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Infra-red Spectral Studies of Diphenylamine

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The infrared spectra of diphenylamine were recorded to discuss the modes of vibrations, overtones and combination frequencies assuming the C_{2v} point group symmetry. The investigations have been discussed with a view to examine the structural pattern and different nature of bonding in the molecule.

Key Words: Infrared spectra, Diphenylamine.

The spectroscopic studies of molecular structure of polyatomic macromolecules require good theoretical[1, 2] and high quality experimental[3] approaches. A study of infrared spectrum gives us most of the required information about the presence or absence of certain vibrational bands or characteristic groups in a molecule and it helps us to establish the nature of bonds or groups present in the molecule.

In continuation of our studies in infrared and ultraviolet-visible spectra of some redox dyes[4–7]; we have selected a typical indicator, diphenylamine. The diphenylamine, an aromatic secondary amine, is a weaker base[8] than aniline. The compound is widely used for qualitative detection of nitric acid and in standardization of dichromate ion[9]

The infrared spectra of diphenylamine have been reported by Randal *et al.*[10] and also by Darmon *et al.*[11]. They studied only the single N—H stretching absorption in dilution salt through a second band at low frequency which is sometimes shown at higher concentrations resulting from H-bonding effect[12–14].

The structural features of diphenylamine $[(C_6H_5)_2\ddot{N}H]$ and its basic nature in addition to its use as redox indicator motivated us to undertake its vibrational analysis.

The diphenylamine was made available from M/S Fluka, Switzerland and used as such without any further purification. Infrared spectrum was recorded on Perkin-Elmer (Model 577) double beam grating spectrometer in the range 4000–200 cm^{-1} using KBr pellets. The source of continuous radiation was Nearnst Glower and the detector was a permanently evacuated thermopile. The measurements of bands were accurate within the range ±4 cm^{-1}.

The different regions of absorption identified in the infrared spectra of diphenylamine are given in Table-1 and the details of infrared absorption bands (cm^{-1}) are given in Table-2.

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TABLE-1
CHARACTERISTIC INFRARED ABSORPTION REGION (cm^{-1}) OF DIPHENYLMINE

Sl. No.	Region	Nature of bands	Indications
1.	*ca.* 3300	No broad and intense	—OH absent
2.	(a) < 3300 (b) > 3000	Strong and Sharp	=C—H present
3.	*ca.* 2200	No absorption	>C=O absent
4.	1780–1650	No absorption	>C=O absent
5.	1600–1500	Broad absorption	Aromatic N—H present
6.	1230–1050	Intense-band	C—C or C—N present
7.	840–690	Weak absorption	Aromatic ring present

TABLE-2

Sl. No.	Frequencies (cm^{-1})	Sl.No.	Frequencies (cm^{-1})
1.	562 m	16.	1510 s
2.	632 m	17.	1590 s
3.	750 s	18.	1610 s
4.	840 m	19.	1790 m
5.	870 s	20.	1850 w
6.	895 w	21.	1880 w
7.	990 s	22.	1960 s
8.	1017 w	24.	2740 w
9.	1020 s	23.	2520 w
10.	1080 w	25.	3020 w
11.	1160 w	26.	3060 w
12.	1170 m	27.	3090 mw
13.	1220 w	28.	3120 mw
14.	1320 s	29.	3160 w
15.	1420 s	30.	3180 w

On the basis of the observation of Tables 1 and 2 and the structure of diphenylamine, the positive features of the survey of the spectrum are summarized as:

The free N—H absorption in secondary amine has been reported to be in the region of 3400 cm^{-1}. The significant fall in the frequency observed is due to association by intermolecular H-bonding in the solid phase spectrum. The frequency change of this order might well arise from change of state due to the possibilities of interactions of hydrogenic vibrations in neighboring molecules in the solid state. It is not possible to do more than indicate the approximate range of 3400–3100 cm^{-1} for associated absorptions of this type. Accordingly we find three N—H absorptions which are all weak at 3120, 310 and 3180 cm^{-1} in the spectrum of diphenylamine.

The N—H deformation absorption is usually very weak in secondary amines.

With secondary aromatic amines having N directly attached to the aromatic ring, the position is further confused by the presence of ring C=C stretching absorptions. In some cases small shifts of bands near 1500 cm^{-1} towards higher frequencies are caused by aromatic secondary amines. The strong bands found at 1610 and 1500 cm^{-1} are thus attributed to this effect of the N—H bond.

The presence of a strong band at 1310 cm^{-1} is assigned to C—N stretching vibration, the frequency of which is largely determined by the aromatic character of the C-atom. The three characteristic bands at 3060, 3090 and 3120 cm^{-1} of medium intensity, constituting a triplet is an ambiguously assigned to =C—H stretching in mono-substituted aromatics.

The spectrum of diphenylamine shows some typical absorptions of medium to strong intensity occurring at 1790, 1850 and 1960 cm^{-1}. These bands are again assigned clearly to mono substituted benzene ring.

The presence of two strong bands at 1590 and 1510 cm^{-1} are again characteristic of aromatic rings and arise due to C=C stretching vibrations. These bands in conjugation with those occurring in the region 3040 cm^{-1} are highly characteristic of the aromatic ring.

The very strong band at 750 cm^{-1} is assigned as due to out of plane C—H bending absorption and is characteristic of mono-substituted aromatics. Two relatively weak bands at 1070 and 1080 cm^{-1} also due to bending vibrations are again characteristic of mono-substituted aromatics.

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