Tetrahedron. Vol. 29, pp. 4175 to 4177. Pergamon Press 1973. Printed in Great Britain

INFRARED SPECTRA OF HETEROCUMULENES—VII[1]

CORRELATIONS OF INFRARED GROUP WAVENUMBERS AND INTEGRATED ABSORPTION INTENSITIES IN SOME HETEROCUMULENES WITH SUBSTITUENT CONSTANTS

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(*Received in the UK* 14 *June* 1973; *Accepted for publication* 30 *July* 1973)

Abstract—A statistical evaluation of the empirical linear relations of the ν_{as}(X=Y=Z) integrated absorption intensities (A) in forty various heterocumulenes with substituent constants σ and σ^+ has been carried out. The correlations of log A with substituent constants show that the positive sign of the slopes ρ and ρ^+ has been observed, suggesting that with all heterocumulenes studied the structure of the X=Y=Z group with cumulative bonds is dominant.

It has long been known that the vibrational wavenumbers and integrated absorption intensities (A) of some chemical bonds with various types of organic compounds can be correlated with substituent constants.[1-10] Since the nature of the substituent generally effects the force constants, bond dipole moments and bond lengths, therefore both the wavenumber and (A) are also influenced though not always in the same way. Several correlations of (A) in *meta*- and *para*-substituted benzene derivatives with σ and σ^+ substituent contents have been suggested.[2-5,11] The best correlation seems to be between the log A and σ, σ^+ or σ^* constants.[2,3,6,11-13] Also, on the basis of a MO theory a correlation between $\sqrt{A}$ in substituted *meta*- and *para*-benzene derivatives has been established.[14,15] A statistical evaluation of these correlations of vibrational wavenumbers and log A of aliphatic and benzene derivatives was made by Rao and Venkataraghavan.[16]

This paper describes the results obtained with C- and N- heterocumulenes which have strong absorption between 2000 and 2300 cm^{-1}. Also, phenyldiazonium salts have been included for comparison. We have also statistically evaluated the correlations of log A of various types of heterocumulenes in order to test the validity of the correlations.

RESULTS AND DISCUSSION

Table 1 summarizes the results obtained on heterocumulenes studied. A statistical evaluation of the correlations of log A with σ and σ^+ constants suggests that σ^+ constants (correlation coefficient r = 0·954) are better suited for the correlations than σ constants (correlation coefficient r = 0·923) which was to be expected since log A are related to electrical properties of chemical bonds. It is known that in the correlations of vibrational wavenumbers of bonds with substituent constants no relation exists between the sign and the magnitude of ρ and the nature of the bond or group involved in the vibrations, as might be expected. Rao and Venkataraghavan[16] reported that in the correlations of log A a negative slope of the log $A-\sigma$ or log $A-\sigma^+$ plot was always observed when the bond or group involved was electron-withdrawing as in thiocyanates,[17] nitriles[18] and diazonium salts.[19] A positive slope is found when the bond or group involved is electron-releasing as in phenols,[20] anilines,[21] isonitriles[22] etc.

The occurrence of shoulders and the complex nature of the ν_{as}(X=Y=Z) bands with all heterocumulenes studied except diazoalkanes, complicates the problem as regards both wavenumber and intensity plots. The complex structure of the bands in the spectra of heterocumulenes studied has been interpreted as being Fermi resonance doublets.[23-25] In spite of this, in considering the variations of (A) of X=Y=Z groups attached to a benzene ring of heterocumulenes in question, it has been found that a roughly linear correlation exists between log A and substituent constants σ and σ^+ with a positive slope ρ. To relate the sign of ρ in the log $A-\sigma$ or log $A-\sigma^+$ plots to the electrical properties of the X=Y=Z bonds of heterocumulenes studied is possible because (A) is itself dependent on the change of the dipole moment during the vibration of the chemical bond. Substituents favouring a dipole of a

Table 1. Correlation of IR integrated absorption intensities in some heterocumulenes and other compounds containing triple bonds with σ and σ^+ constants

Compounds	XYZ	σ_p	log A_0	ρ	r	s	log A_0	ρ^+	r	s^+	n
Isocyanates	—N=C=O	0·19	5·133	0·129	0·924	0·027	5·152	0·100	0·971	0·012	6
Isothiocyanates	—N=C=S	0·20	5·178	0·147	0·874	0·033	5·206	0·077	0·857	0·021	8
Isoselenocyanates	—N=C=Se	0·31	5·277	0·143	0·962	0·029	5·291	0·065	0·999	0·002	4
Carbodiimides	—N=C=N—	—	5·212	0·449	0·988	0·041	5·250	0·247	0·970	0·036	5
Keteneimines	$>$C=N=N—	—	4·799	0·175	0·958	0·026	4·823	0·128	0·970	0·016	6
Diazoalkanes	$>$C=N=N	—	4·612	0·269	0·951	0·044	4·666	0·126	0·996	0·006	6
Azides	—N=N=N	0·15	4·715	0·201	0·805	0·085	4·717	0·201	0·914	0·052	5
Thiocyanates[17]	—S—C≡N	0·699	3·581	−0·170	0·963	0·028	3·531	−0·109	0·995	0·006	5
Nitriles[18]	—C≡N	0·628	—	−0·787	0·930	0·088	—	−0·461	0·982	0·033	7
Isonitriles[22]	—N=Cl		3·419	0·389	0·938	0·072	3·488	0·224	0·976	0·025	6
Diazonium salts[19]	$-\overset{\oplus}{N}\equiv N$	1·9	—	—	—	—	4·103	−0·42	0·980	—	7

The spectra of compounds, except thiocyanates, isonitriles and diazonium salts, were recorded in CCl_4; thiocyanates in $CHCl_3$; isonitriles in C_6H_6 and diazonium salts in MeOH:

σ—substituent constants of groups involved.

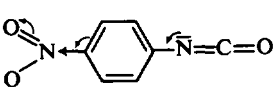
A—integrated absorption intensity, ρ and ρ^+ are slopes of log A − σ and log A − σ^+.

r—correlation coefficient.

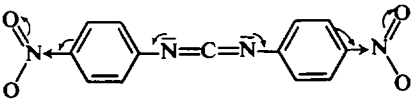
n—number of compounds in the correlation.

s—standard deviation.

bond always increase their integrated absorption intensity (A), for instance



$A = 17{\cdot}1 \times 10^4.l.mol^{-1}.cm^{-2}$



$A = 25{\cdot}7 \times 10^4.l.mol^{-1}.cm^{-2}$

The magnitude of the slope varies in proportion to the electron-withdrawing or electron-releasing power of the X=Y=Z group. The slope of the log A − σ or log A − σ^+ decreased if the electron-withdrawing power of the group is increased. The highest slopes were found with carbodiimides which is in accord with the structure of these compounds because two nitrogen atoms directly attached to benzene rings are very sensitive to electrical effects of substituents.

A positive slope of log A − σ or log A − σ^+ found in all heterocumulenes studied should be in accordance with the assumption that the X=Y=Z group is of an electron-releasing nature. However positive values of substituent constants of the X=Y=Z groups point out that those are electron-withdrawing:

σ_p NCS = 0·20 $\quad \sigma_p$ NCSe = 0·31 $\quad \sigma_p$ NCO = 0·19

Therefore, generalizations in the correlations of log A suggested[16] cannot be applied to heterocumulenes studied. These generalisations can only be applied to simple groups exhibiting well resolved bands. With heterocumulenes four main points must be taken into consideration:

(a) The complex nature of the ν_{as}(X=Y=Z) bands which is due to vibrational coupling between ν(X=Y) and ν(Y=Z) of the cumulative system.

(b) The doubling of the bands due to Fermi resonance.

(c) The presence of shoulders on both sides of the doubled band.

(d) Substituent constants of the X=Y=Z groups which have positive values indicating the electron-withdrawing power of these groups.

The wavenumber splitting in heterocumulenes studied corresponds to the existence of cumulated double bonds e.g. the s_p hybrid character of the central atom of the X=Y=Z group. Evidently, no mesomeric interaction can be expected in the cumulative system of double bonds between the lone electron pair on the X atom and π-electrons of the Y=Z bond. From our results the following points emerge:

(a) A positive slope of the log A − σ or log A − σ^+ is always found when the group contains a cumulative system of double bonds or a lone electron pair on the atom attached directly to the benzene ring.

(b) The sign of the slope of the correlations of log A with substituent constants can only be related to simple groups such as OH, NH_2, CN etc. as reported in literature.[16]

EXPERIMENTAL

IR spectra were recorded with a UR-20 Carl Zeiss instrument using LiF optics. The calibration was checked against the spectrum of polystyrene after each group of measurements. The theoretical spectral slit width was 2·2 cm^{-1}. The intensities were measured on bands of not less than 0·05 absorbance.

Integration was performed by redrawing the absorption band on tracing paper and by weighting the paper. The true integrated intensities (A) were obtained by extrapolation of the dependences of apparent integrated absorption intensities (B) on c.d. Extrapolation was carried out by a programme calculator, Hewlett Packard 9100 B. The range of integration was 300 cm^{-1} (150 cm^{-1} on both sides from the maximum of absorption).

Materials. Analar CCl_4 and MeOH (spectroscopic grade) were used without further purification. Analar $CHCl_3$ was dried several times by passage through a column of blue silica gel before direct use. Compounds used in our investigation were prepared and purified and were analytical purity and their constants agreed well with those in literature.

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