Electron Donating Properties of Phenothiazine & Methylphenothiazine

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The interaction of electron donors, phenothiazine and N-methylphenothiazine, with 7,7,8,8-tetracyanoquinodimethane, tetracyanobenzene and tetracyanoethylene has been studied employing electronic spectroscopy. Equilibrium constants and enthalpies of formation of electron donor-acceptor complexes of phenothiazines show that N-methylphenothiazine is a poor electron donor compared to phenothiazine.

IN view of the physiological activity of phenothiazine derivatives, considerable interest has been shown in phenothiazine (PTZ) drugs[1-4]. Calculations of the energies of the highest occupied orbital of phenothiazine and substituted phenothiazines indicate that these molecules could be strong electron donors[5], although the estimate is somewhat modified when sulphur d-orbitals are taken into account[2]. It is expected that the electronic effect of replacing the amino H by Me would enhance the electron donating properties. But Bloor and coworkers[6] are of the opinion that N-methylphenothiazine (MePTZ) may not be a better electron donor compared to phenothiazine. So we have investigated the electron donating properties of PTZ and MePTZ towards strong electron acceptors like 7,7,8,8-tetracyanoquinodimethane (TCNQ) by determining the spectroscopic and thermodynamic properties of these complexes to see whether MePTZ is a better electron donor than PTZ.

Phenothiazine and tetracyanoquinodimethane were available commercially (Aldrich) and were purified by recrystallization and vacuum sublimation. N-methylphenothiazine was prepared and purified by the method described in the literature[7]. Tetracyanobenzene (TCNB) was purified by sublimation *in vacuo*. Spectroscopic grade (BDH) dichloromethane was used as such.

The solution spectra of the complexes in dichloromethane were recorded on a Hitachi EPS-24 and Cary 14R spectrophotometer fitted with a variable temperature cell compartment. The 1:1 equilibrium constant was determined employing the modified Scott equation[8]. The uncertainty in K values is within $\pm$ 10%. The donor concentrations were sufficiently high as required by the criteria proposed by Person[9].

Interaction of concentrated solution of PTZ with TCNQ gives rise to a charge-transfer (CT) band at 1053 nm. The absence of any band in 600-800 nm region indicates that there is no TCNQ$^-$ species in the system[10]. Foster and Hanson[3] failed to detect CT bands in similar cases which seems to be due to a small amount of complex present in the systems. Our attempts to analyse the absorption band in 350-600 nm region were not successful due to the overlapping of the weak CT band and a very intense

{[Donor] $= 5 \cdot 0 \times 10^{-3}$-$5 \cdot 0 \times 10^{-2} M$; [Acceptor] $= 1 \times 10^{-3} M$}

Acceptor	λ_{CT} (nm)	K (litre mole^{-1})	ϵ_{CT} (litre mole^{-1} cm^{-1})	$-\Delta H°$ (kcal mole^{-1})
DONOR: PHENOTHIAZINE				
TCNQ	1053	4·5	4300	4·2
TCNB*	575	1·8	500	2·0
TCNE*	850	5·8	4140	5·6
DONOR: N-METHYLPHENOTHIAZINE				
TCNQ	945	1·5	2500	3·0
TCNB*	555	1·1	580	1·5
TCNE*	826	1·8	2560	3·5

*Part of the data from ref. 4.

band of TCNQ (400 nm)*. The MePTZ.TCNQ complex absorbs at 945 nm in dichloromethane. The equilibrium constant (K), extinction coefficient (ϵ) and enthalpy ($\Delta H°$) are given in Table 1. As the meaningful separation of K and ϵ are not feasible for weak molecular complexes, these values cannot be considered to give anything better than the order of magnitude[11]. N-Methylphenothiazine complex absorbs at higher energy and the K and $\Delta H°$ values are smaller compared to those of PTZ.TCNQ complex. The higher energy CT absorption and the low values of K and $\Delta H°$ clearly show that MePTZ is a weaker electron donor compared to PTZ. This trend is observed even when tetracyanoethylene (TCNE) and TCNB are used as electron acceptors.

Tetracyanobenzene is a weaker electron acceptor ($E_A = 0 \cdot 4$ eV) compared to the other tetracyano compounds. The PTZ and MePTZ complexes of TCNB absorb at 575 and 555 nm respectively; the valves of K and $\Delta H°$ also show that electron donating power of MePTZ is reduced. This can be visualized in terms of steric interactions which result in increased folding of the molecule and corresponding reduction of the interaction of the N lone pair with π-electrons of the rest of the molecule[12]. The work of Aroney and coworkers[13] on the molecular polarizability of PTZ and MePTZ supports our finding that MePTZ is a weaker electron donor compared to PTZ.

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*The polarized absorption spectra of single crystals of PTZ, TCNQ and MePTZ.TCNQ show two CT bands in each case, namely at 540, 1220 and 500 and 1150 nm respectively [Bhat, S. N. & Kuroda, H., *Bull. chem. Soc. Japan,* in press].

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Assignment of C-CF₃ Stretching Vibration in Substituted Benzotrifluorides

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On the basis of a detailed study of substituted benzotrifluorides specially the p-(CF₃C₆H₄CF₃) an unambiguous assignment of the frequency of C-CF₃ stretching mode has been proposed.

VIBRATIONAL spectra of benzotrifluorides has been extensively studied and the assignment of fundamentals have been proposed. In spite of extensive work there is an ambiguity about the assignment of the C-CF₃ stretching vibration. The present paper gives briefly evidence to resolve this ambiguity from the study of substituted benzotrifluorides.

The compound, viz. isomeric cyano-benzotrifluorides (CN C₆H₄CF₃) and *meta*- and *para*-bis(trifluo)-xylenes (CF₃C₆H₄CF₃), were obtained from PCR-Flourida, Fluka, Switzerland and Schuchardt, Germany, as pure compounds. At room temperature all the compounds are colourless liquids, except p-(CN C₆H₄CF₃), which is solid, m.p. 36°.

The infrared spectra from 2 to 40 μ were recorded on a Perkin-Elmer model 457 grating spectrophotometer. Raman spectra were obtained on Spex Ramalog instrument, with depolarization ratios of the bands at BARC, Bombay.

Narasimham et al.[1] assigned the peak at 1028 cm⁻¹ to vC-CF₃ whereas Scott et al.[2] located it at 1072 cm⁻¹. Cave and Thompson[3] reported the excited state frequency as 1035 cm⁻¹. However, Sponer and Lowe[4] assigned 751 cm⁻¹ in the excited state, the corresponding ground state of which from

the fluorescence studied was found to be 771 cm⁻¹ by Sponer and Sastri[5]. Recent calculations by D'Cunha[6] gave it as 1327 cm⁻¹ in benzotrifluoride and 1270 cm⁻¹ in the deuterated analogue. Further Varsanyi[5] assigned 338 cm⁻¹, which was the calculated value for the 6a mode, to this vibration.

Of the present molecules, p-(CF₃C₆H₄CF₃) is very characteristic in so far as the two C-CF₃ vibrations would couple to give two split components. Since this molecule has been shown to belong to D_{2h} point group[8], of two split components one would be Raman active and the other infrared active. In case the corresponding mode is mixed with other normal modes, instead of complete mutual exclusion the reversal of relative intensities in the Raman and in the infrared spectra is expected. No such components with expected characteristics were observed in 1300 or 1000 cm⁻¹ region in the spectra of p-(CF₃C₆H₄CF₃) or in any other molecule. This hence does not support the proposed assignments either of D'Cunha or of Narasimham and of Scott. Even the 338 cm⁻¹ assignment seems to be quite low.

In benzotrifluoride one observes a strong band at 770 cm⁻¹ in the infrared and Raman spectra. Raman spectrum of p-(CF₃C₆H₄CF₃) has a strong band at 624 cm⁻¹ and the IR spectrum shows a strong band at 803 cm⁻¹. From the mutual exclusion principle this shows that these two bands are the split components and correspond to the 770 cm⁻¹ band of benzotrifluoride. Thus 624 cm⁻¹ are assigned to the C-CF₃ stretching modes of the said molecule. In m-(CF₃C₆H₄CF₃) the 810 and 780 cm⁻¹ are the two C-CF₃ stretching modes, the former being strong in Raman and the latter in IR. This assignment is substantiated from the study of other substituted benzotrifluorides. The frequency 770 cm⁻¹ lies between the limits of C-X stretching vibration for heavy and light substituents as proposed by Varsanyi. The C-CF₃ stretching frequency in all the cyano- and amino-benzotrifluorides is near about 770 cm⁻¹ (that of benzotrifluoride), as given in Table 1.

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TABLE 1 — C-CF₃ STRETCHING FREQUENCIES (cm⁻¹) OF CYANO- AND AMINO-BENZOTRIFLUORIDES

Mode No.	C₆H₅CF₃	CNC₆H₄CF₃			NH₂C₆H₄CF₃			CF₃C₆H₄CF₃	
		ortho	*meta*	*para*	*ortho*	*meta*	*para*	*meta*	*para*
7a	770	740		780	754		754	810	803
7b			808			755		780	
13									624