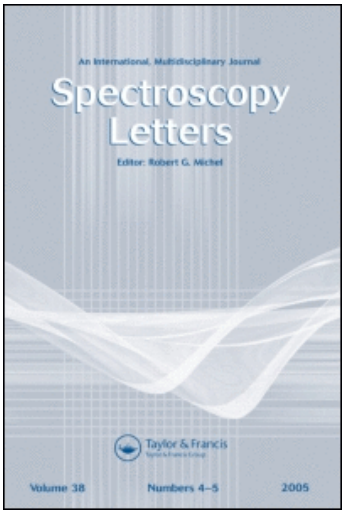

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

Substituent Effects on the Bands Near 1600 cm^{-1} in The Ir Spectra of Azobenzene and Some Substituted Azobenzenes

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To cite this Article Deb, K. K. , Zielinski Jr., W. L. and Casper, J. M.(1973) 'Substituent Effects on the Bands Near 1600 cm^{-1} in The Ir Spectra of Azobenzene and Some Substituted Azobenzenes', Spectroscopy Letters, 6: 10, 585 — 589
To link to this Article: DOI: 10.1080/00387017308060848
URL: http://dx.doi.org/10.1080/00387017308060848

SPECTROSCOPY LETTERS, 6(10), 585-589 (1973)

SUBSTITUENT EFFECTS ON THE BANDS NEAR 1600 cm^{-1} IN THE IR SPECTRA OF AZOBENZENE AND SOME SUBSTITUTED AZOBENZENES[1]

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ABSTRACT

The mean positions and apparent extinction coefficients of the ring stretching bands near 1600 cm^{-1} in the IR spectra of trans azobenzene and some substituted trans azobenzenes are reported. These results are discussed in relation to values reported for substituted benzenes.

INTRODUCTION

It is well known that the position and intensity of the bands of substituted benzenes depend upon the substituents.[2] Katritzky[3-4] observed that the intensities of the ring stretching bands in six-member aromatic rings which appear at about 1600 and 1585 (ν_{16a} and ν_{16b} using Herzberg's notation) should be a function of charge distrubance in the ring. This observation was reported for a large number of various substituted benzenes.[5-9] However, only one substituted azobenzene compound was reported.[5] It was decided, therefore, to investigate the 1600 cm^{-1} region of the infrared spectra of several azobenzene compounds to see if

the intensities are related to charge disturbance in these highly conjugated molecules. It was also of interest to see if the intensities could be predicted by taking one of the rings as a nucleus and considering the remaining portions of the molecule as substituents. Symmetrically substituted compounds were chosen so that the spectral region of interest would not be complicated by different stretching frequencies from the two regions. The fundamental vibrations of the N=N, C-N, N-O, and side chains are known[2,10-14] to fall outside of the 1600 cm^{-1} region.

EXPERIMENTAL SECTION

The trans isomers of the following compounds are investigated: stilbene, azobenzene, azoxybenzene, 4,4'-azophenetole, 4,4'-azoxyphenetole, 4,4'-azoxydianisole, 2,2'-azophenol, and m-azotoluene. All the compounds were commercially available materials in high purity.

The infrared spectra of the samples were recorded in CCl_4 solution using a Perkin-Elmer Model 180 spectrometer. The thickness of the absorption cell was usually 1mm with occasional use of a 2mm cell for the less soluble compounds. Suitable compensation cells were used in the reference beam while recording the absorption spectra. The positions and intensities were measured separately for three solutions of each compound. The mean frequencies and apparent extinction coefficients (calculated without correction for finite slit width or refractive index[5,15]) are listed in Table I.

DISCUSSION

It is apparent from Table I that the frequencies and positions of the ν_{16} bands vary considerably from compound to compound. The position of the bands do not seem to be correlated with the intensities. The intensities correlate approximately with the type of substitution as predicted by comparison with substituted benzenes.

Stilbene, azobenzene and azoxybenzene may be considered monosubstituted benzenes. The frequency and apparent extinction coefficient of stilbene have been previously reported[5], and the values reported here are in reasonable agreement. It is expected[5-6,9] that the intensities of the ν_{16} bands will be low for all monosubstituted benzenes except those with strong electron donating groups. However, it has also been reported[5-6] that unsaturated carbon substituents should give the weakest bands with electron withdrawing groups giving stronger bands. On the basis of this prediction, the intensities of the monosubstituted compounds in this study should be in the opposite order of those observed. The observed order could be explained if the azo-and azoxy-substituents acted as unsaturated carbon systems but this is not consistent with values found for the other compounds in this study. The two ν_{16b} bands are weaker than and in the same order as the ν_{16a} bands similar to monosubstituted benzenes.[5-6]

4,4'-azophenetole, 4,4'-azoxyphenetole, and 4,4'-azoxydianisole may be considered as paradisubstituted benzenes. The observed intensities of the ν_{16} bands are in agreement with expectation[6] for donor-acceptor pairs but too intense for donor-unsaturated carbon pairs. The order of the intensities is not that predicted[6] on the basis of the greatest difference in the mesomeric effects of the donor-acceptor pair. It is likely that for these para compounds only the order of magnitude of the ν_{16a} band intensities is a meaningful indication of electron disturbance since these high values of the apparent extinction coefficients are outside the optimum range and must be considered approximate.[16] The order of intensities of the ν_{16b} bands does not follow that of the ν_{16a} bands. Both the frequency and intensity of the ν_{16b} bands of the azoxy compounds are low for donor-acceptor para disubstituted benzenes.[6]

The frequencies and intensities of the ν_{16} bands of 2,2'-azophenol and m-azotoluene are in agreement with expected values for donor-acceptor

TABLE I. Mean Positions and Apparent Extinction Coefficients of the ν_{16a} and ν_{16b} Modes of Some Trans Azobenzenes[a]

Compound[b]	$\nu_{16a}(cm^{-1})$	ε_A	$\nu_{16b}(cm^{-1})$	ε_A
Stilbene[c]	1598	60	1580	20
Azobenzene	1586	25	--	--
Azoxybenzene	1600	12	1590	11
4,4'-azophenetole	1602	564	1585	300
4,4'-azoxyphenetole	1598	654	1571	82
4,4'-azoxydianisole	1598	476	1570	103
2,2'-azophenol	1620	318	1585	160
m-azotoluene	1606	52	1580	18

a. Designation 16a and 16b is according to Herzberg's notation for six-member aromatic rings.

b. All spectra were recorded as CCl_4 solutions of the compounds.

c. Ref. 5 reports $\nu_{16a}(1607\ cm^{-1})$, $\varepsilon_A(50)$ and $\nu_{16b}(1582)$, $\varepsilon_A(15)$ for this compound in $CHCl_3$ solution.

ortho[8]-and weak-acceptor meta[9] disubstituted benzenes, respectively.

CONCLUSION

It appears, for the compounds studied, that the intensities of the ν_{16} bands of azo compounds cannot be rigorously correlated with substituent effects as proposed for substituted benzenes. However, when the apparent extinction coefficients are taken as indicating a range of values, there is

good agreement with values predicted[5-8] by considering one of the benzenes as a nucleus and the remaining portions of the molecule as substituents. The frequencies do not appear to be correlated with the substituents.

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Received September 15, 1973

Accepted September 20, 1973