nu_{\text{as}}(\text{NCN})$ of carbodiimides with σ and σ^+ constants was made. A linear relationship was found between $\log A$ and σ and σ^+ constants, respectively ($\rho = 0.449$, $r = 0.988$ and $\rho^+ = 0.247$, $r = 0.970$). The high value of the slope ρ points to the high sensitivity of the $-\text{N}=\text{C}=\text{N}-$ group to the influence of substituents.

Rao *et al.* [7] investigated statistically the correlations of this type ($\log A - \sigma$) and reported that in the correlations of $\log A$ a positive slope is always found when the bond or the group involved is electron-donating in nature, as in phenols, anilines, *etc.* As negative slope is observed when the bond or the group involved is electron-withdrawing in character, as in nitriles, nitro compounds, *etc.* Admitting the validity of this statistically found relation one can consider that the NCN group of carbodiimides studied is of electron-releasing nature.

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