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DIPOLE MOMENTS OF IODINE AND IODINE CYANIDE COMPLEXES WITH SOME PHOSPHORYL COMPOUNDS*

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The dipole moments of iodine and iodine cyanide complexes with six phosphoryl compounds have been determined at 20 °C. The dipole moments of the present complexes have been compared with the dipole moments of the complexes between the corresponding phosphoryl compounds and phenol.

The vectorially calculated dipole moments of the iodine and iodine cyanide complexes were found to be smaller than the corresponding dipole moments obtained experimentally.

Keywords: Iodine and iodine cyanide complexes, phosphoryl complexes.

INTRODUCTION

Previously we have determined the dipole moments of several phosphoryl,¹ carbonyl² and pyridine compounds,³ and of their hydrogen-bonded complexes with phenol. The dipole moments were related to hydrogen bond strength and to the ability of the proton acceptors to associate with phenol. To our knowledge, however, no dipole moments of the complexes between iodine cyanide and phosphoryl compounds and only a few of the corresponding iodine complexes have appeared in the literature.^{4,5}

RESULTS AND DISCUSSION

μ_{-DA-}^{exp} . The experimental dipole moments, μ_{DA}^{exp} , of the complexes between some phosphoryl compounds (OPC) and iodine or iodine cyanide are listed in the Tables I and II. As can be seen, the dipole moments of the iodine cyanide com-

* Dedicated to Professor Robert Wolf on the occasion of his 70th birthday.

plexes are much larger than of the corresponding iodine complexes. Since the enthalpy of association, $-\Delta H^\circ$, of the corresponding iodine and iodine cyanide complexes is equal to within experimental uncertainty, the difference in the dipole moments of the complexes might be ascribed to the larger dipole moment of the iodine cyanide (3.83 D) as compared with iodine (0.24 D). The difference between the dipole moments of corresponding iodine cyanide and iodine complexes corresponds in general well with the difference of 3.59 D found between iodine cyanide and iodine. Furthermore, it appears from the K_{assn} and $-\Delta H^\circ$ values in the Tables that the phosphoryl compounds interactions with phenol are stronger than with iodine, but the dipole moments of the iodine complexes and the corresponding phenol complexes are comparable. This means that the iodine as it occurs in the complex, is strongly polarized and hence contributes substantially to the dipole moment of the complex. We have previously¹ shown that the experimental dipole moments of the hydrogen-bonded complexes between phenol and the phosphoryl compounds form a scatter diagram with the enthalpy of association $-\Delta H^\circ$, the ability of phenol, $\log K_{\text{assn}}$, to associate with the phosphoryl compounds, or with the O-H stretching frequency shift, $\Delta\nu_{\text{OH}}$, accompanying the formation of a hydrogen bond with phenol ($\Delta\nu_{\text{OH}}$ = IR stretching frequency of free phenol O-H bond minus the frequency of the hydrogen-bonded O-H). Similar correlations have been carried out with the dipole moments of the iodine and iodine cyanide complexes. The correlations were found to be non-linear, but there is in general an increase in the dipole moment with increasing K_{assn} , $-\Delta H^\circ$ and spectral shifts $\Delta\lambda_{\text{I-I}}$ and $\Delta\nu_{\text{I-C}}$ ($\Delta\lambda_{\text{I-I}}$ = blueshift of the wavelength of the iodine visible band;⁶ $\Delta\nu_{\text{I-C}}$ = IR stretching frequency shift upon complexation).⁷

$\mu_{\text{DA}}^{\text{calc}}$ and $\Delta\mu$. and $\Delta\mu$. The difficulty in our calculation of the dipole moments of the complexes between the phosphoryl compounds and iodine or iodine cyanide, $\mu_{\text{DA}}^{\text{calc}}$, is that we do not know the dipole moments of the electron donor and acceptor molecules as they occur in the complex. However, by using the experimental dipole moments of the uncomplexed donor and acceptor we obtained vectorially calculated dipole moments of the complexes which, when compared with the experimental values, gave us important information about the polarization within the complexes. In our calculations we have assumed that the direction of $\mu_{\text{B}}^{\text{exp}}$ in the phosphoryl compounds of the type X_3PO which possess C_3 symmetry, lies along the C_3 axis i.e., is coincident with the $\text{P}=\text{O}$ direction. Furthermore, to calculate the dipole moment of the complex we also need to know the structure. As a geometrical model for the complexes $\text{I}_2/\text{X}_3\text{PO}$ and $\text{ICN}/\text{X}_3\text{PO}$, we

have used the crystal structure of the addition compound between bromine and acetone of Hassel et al.⁸ The C=O...Br angle was found to be 125°. The vectorially calculated dipole moments, μ_{DA}^{calc} , of the various complexes are presented in Table III. The calculated dipole moments were found to be smaller than the corresponding experimental values. This finding demonstrates clearly that the formation of a complex brings about displacement of electrons. Strong support is also obtained that the visible iodine band⁶ and the IR spectra of the phosphoryl compounds and of the iodine cyanide⁷ are greatly perturbed on complexation. The vectorial difference between the experimental dipole moment and the vectorial sum of the components can be expressed in terms of a dipole increment, $\Delta\mu$, defined by the vector equation (1)

$$\Delta\mu^+ = \mu_{DA}^{exp} - \mu_{DA}^{calc} = \mu_{DA}^{exp} - (\mu_D^{exp} + \mu_A^{exp}) \quad (1)$$

TABLE I Experimental dipole moment, μ_{DA}^{exp} , the corresponding total polarization, P_∞ , molar refraction, R_D , the parameters α , β , γ and spectroscopic data of the addition compound between iodine and some phosphoryl compounds at 20 C°. Solvent: carbon tetrachloride

Electron donor (D)	$\Delta\lambda_{I-I}$ / nm	K_{assn} / M^{-1}	α	β	γ	P_∞	R_D	μ_{DA}^{exp} / D
1 Diethoxy (dichloromethyl) phosphine oxide	65	1.3	3.5000	-2.2857	-1.4545	-54.323	-297.843	3.83
2 Trimethyl phosphate	68	2.6	8.3333	-0.1923	1.3750	443.823	70.115	4.24
3 Triethyl phosphate	72	6.2	9.2593	-0.3871	0.8979	456.078	72.329	4.39
4 Diethoxy (diethyl- amino)phosphine oxide	73	7.2	10.4000	-1.2800	0.5384	419.523	-54.779	4.77
5 Triphenyl- phosphine oxide	78	22.3	19.3103	-1.0455	1.3913	1017.713	21.391	6.92
6 Triethyl- phosphine oxide	86	83.2	28.5714	-0.1765	0.5609	1012.293	69.293	6.74
Iodine (A)	-	-	0.3125	-0.3182	0.3055	31.448	30.256	0.24 ^a

^a Means the μ_A^{exp} value. The $\Delta\lambda_{I-I}$ and K_{assn} data at 20 C° for the association of the phosphoryl compounds with iodine are from Ref. 5. The experimental dipole moments of the phosphoryl compounds 1, 2, 3, 4, 5 and 6 are respectively 3.20, 3.03, 3.07, 3.24, 4.61 and 4.52 D. The dipole moments of the corresponding hydrogen-bonded complexes with phenol are 4.07, 4.24, 4.28, 4.73, 6.31 and 5.72 D (Ref. 1).

The calculations of the μ_{DA}^{calc} and $\Delta\mu$ values of the complex iodine/ /triphenyl-phosphine oxide are shown in Figure 1. In these calculations we have assumed

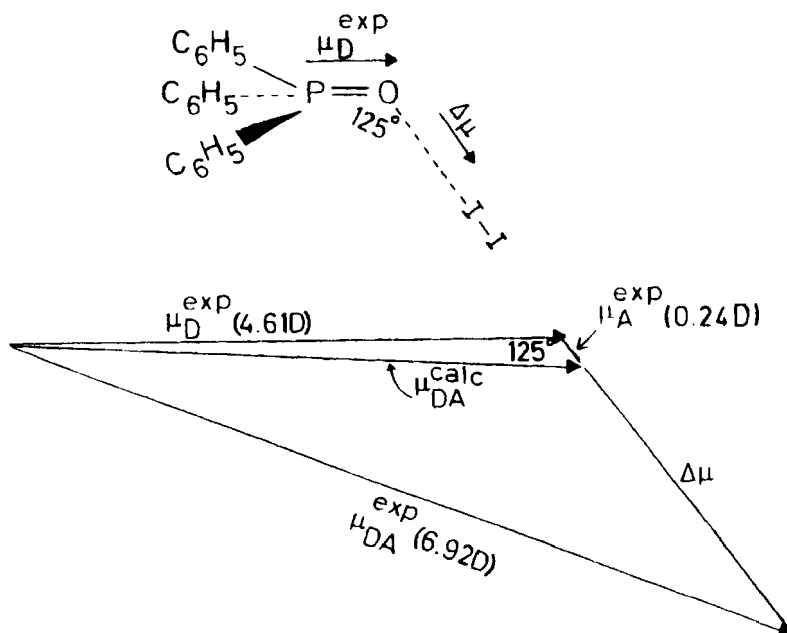


FIGURE 1 The complex between iodine and triphenylphosphine oxide

the $\text{P}=\text{O}\cdots\text{I}$ angle to be 125° and further that the additional dipole moment, $\Delta\mu$, is caused only by electronic displacement along the $\text{O}\cdots\text{I}$ and the $\text{I}-\text{I}$ bonds, i.e., we have not taken into account possible electronic redistribution in other parts of the complex. The $\Delta\mu$ values of the various systems are tabulated in Table III. By increasing the $\text{P}=\text{O}\cdots\text{I}$ angle from 125° to 141° , which corresponds to the $\text{P}=\text{O}\cdots\text{H}$ angle found in the hydrogen-bonded complex between pentafluorophenol and triphenylphosphine oxide,¹ the $\mu_{\text{DA}}^{\text{calc}}$ value for the complex $\text{I}_2/(\text{C}_6\text{H}_5)_3\text{PO}$ is increased from 4.75 to 4.80 D and $\Delta\mu$ is decreased from 2.92 to 2.46 D, and for the complex $\text{ICN}/(\text{C}_6\text{H}_5)_3\text{PO}$ from 7.41 to 7.86 D and from 1.80 to 1.23 D. Similar results were also obtained for the other complexes. This means that the discussion in this work is not influenced by small variation of the $\text{P}=\text{O}\cdots\text{I}$ angle. Furthermore, the $\Delta\mu$ values of the $\text{I}_2/\text{X}_3\text{PO}$ and $\text{ICN}/\text{X}_3\text{PO}$ complexes are much larger than the values of the corresponding $\text{C}_6\text{H}_5-\text{OH}/\text{X}_3\text{PO}$ complexes in spite of the fact that phenol is a stronger electron acceptor.^{6,7} The reason for this might be that the $\text{O}\cdots\text{I}$, $\text{I}-\text{I}$ and $\text{I}-\text{C}$ bonds are strongly polarized in the complex. Unfortunately no solid addition compounds between phosphoryl compounds and halogens or interhalogens are known since it would be of considerable interest to compare the interatomic distances in this with the experimental dipole moments. Hassel et al.⁹ have shown, however, that there is a considerable lengthening of the $\text{I}-\text{I}$ bond on complexation of iodine with 4-methylpyridine,

from 2.67 Å in the free iodine to 2.83 Å in the complex. The N...I distance was observed to be 2.31 Å (the sum of the covalent radii and of the van der Waals radii are 2.03 and 3.65 Å, respectively). Ratajczak and Orville-Thomas have shown¹⁰⁻¹² by using an extension of Mulliken's charge-transfer theory, that there exists for structurally similar complexes, a linear correlation between the square root of the additional dipole moment, $\Delta\mu^{1/2}$, and the enthalpy of formation, $-\Delta H^\circ$. A similar linear correlation has not been observed in this work. The reason for the non-linearity might be that on complexation the enhancement of the various bond moments in the donor molecules contribute differently to the dipole moment of the complex.

TABLE II Experimental dipole moment, μ_{DA}^{exp} , the corresponding total polarization, P_∞ , molar refraction, R_D , the parameters α , β , γ and IR data of the addition compounds between iodine cyanide and some phosphoryl compounds at 20 C°. Solvent: benzene

Electron donor	$\Delta\nu_{I-I}/\text{cm}^{-1}$	K_{assn}/M^{-1}	α	β	γ	P_∞	R_D	μ_{DA}^{exp}/D
1	12	7.5	14.7727	-1.4583	0.1547	1002.308	-23.147	7.02
2	16	14.8	18.9394	-0.3571	0.1613	1108.193	76.886	7.04
3	16	17.7	19.6078	0.5863	0.1103	1286.309	62.092	7.67
5	26	118.9	21.3333	-0.0125	0.3467	1864.466	171.841	9.02
6	31	168.3	40.0000	-0.3843	0.1424	2212.028	69.856	10.15
Iodine cyanide	-	-	10.5882	-0.7742	-0.0720	319.499	14.513	3.83 ^a

^a Means the μ_A^{exp} value. The $\Delta\nu_{I-I}$ and K_{assn} data at 20 C° for the association between the phosphoryl compounds and iodine cyanide at 20 C° are from Ref. 5.

TABLE III Vectorially calculated dipole moment, μ_{DA}^{calc} , and additional dipole moment, $\Delta\mu$, of the complexes formed between some symmetrical phosphoryl compounds and iodine, iodine cyanide and phenol at 20 C°

Electron donor	Iodine			Iodine cyanide			Phenol				
	$-\Delta H^\circ/\text{kJ mol}^{-1}$	μ_{DA}^{calc}/D	$\Delta\mu/D$	$-\Delta H^\circ/\text{kJ mol}^{-1}$	μ_{DA}^{calc}/D	$\Delta\mu/D$	$\Delta\nu_{OH}/\text{cm}^{-1}$	K_{assn}/M^{-1}	$-\Delta H^\circ/\text{kJ mol}^{-1}$	μ_{DA}^{calc}/D	$\Delta\mu/D$
2	8.8	3.17	1.46	12.5	6.19	0.92	305	183	22.2	3.99	0.27
3	13.8	3.21	1.48	15.1	6.25	1.53	330	268	24.7	4.03	0.27
5	19.2	4.75	2.92	20.9	7.41	1.80	410	1055	28.4	5.51	0.88
6	20.5	4.66	2.80	20.5	8.03	2.41	468	2522	29.3	5.42	0.33

The $\Delta\nu_{OH}$, K_{assn} and ΔH° data are from Ref. 5 and the μ_{DA}^{calc} and $\Delta\mu$ for the association between phenol and the phosphoryl compounds are from Ref. 1.

EXPERIMENTAL

The purification of the chemicals and the method of evaluation of the dipole moments of the complexes were the same as reported elsewhere.^{13,14} The concentration range of the iodine in carbon tetrachloride and of the iodine cyanide in benzene was $0.17 \times 10^{-1} - 4.77 \times 10^{-2}$ M, and of the phosphoryl compounds $0.18 \times 10^{-2} - 6.18 \times 10^{-2}$ M. The experimental polarization data α , β , γ , P_∞ , R_D (α , β , γ are the coefficients of the equations $\epsilon = \epsilon_1 + \alpha w$, $v = v_1 + \beta w$, $n^2 = n_1^2 + \gamma w$, for details see Ref. 14) and the corresponding dipole moments of the iodine and iodine cyanide complexes, μ_{DA}^{exp} , are tabulated in the Tables I and II. The μ_{DA}^{exp} values were estimated to be accurate to within ± 0.20 D. Our data are, when a comparison is possible, in fairly good agreement with literature values.^{4,5}

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