

Intramolecular Charge Transfer Phenomena & Structure of Substituted Picryl Phenyl Ethers

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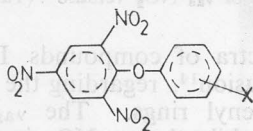
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Received 15 June 1978; revised 26 December 1978; accepted 15 February 1979

The UV spectra of some picryl phenyl ethers (I-IX) display mainly three absorption bands (A, B and C) near 225, 255 and 320 nm in different organic solvents. The band B is assigned to the transition (${}^1L_b \leftarrow {}^1A$) and to CT from the substituted phenoxy moiety as donor to the picryl moiety as acceptor, while the band (C) is attributed to $n-\pi^*$ transition. The dielectric constant and the hydrogen bond formation] capacity of the solvents are the main factors affecting the displacement of the band position. The IR spectra of the compounds have also been discussed.

THE spectra of a large number of substituted phenols¹, and their corresponding methyl ethers have been analysed in terms of their structures but only a few studies have been reported on the spectra of picryl ethers². To elucidate the structural features of substituted phenyl ethers, the UV spectra of a number of picryl phenyl ethers have now been examined in organic solvents of varying polarities. The solvent induced shifts in the absorption bands have been noted and correlated with the various solvent properties. Also, the charge transfer (CT) bands as well as some of the bands in the IR region have been correlated with molecular structure.

The picryl ether derivatives (I-IX) were prepared as described elsewhere³.



where X = H(I), *p*-CH₃ (II), *m*-CH₃ (III), *o*-CH₃ (IV), *p*-Cl (V), *o*-Cl (VI), *p*-Br (VII), *p*-CHO (VIII), and *p*-NO₂ (IX).

The organic solvents were purified according to recommended procedures⁴. The UV spectra were scanned on a UNICAM SP 8000 spectrophotometer using 1 cm matched silica cells. The IR spectra of the compounds were recorded as KBr discs on a UNICAM SP 200 spectrophotometer.

The UV spectra† of compounds I, II and IX were recorded in DMF, H₂O₂, EtOH, isopropanol, ether, chloroform, *n*-octane, dioxane, 1,2-dichloroethylene, carbon tetrachloride, *n*-hexane and cyclohexane while those of III-VII in EtOH, ether, H₂O, CHCl₃, CCl₄ and cyclohexane and of VIII in EtOH alone.

The UV spectra of the picryl phenyl ethers in ethanol show mainly three broad bands (A, B and C)

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†The detailed UV data of compounds I-IX in solvents of different polarities can be had from the authors on request.

in the 210–350 nm region. The band (A) is located at 225 nm having ϵ values amounting to $(2.3-0.6) \times 10^4$ mol⁻¹ litre cm⁻¹. Surprisingly, the band (A) is solvent-sensitive. The plot of Taft's substituent constant (σ^*) versus λ_{\max} is linear (Fig. 1). The spectra of III, IV and VIII show two bands in this region near 215 and 225 nm which can be assigned to the transitions ${}^1B_b \leftarrow {}^1A$ and ${}^1L_a \leftarrow {}^1A$ of the phenyl ring. The 1B_b band of the remaining compounds may interact with 1L_a to give a broad band at 225 nm⁵.

The band (B), observed in 250–260 nm region, is broad and shows a reasonable variation in its position under the influence of the substituent X (Fig. 1). This band is also solvent-sensitive and shows high ϵ_{\max} values, supporting the $\pi-\pi^*$ nature of the electronic transition leading to this band⁶. The shift of the band (B) under the influence of solvent is governed by the relations given by Suppan⁷.

$$f(D) = \frac{2(D-1)}{(2D+1)} \text{ and } \phi(D) = \frac{D-1}{D+2}$$

The plots of λ_{\max} of the band (B) of compound (II) versus $f(D)$ and $\phi(D)$ (Fig. 2) are linear with a positive slope. The band is composite and can be assigned to transition (${}^1L_b \leftarrow {}^1A$) of the phenyl moiety, similar to that observed in the case of substituted benzene derivatives⁸. Also, the band involves absorption corresponding to an intramolecular CT. This charge migration could be either from the ether oxygen atom or from the phenoxy moiety depending

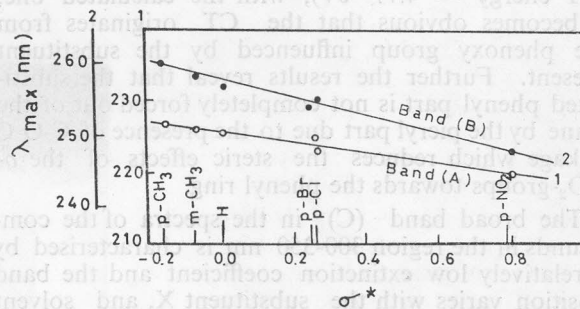


Fig. 1 — Plots of σ^* (Taft's constant) versus λ_{\max} of bands A and B.

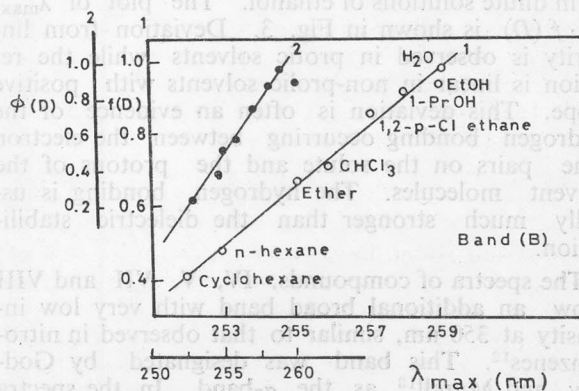


Fig. 2 — Plots of the functions $f(D)$ and $\phi(D)$ versus λ_{\max} of band (B) of compound (II) in different solvents.

TABLE 1 — CALCULATED AND OBSERVED VALUES OF E_{CT} FOR VARIOUS PICRYL PHENYL ETHERS

Compound	Donor system	I_p eV	E_{CT} (eV)		Difference
			Obs.	Calc.	
I Phenyl		9.245	4.78	5.045	+0.265
II Toluene		8.820	4.87	4.620	-0.250
III -do-		8.820	4.810	4.620	-0.190
IV -do-		8.82	4.810	4.620	-0.190
V Chlorobenzene		9.070	4.770	4.870	+0.100
VI -do-		9.070	4.910	4.870	-0.040
VII Bromobenzene		8.980	4.870	4.780	-0.090
VIII Benzaldehyde		9.530	4.830	5.330	+0.500
IX Nitrobenzene		9.92	5.000	5.72	+0.720

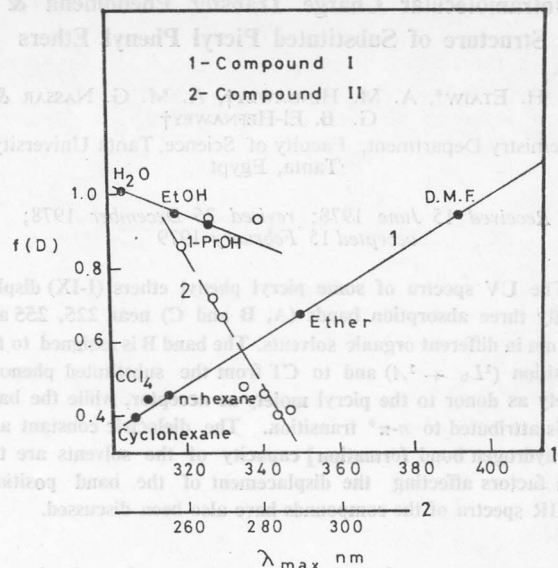
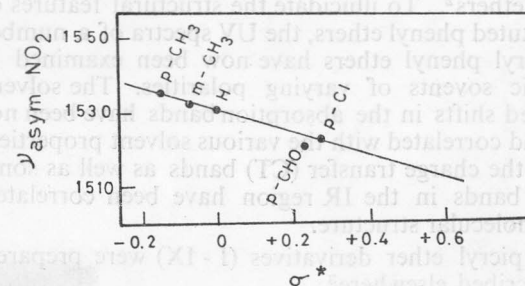
on whether the substituted phenyl attains the plane defined by the rest of the molecule or not. A convenient support for the CT origin of such a band could be obtained from the calculation of the energy of CT (Table 1), from the equation^{9,10}:

$$E_{CT} = (I_p - E_A) + C$$

If the ether oxygen atom is the origin of the CT, then using I_p of oxygen atom = 13.6 eV, the above equation value gives a value of 9.44 eV as the energy of CT. On the other hand, if the substituted phenoxy group is the origin of CT ($I_p = 9.07$ eV for compound V)¹¹, the CT energy is 4.87 eV. On comparing the experimental value obtained from the spectra of V in cyclohexane (CT energy = 4.77 eV), with the calculated one, it becomes obvious that the CT originates from the phenoxy group influenced by the substituent present. Further the results reveal that the substituted phenyl part is not completely forced out of the plane by the picryl part due to the presence of C-O-C linkage which reduces the steric effects of the *o*-NO₂-groups towards the phenyl ring.

The broad band (C) in the spectra of the compounds in the region 300-350 nm is characterised by a relatively low extinction coefficient and the band position varies with the substituent X, and solvent polarity. All these facts reveal that this band is most probably due to $n - \pi^*$ transition. This is supported by the fact that it disappears in HCl as solvent as well as in dilute solutions of ethanol. The plot of λ_{max} vs. $f(D)$ is shown in Fig. 3. Deviation from linearity is observed in protic solvents while the relation is linear in non-protic solvents with positive slope. This deviation is often an evidence of the hydrogen bonding occurring between the electron lone pairs on the solute and the protons of the solvent molecules. The hydrogen bonding is usually much stronger than the dielectric stabilisation.

The spectra of compounds, IV, V, VII and VIII show an additional broad band with very low intensity at 350 nm, similar to that observed in nitrobenzenes¹². This band was designated by Godfrey and Murell¹³ as the α -band. In the spectra of the remaining compounds the (C) band masks the weaker α -band.


 Fig. 3 — Plots of the function $f(D)$ versus λ_{max} of compounds (I) and (II) in different solvents.

 Fig. 4 — Plot of $\nu_{asym} NO_2$ versus σ^* (Taft's constant).

The IR spectra of compounds I-IX confirm the previous conclusion¹⁴ regarding the non-coplanarity of the two phenyl rings. The $\nu_{asym} NO_2$ appears around 1545 while the $\nu_s NO_2$ is located at 1355-1358 cm^{-1} . On the other hand, the spectra display the ν_{C-O-C} at 1230-1246 cm^{-1} . The plot of $\nu_{asym} NO_2$ versus Taft's substituent constant is linear (Fig. 4) indicating the transfer of polar effect from the substituted phenyl to the electron deficient picryl ring through the C-O-C linkage.

For the halogen derivatives the NO₂ bands shift to lower frequencies indicating a decreased acceptor character of the halogen. This would favour the charge migration to the oxygen atom, and then to *p*-NO₂ group of the picryl part, hence lowering —N=O bond order in accordance with previous studies with *p*-nitrobenzyl derivatives¹⁵.

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Molecular Chalcogenide, Tetraselenium Tetrasulphide : Some Comments

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Received 21 July 1979

It is pointed out that the spectra of Datta and Krishnan [*Indian J. Chem.*, **16A** (1978), 3351] as compared to our own data indicate the presence of chemical species with homonuclear S-S and Se-Se bonds as well as Se-S bonds in their sample. Thus the possibility of isolation of a pure isomer S_4Se_4 with S and Se atoms at alternate positions from a melt of equivalent amounts of Sulphur and selenium remains doubtful.

IN a recent paper¹ published in this journal, Datta and Krishnan claimed to have isolated a pure isomer of S_4Se_4 consisting of S and Se atoms at the alternate positions only. This result would be very unusual since normally one obtains a homogeneous mixture of many different $Se_n S_{8-n}$ molecules by the method of preparation employed. The purpose of this communication is to point out that the data given in their paper do not warrant the above conclusion. In our opinion, the authors' own data indicate the presence of chemical species with homonuclear S-S and Se-Se bonds in their sample as can be seen from the following brief discussion.

The symmetric stretching modes of homonuclear S-S and Se-Se bonds in pure S_8 and Se_8 appear in the Raman spectra ~ 470 and 250 cm^{-1} respectively²⁻⁵. As long as S-S and Se-Se bonds are present, the peak positions of bands due to their stretching vibrations do not vary appreciably when S is inserted in a Se_8 ring (or vice versa) but a new band occurs $\sim 360\text{ cm}^{-1}$ due to the Se-S bond^{2,3}. It is clear from Fig. 1 in ref. 1 that the spectrum of ' Se_4S_4 ' clearly

contains bands which are easily assigned to $\nu S-S$ and $\nu Se-Se$ in addition to S-Se vibrations and the deformation modes. Datta and Krishnan have not discussed the band $\sim 466\text{ cm}^{-1}$ (Fig. 1, ref. 1) which must be assigned to $\nu S-S$. This indicates that their sample must contain molecules with at least two adjacent S atoms. A very small lowering in the frequency of the S-S vibration, as compared to its value of $470-474\text{ cm}^{-1}$ in S_8 (ref. 8), is due to the presence of heavier Se atoms in the rings containing homonuclear S-S bonds. Similarly the band $\sim 262\text{ cm}^{-1}$ indicates a $\nu Se-Se$ (ref. 2). Therefore, their sample has molecules containing adjacent selenium atoms as well. Slight increase in the frequency of $\nu Se-Se$ as compared to 254 cm^{-1} in Se_8 (ref. 5), is due to the fact that $\nu Se-Se$ seen in their sample are mainly due to Se-Se homonuclear bonds in $Se_n S_{8-n}$ moieties and not Se_8 impurity.

In fact a sample of macroscopic composition S_4Se_4 must contain equal number of S-S and Se-Se homonuclear bonds, if any of them are present. Although a system with a composition S_4Se_4 will have equal number of S-S and Se-Se bonds the strength of the Raman bands due to their stretching vibrations will not be equal due to the differences in their polarizabilities. Our studies using an internal standard indicate that the Se-Se bonds are nearly ten times stronger Raman scatterers than the S-S bonds in these mixed crystals if one uses 6328Å radiation for exciting the Raman spectrum².

Furthermore we would like to point out that the symmetry considerations of Datta and Krishnan do not hold. If one really could assume that the only molecular species present in the sample was the single isomer of $Se_4 S_4$ having C_{4v} molecular symmetry as claimed by Datta and Krishnan then group theory would predict 13 Raman active modes ($3A_1$, $3B_1$, $3B_2$ and $4E$) of which 7 modes ($3A_1$ and $4E$) are also IR active. The A_2 mode is not active in both IR and Raman. Datta and Krishnan give different numbers and activities¹. It is not possible to deduce the molecular structure and symmetry from the number of bands in the Raman spectrum of polycrystalline solid alone. This limitation is particularly important in the present example where one has to prove the 'purity' of the sample at the same time. If the preparation of chemically pure species could be realized, it would be necessary to measure polarized spectra of single crystal and/or solution spectra in order to obtain the symmetry assignment of the bands and establish the molecular symmetry.

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