

LETTERS TO THE EDITOR

THE NEAR ULTRAVIOLET ABSORPTION SPECTRA OF 2, 6- AND 3, 5-DICHLOROBENZONITRILES

THE vibrational analysis of the infrared and ultraviolet absorption spectra of benzonitrile has been carried out by Hert and Howe¹ and Bass². The effect of monohalogen substitution on the spectra of benzonitrile has been extensively studied by other

obtained in the two molecules have been given in Table I. These fundamentals have also been correlated with the infrared fundamentals⁹. The assignments to these fundamentals have been made on the basis of correlation with other substituted benzonitriles. All the observed bands have been explained as the combination of fundamentals and ν - ν transitions and their overtones.

TABLE I

2, 6-DCBN			3, 5-DCBN			Assignment
G.S.	E.S.		G.S.	E.S.		
I.R. cm^{-1}	U.V. nm	U.V. nm	I.R. cm^{-1}	U.V. nm	U.V. nm	
275	255	..	258	C-Cl, O.P. bending
404	..	290	458	446	420	a_1 component of e_{2g} (608 cm^{-1})
716	..	528	662 } 717 }	C-Cl, stretching
983	..	923	994	..	967	C-C-C, trigonal bending
1433	..	1183	1412	..	1220	a_1 component of e_{1u} (1485 cm^{-1})

investigators³⁻⁸. In the present communication, the near ultraviolet absorption spectra of 2, 6- and 3, 5-dichlorobenzonitriles (abbreviated as 2, 6-DCBN and 3, 5-DCBN) are reported.

The ultraviolet absorption spectra of both the molecules were photographed in the vapour phase on a Hilger medium quartz spectrograph. The hydrogen arc lamp was used as the source of continuous radiation. Well-defined absorption bands were obtained with a path length of 225 cm at the vapour temperature 20° to 100° C.

Both the molecules have C_{2v} symmetry. The ultraviolet absorption spectra of both molecules were found to be due to the $A_1 - B_1$ transition which corresponds to the $A_{1g} - B_{2u}$ transition of benzene. The strong band at 34015 cm^{-1} and 34262 cm^{-1} in 2, 6- and 3, 5-DCBN respectively have been taken as 0, 0 band. About 37 bands have been observed for 2, 6-DCBN and 55 bands for 3, 5-DCBN. The bands are degraded towards red but are sharp in general. The ground and excited state fundamentals

TABLE II

Molecules	Position of 0, 0 bands in cm^{-1}	Shift with respect to benzonitrile in cm^{-1}
Benzonitrile ^{1,2}	36516	..
<i>o</i> -chlorobenzonitrile ⁶	35156	1360
<i>m</i> -chlorobenzonitrile	35239	1277
<i>p</i> -chlorobenzonitrile ¹	36327	189
2, 6-DCBN	34015	2401
3, 5-DCBN	34262	2254

} Present work

Table II shows the position of 0, 0 band in *o*-, *m*- and *p*-chlorobenzonitriles and in the present mole-

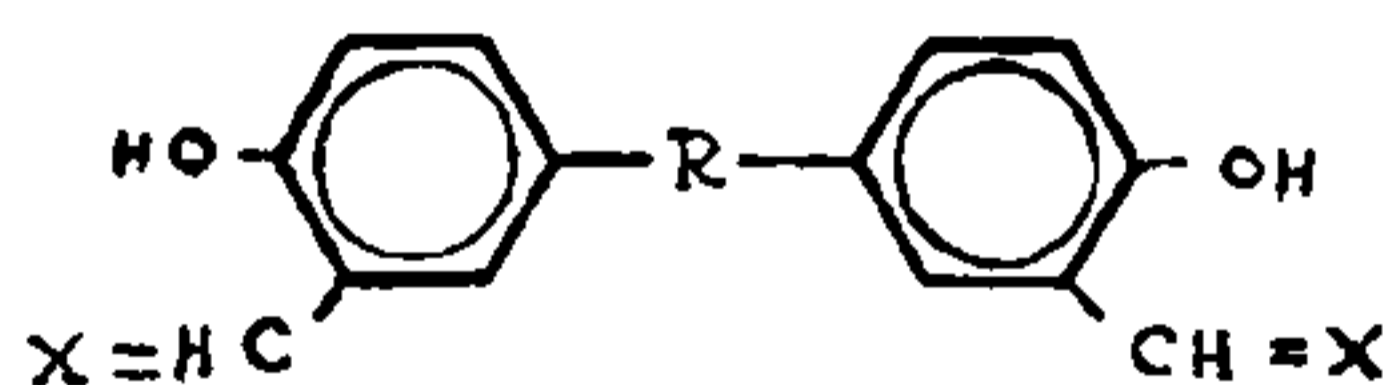
cules. The red shift in *o*-, *m*- and *p*-chlorobenzonitriles is in the order of *o*- > *m*- > *p*-CBN. In the present molecules, red shift is in the order of 2,6- > 3,5-DCBN. From these observations, it can be concluded that as the distance of substituent atom from nitrile (CN) group increases, 0,0 band shifts towards the shorter wavelengths.

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NICKEL CHELATES OF 5-SUBSTITUTED SALICYLALDEHYDE AND 5-SUBSTITUTED SALICYLALDOXIME LIGANDS

CHELATE polymers of *bis*-bidentate salicylaldehyde derivatives such as salicylaldehyde derivative (I-a) and salicylaldimine derivative (I-b) have been well investigated¹⁻⁴. We present here our studies on the chelates of nickel with salicylaldehyde derivative (I-c) and salicylaldoxime derivative (I-d).



(I)

X =	R =
a. O	CH ₃ ; SO ₂
b. NH	CH ₃ ; SO ₂
c. O	N ₅ C ₆ H ₄ C ₆ H ₄ N ₅
d. NOH	N ₅ C ₆ H ₄ C ₆ H ₄ N ₅

Experimental Procedure.—4-4' bis (m-formyl-p-hydroxy phenyl azo) biphenyl (H₂ BASA) and its dioxime (H₂ BASAO) were prepared by the method of Sen and Ghosh⁵.

Nickel chelates of 4-4' bis (m-formyl-p-hydroxy-phenyl azo) biphenyl and its dioxime (HBASA)₂ Ni and (BASAO) Ni.—When the solution of nickel acetate in pyridine was mixed with the solution of the ligand (H₂ BASA or H₂ BASAO) in pyridine (salt : ligand : : 1 : 1), the mixture became turbid,

slowly forming slimy precipitates when left overnight. The precipitates were filtered, washed with a little pyridine and alcohol and dried. They were insoluble in water and in all common organic solvents except dimethyl formamide and pyridine in which they were slightly soluble.

Magnetic susceptibility (X_g) of these chelates was determined on Gouy's magnetic balance at room temperature. Thermal analysis (T.G.A.) of the chelates was carried out in nitrogen atmosphere using Lenseis Model. Visible absorption spectra of the nickel chelates in dimethyl formamide were measured on a Spekol spectrophotometer.

Discussion

(HBASA)₂ Ni—The chelate is orange-red in colour and does not melt upto 300° C. The stoichiometry of the chelate indicates the ratio of metal to nitrogen as 1 : 9 [Analysis : Found : % Ni : 5.42 ; % N = 11.52 (C₅₇H₄₇N₉O₁₂) Ni required % Ni : 5.34 ; % N : 11.47]. Further it gives the smell of pyridine on heating. Hence it is formulated as monomeric nickel chelate Ni(HBASA)₂ py aq₄. Nickel is not precipitated from its dilute solution in dimethyl formamide by hydrogen sulphide. The solution gives the visible absorption spectrum which is characteristic of an azo compound.

The stepwise weight loss observed in T.G.A. studies indicates that the chelate (i) loses pyridine and part of water over a temperature range of 70–150° and (ii) loses the remaining amount of water sharply at 475–80° C. The total weight loss observed is about 14%. The residue left in this study is anhydrous nickel chelate but upto 475° C, the two water molecules are strongly held by the molecule, forming octahedral chelate molecule.

Its magnetic susceptibility is found to be 2.8 × 10⁻⁶ C.G.S. unit at 29° C. Hence magnetic moment per nickel atom is calculated as 2.86 B.M. It confirms the octahedral nature of the chelate.

Although we could not prepare the anticipated thermally stable polychelate, the monomeric chelate obtained is quite stable thermally.

(BASAO) Ni.—It is orange red in colour and does not melt upto 300° C. The stoichiometry of the chelate indicates the ratio of metal to ligand as 1 : 1 [Analysis : Found : % Ni = 10.31 ; % N = 15.13. (C₂₀H₂₀N₄O₅) Ni required % Ni = 10.53 ; N = 15.15]. It gives no smell of pyridine on heating. Hence it is formulated as linear chain [Ni(BASAO)aq]_n.

Nickel is not precipitated from its dilute solution in dimethyl formamide by hydrogen sulphide. The solution gives the visible absorption spectrum which is characteristic of an azo compound.