

## SOLID CHARGE TRANSFER COMPLEXES OF 4-NITROQUINOLINE-1-OXIDE WITH $\text{Ph}_3\text{M}$ (M=P, As, Sb)

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### ABSTRACT

The subject matter in this paper is aimed to isolate solid complexes of 4-NQO with  $\text{Ph}_3\text{M}$  (M=P, As, Sb) and to characterize them in order to establish the site of interaction.]

**KEYWORDS:** 4-NQO, Donors {Triphenylphosphine ( $\text{Ph}_3\text{P}$ ), Triphenylarsine ( $\text{Ph}_3\text{As}$ ) and Triphenylstilbene ( $\text{Ph}_3\text{Sb}$ ) and Tryphenylstilbene ( $\text{Ph}_3\text{Sb}$ )}

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### INTRODUCTION

It has been observed that 4-NQO forms charge transfer complexes in solution with  $\pi$ - and n-donor compounds of biological interest, thereby suggesting that molecular interaction of chemical carcinogens with biomolecules may be possible step in the chemical initiation of cancer. By differential refractometric technique has been used to investigate the interaction of 4-NQO with  $\text{Ph}_3\text{M}$  (M=P,As,Sb) in solution. These interaction have shown formation of stronger molecular complexes than others described. Thus there is possibility to isolate them in solid form.

### EXPERIMENTAL

#### Materials

The donors, triphenylphosphine ( $\text{Ph}_3\text{P}$ ), triphenylarsine ( $\text{Ph}_3\text{As}$ ) and triphenylstilbene ( $\text{Ph}_3\text{Sb}$ ) and tryphenylstilbene ( $\text{Ph}_3\text{Sb}$ ) (Fluka) were purified by recrystallization<sup>1,2</sup>. Chloroform and carbon tetrachloride (B..D.H. AR) was used after distilling thrice. 4-Nitroquinoline-1-oxide was obtained commercially form Sigma and used as such.

All melting points were taken on Fisher Jons melting point apparatus and are uncorrected. The recrystallized products were kept in vacuum desiccator for 2-3 weeks in order to remove last traces of solvent. The solid complexes were analyzed for C, H and N at I.I.T., Kanpur. Identity of the products was established on the basis of IR spectral data, mixed melting points and melting points and elemental analyses.

#### Spectral Measurements

The infrared spectra in the region  $4000\text{-}200\text{ cm}^{-1}$  were recorded on a Perkin-Elmer model 621 spectrophotometer. Samples were run as nujols mulls. The main infrared spectral bands are presented in Table 1.2.

### Preparation of Molecular Complexes

The solid complexes of 4-NQO with Ph<sub>3</sub>P, Ph<sub>3</sub>As, Ph<sub>3</sub>Sb were prepared as described below:

#### Ph<sub>3</sub>P:4-NQO

0.524g Ph<sub>3</sub>P (0.002 M) was dissolved in 5 ml chloroform and 0.380 g 4-NQO (0.002M) was also dissolved in 5 ml chloroform. The two solutions were mixed and stirred at room temperature. The yellow color of the reaction mixture changed to pink after 12 hrs. This solution was kept for a few days. Pink-plated like crystals formed were separated and dried in vacuum over P<sub>2</sub>O<sub>5</sub>.

#### Ph<sub>3</sub>As:4-NQO

0.305 g Ph<sub>3</sub>As (0.001M) was dissolved in 5ml chloroform and 0.190 g 4-NQO (0.001 M) was dissolved in 5 ml chloroform. The two solutions were mixed and stirred at room temperature. The color of the reaction mixture did not change. After one weak yellow crystals were formed. These were filtered and dried in vacuum over P<sub>2</sub>O<sub>5</sub>.

#### Ph<sub>3</sub>Sb:4-NQO

0.353g Ph<sub>3</sub>Sb (0.001M) was dissolved in 5 ml chloroform and 0.190g 4-NQO (0.001M) was dissolved in 5 ml chloroform. The two solutions were mixed and stirred at room temperature. The yellow color to the reaction mixture change to pink after 3hrs. The solutions were kept for one week and the crystals obtained were filtered and dried in vacuum over P<sub>2</sub>O<sub>5</sub>.

### RESULTS AND DISCUSSIONS

4-NQO is a colourless crystalline compound having m.p. 154-156 °C while donors triphenylphosphine, triphenylarsine, triphenylstilbene are colourless compounds having m.p. 79-81 °C, 60-62 °C and 52-54 °C, respectively. When solutions of triphenylphosphine and 4-NQO solution were mixed, the yellow color of the reaction mixture changed to pink after 12hrs. which gave pink plate-like crystals having m.p. 135 °C. This m.p. is quite different from parent compounds. Similar results have been obtained for Ph<sub>3</sub>As:4-NQO, Ph<sub>3</sub>Sb:4-NQO complexes (Table 1.1).

The elemental analyses of solid complexes (Table 1.1) indicate that 1:1 molecular complexes have been formed between Ph<sub>3</sub>M(M=P, As, Sb) and 4-NQO.

#### Infrared Spectra

The main infrared absorption frequencies of Ph<sub>3</sub>M, 4-NQO and their molecular complexes in the region 2000-400 cm<sup>-1</sup> with possible assignment are recorded in Table 2. These assignments are based on the classic work of Whiffen<sup>3</sup> on the halobenzenes and the results of Jensen and Nielsen.<sup>4</sup> Only minor modifications to their original assignments have subsequently been suggested.<sup>5</sup> The assignment of phenyl vibrations in Ph<sub>3</sub>M has been discussed in detail by Mackay, Sowerby and Young.<sup>6</sup> As can be seen from Table 2 the absorptions of Ph<sub>3</sub>M in the complexes are observed-

**Table 1: Analytical Data of Ph<sub>3</sub>M: 4-NQO Complexes**

Complex	Colour	M.P. (°C)	Percentage					
			C		H		N	
			Calc.	Obsd. I	Calc.	Obsd. I	Calc.	Obsd.
(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> P:C <sub>9</sub> H <sub>6</sub> ON <sub>2</sub> O <sub>2</sub>	Pink	135	71.61	71.00	4.64	4.58	6.18	6.10
(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> As:C <sub>9</sub> H <sub>6</sub> ON <sub>2</sub> O <sub>2</sub>	Yellow	120	65.30	64.69	4.23	4.20	5.64	5.52
(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> Sb:C <sub>9</sub> H <sub>6</sub> ON <sub>2</sub> O <sub>2</sub>	Pink	105	59.67	59.02	3.86	3.75	5.10	5.05

**Table 2: Infrared Spectral Data with their Possible Assignment of Ph<sub>3</sub>M and 4-NQO and their Molecular Complexes**

4-NQO	Ph <sub>3</sub> P	Ph <sub>3</sub> P: 4-NQO	Ph <sub>3</sub> As	Ph <sub>3</sub> As 4-NQO	Ph <sub>3</sub> Sb	Ph <sub>3</sub> Sb 4-NQO	Possible Assignments
-	425(vw)	430 (w)	-	-	-	-	t
-	515 (sh)	510 (w)	473 (vs)	473 (ms)	453 (ms)	458 (ms)	Y
-	-	-	695 (vs)	695 (vs)	652 (w) 670 (sh)	660 (w) 665 (sh)	r
-	-	-	695 (vs)	695 (vs)	694 (vs)	695 (vs)	Phenyl
-	1089 (s)	1095 (m)	1081 (sh) 1072 (ms)	1075 (w) 1085 (sh)	1063 (vs)	1070 (m)	q
1300 (m)	-	1300 (m)	-	1300 (m)	-	1300 (m)	N-O
1500 (m)	-	1505 (w)	-	1500 (sh)	-	1510 (w)	asv (C-NO <sub>2</sub> )

vs= very strong; s=strong; ms=medium strong;

m-medium; w-weak; vw=very weak; sh=shoulder In the expected regions with good correspondence to those of free Ph<sub>3</sub>M expect slight shift. It diminishes absorption intensity of phenyl  $\nu$ (C-C) vibrations to a great extent. This phenomenon is characteristic of such molecular complexes.<sup>7-10</sup>

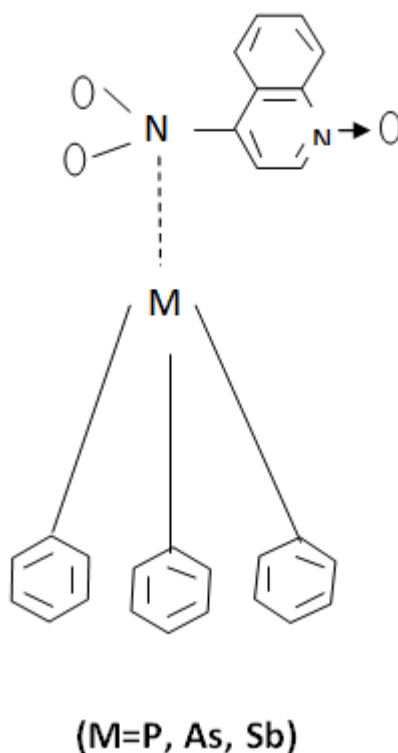
In the infrared spectra of Ph<sub>3</sub>M (Table 2), the M- sensitive modes q, r and t are due to Ph-M bending vibrations and y, u and x modes due to Ph-M stretching vibrations.<sup>4,6,11,12</sup> These bands are mainly influenced on complexation with 4-NQO. In the infrared spectra of Ph<sub>3</sub>Sb, bands at 1063 and 453 cm<sup>-1</sup> have been assigned q and y modes, respectively. Two bands at 652 and 670 cm<sup>-1</sup> are due to r mode. On complexation, q, y and r bands of Ph<sub>3</sub>Sb are shifted to higher region (ca. 10 cm<sup>-1</sup>). In the case of Ph<sub>3</sub>As:4-NQO complex, the shifting of these bands is also observed. In Ph<sub>3</sub>P:4-NQO complex slight positive shift in q, y and r bands was noticed.

In the infrared spectra of Ph<sub>3</sub>As, bands at 1081, 1072 and 473 cm<sup>-1</sup> have been assigned to q and y modes, respectively. One band at 695 cm<sup>-1</sup> is due to r mode. On complexation q, y and r bands of Ph<sub>3</sub>As are shifted to higher region. In the infrared spectra of Ph<sub>3</sub>P, bands at 1089 and 515, 425 cm<sup>-1</sup> have been assigned to q and y modes, respectively. The band at 425 cm<sup>-1</sup> is due to t mode. On complexation q, y and t bands of Ph<sub>3</sub>P are shifted to higher region.

In the infrared spectra of 4-NQO, bands at 1500 and 1300 cm<sup>-1</sup> have been assigned to  $\nu_{asy}$  (C-NO<sub>2</sub>) and  $\nu$ (NO) vibrations, respectively. On complexation, no change in the position of  $\nu$ (N-O) mode was noticed. This clearly indicates that oxygen atom attached to heterocyclic nitrogen atom does not take part in complexation. The  $\nu_{asy}$  (C-NO<sub>2</sub>) band for 4-NQO is influenced on complexation and shifts to higher region. The positive shift in M-sensitive bands of Ph<sub>3</sub>M (M=P, As, Sb) suggests that nonbonding electrons of Ph<sub>3</sub>M are involved in the interaction.

The 4-NQO in chloroform shows a peak at 386 nm and in the case of Ph<sub>3</sub>M (M=P, As, Sb) the electronic transition bands in the UV region are observed below 300 nm. But in Ph<sub>3</sub>Sb:4-NQO complex bands at 316, 329, 360 and 430 nm are observed. The presence of these bands may be due to the formation of ionic species. The change in conductance and respective indices was also noticed on keeping the solution (donor + acceptor) for longer duration.

From infrared and electronic spectral results, it may be concluded that the charge-transfer takes place between a non-bonding orbital of the M atom of the  $\text{Ph}_3\text{M}$  and nitro group of 4-NQO. The localized  $n\text{-}\pi^*$  charge-transfer may be proposed from the significant increase in asymmetric stretching vibration of  $\text{NO}_2$  group and electronic spectra of the complexes. A probable model for these interactions has been proposed below:



**Figure 1**

## CONCLUSIONS

In this paper solid complexes of 4-NQO with  $\text{Ph}_3\text{M}$  (M=P,As,Sb) have been isolated and they have been characterized by elemental analysis, infrared and UV-VIS spectral studies. From the significant increase in  $\nu_{\text{asy}}$  (C- $\text{NO}_2$ ) and M-sensitive bands,  $n\text{-}\pi^*$  type of charge transfer has been proposed in  $\text{Ph}_3\text{M}$ :4-NQO systems.

From above discussions, it is evident that the model proposed by differential refractometric<sup>13</sup> Studies and conductometric<sup>14</sup> studies, finds further support from present investigation, where the charge transference from  $\pi$ -orbital of the donor (HOMO) is taking place to the  $\pi^*$ -orbital of nitrogen in the 4-nitro group of 4-NQO, which is lowest unoccupied molecular orbital (LUMO) of the acceptor.<sup>15</sup>

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