

# Infrared spectra of heterocumulenes. III. Vibrational wavenumbers and integrated absorption intensities of the diazo group of some diphenyldiazomethanes

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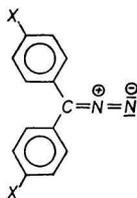
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The influence of substituents on the  $\nu_{as}(\text{CCN})$  bands of diphenyldiazomethanes has been studied. Spectral data of some diphenyldiazomethanes and arenediazonium compounds have been compared. A linear dependence of integrated absorption intensities ( $\log A$ ) of the  $\nu_{as}(\text{CNN})$  and the  $\nu(\text{NN})$  bands, respectively, on Hammett  $\sigma_p^+$  substituent constants has been found ( $\rho^+ = +0.126$  and  $\rho^+ = -0.42$ , respectively). The slope  $\rho$  of this dependence suggests the different nature of the diazo group of both types of the compounds investigated.

Although infrared spectral data of various diazo compounds were reported by several authors [1–7], only the spectrum of diazomethane was interpreted in detail [8]. Other papers dealing with the infrared spectra of diazomethane derivatives with the exception of diazo ketones and diazo esters, report wavenumbers of the stretching vibrational band of the diazo group. *Yates et al.* [1] assigned very strong absorption bands in the i.r. spectra of diazo compounds, such as diazoalkanes, diazo ketones, and diazo esters in the range of 2000–2100  $\text{cm}^{-1}$  to the stretching vibration of the CNN group.

This paper describes the i.r. spectra of six bis-[4-phenyl] substituted diazomethanes (I–VI) and two phenyldiazomethanes (VII and VIII) (Scheme 1).



X = $(\text{CH}_3)_2\text{N}$	I
$\text{CH}_3\text{O}$	II
$\text{CH}_3$	III
H	IV
Cl	V
Br	VI
4-Nitrophenyldiazomethane	VII
Phenyldiazomethane	VIII

*Scheme 1*

Spectra of diphenyldiazomethanes studied have been compared with the spectra of similar compounds — diazonium salts.

### Experimental

All diphenyldiazomethanes were prepared by oxidizing the appropriate hydrazones with yellow HgO [9]; phenyldiazomethanes were prepared by the reaction of the respective tosylhydrazones with sodium methoxide according to [10].

Infrared spectra of the compounds studied were recorded with a UR-20 (Zeiss, Jena) instrument. The experimental conditions and the method used in the determination of integrated absorption intensities of the  $\nu(\text{NN})$  bands are described in [11].

### Results and discussion

As can be seen from the i.r. spectra of diazomethanes intensive single absorption bands in the range of 2030–2070  $\text{cm}^{-1}$ , assigned to the stretching vibration of the NN group are observed (Table 1; Fig. 1). The wavenumber of these bands increases with the increasing electron-withdrawing power of the substituents.

Fig. 1. Infrared spectra of substituted diphenyldiazomethanes.

I.  $(\text{CH}_3)_2\text{N}$ ; II.  $\text{CH}_3\text{O}$ ; III.  $\text{CH}_3$ ; IV. H; V. Cl; VI. Br.

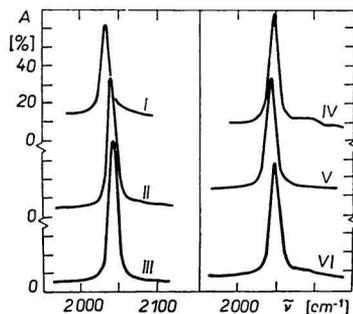


Table 1

Infrared spectral data of substituted diphenyldiazomethanes and phenyldiazomethanes

No.	$\bar{\nu}_{\text{max}}$	$\epsilon$	$\Delta\nu_{1/2}$	$A \cdot 10^{-4\alpha}$	$A \cdot 10^{-4}$
I	2031	501	12.5	2.1	1.7
II	2038	650	13.0	3.3	3.0
III	2039	946	14.0	4.3	4.1
IV	2046	760	16.0	4.2	4.4
V	2046	1015	15.0	5.4	4.9
VI	2049	803	16.0	5.6	5.1
VII	2073	2532	13.0	10.8	—
VIII	2065	842	12.0	4.2	—

a) Values obtained by a direct integrated method;  $\bar{\nu}$  and  $\Delta\nu_{1/2}$  in  $\text{cm}^{-1}$ ;  $\epsilon$  in  $\text{l mol}^{-1} \text{cm}^{-1}$ ;  $A$  in  $\text{l mol}^{-1} \text{cm}^{-2}$ .

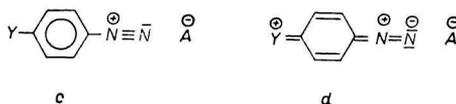
The bands assigned to the stretching vibration of the NN group in benzenediazonium salts are observed at higher wavenumbers than those in diazomethanes. The wavenumber of the NN bonds evidently depends on the nature of the CNN group in both types of the compounds investigated.

One can imagine that diazomethane and its derivatives can exist in the form of some resonance structures, of which structures *a* and *b* are predominant (Scheme 2).



Scheme 2

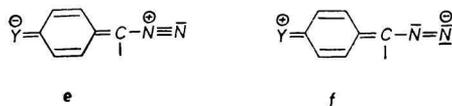
These structures were determined on the basis of X-ray studies [12] and dipole moments of the substituted diazomethanes [13]. The wavenumber of the absorption band of diazomethane, which is lower than that of diazonium salts, can be explained on the basis of these structures. It can be assumed that structure *d* of diazonium salts is less probable than *b* of diazomethanes in consequence of a distortion of an aromatic system resulting in structure *d* (Scheme 3).



Scheme 3

Therefore the electron density in the NN bond in diazomethane is lower than that in the diazo group of diazonium salts (*c*) which results in lower wavenumbers of the bands of the  $\nu(\text{NN})$  in diazomethanes.

With aryl substituted diazomethanes structures *e* and *f*, depending on the nature of the substituent attached to the benzene ring, can be assumed (Scheme 4).



Scheme 4

In the case of an electron-withdrawing substituent (Y) (e.g.  $\text{NO}_2$  group) the structure *e* plays a predominant role leading to a shift of the  $\nu(\text{NN})$  band to higher wavenumbers. In the case of an electron-releasing substituent (e.g.  $(\text{CH}_3)_2\text{N}$ ,  $\text{CH}_3\text{O}$  groups) a double bond character of the NN group can be expected (*f*) resulting in a shift in the opposite sense. Similar dependences were observed in the case of the asymmetrical stretching vibration of the NNN group in azides [14]. The wavenumbers of the  $\text{N}\equiv\text{N}$  bonds in diazonium salts [15, 16] are only slightly influenced by electron-withdrawing substituents.



group of aryldiazomethanes is electron-releasing in nature, whilst the diazo group of benzenediazonium salts is electron-withdrawing, which is in accord with the high Hammett constant of the  $-\overset{\oplus}{\text{N}}\equiv\text{N}$  group ( $\sigma_p = +1.91$ ).

The high integrated absorption intensities of the  $-\overset{\oplus}{\text{N}}\equiv\text{N}$  group in diazonium salts containing the  $(\text{CH}_3)_2\text{N}$  or  $\text{H}_2\text{N}$  groups can be explained by the presence of structure *d* similar to the structure of quinone diazides [15]. Integrated absorption intensities of the bands in the spectra of these compounds are close to those of compounds containing a typical cumulative system of double bonds, such as carbodiimides, isothiocyanates, etc. [19].

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