Acta Chemica Scandinavica B 31 (1977) 345—353

Studies of Hydrogen Bonding. Part XXVIII.* Hydrogen Bond Association of Phenol with 5,5-Dimethyl-2-oxo-1,3,2-dioxaphosphorinanes and Diethylphosphonates

THOR GRAMSTAD and KJELL TJESSEM

Department of Chemistry, University of Bergen, N-5014 Bergen-Univ., Norway

The association constant and enthalpy of formation of the equilibrium between phenol and twelve 5,5-dimethyl-2-oxo-1,3,2-dioxaphosphorinanes and six diethylphosphonates have been determined. It has been found that the association constant, K_{ass}, enthalpy of association, ΔH, half band width, $\nu_{\frac{1}{2}}$, of the complexed O–H bond, P=O bond moment, μ_{PO}, and excess charge density, Δ_q, on the phosphoryl oxygen give linear relationships with the O–H frequency shift, $\Delta\nu_{OH}$. The calculated P=O bond moment in the axial and equatorial position gives a linear correlation with the experimental P=O stretching frequency. Furthermore, the square root of the additional dipole moment, $\Delta\mu^{\frac{1}{2}}$, due to hydrogen bond formation, correlates linearly with the association constant, the O–H frequency shift, and with the half band width. These findings indicate a close relationship between band width of the complexed O–H bond and the strength and polarity of the hydrogen bonded complex.

Since we previously [2] have carried out conformational studies of 5,5-dimethyl-2-oxo-1,3,2-dioxaphosphorinanes, we found it of interest to extend our study to include the dipole moment and structure of the complex formed with phenol and further to correlate the hydrogen bond data with P=O bond moment, excess charge density on the phosphoryl oxygen and with the square root of the additional dipole moment, $\Delta\mu^{\frac{1}{2}}$, *i.e.* with the difference between the dipole moment of the complex and the vector sum of the individual moments of the components.

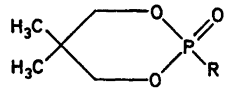
* For Part XXVII see Ref. 1.

EXPERIMENTAL

Materials. Phenol was purified by several recrystallizations from light petroleum and the white needles obtained were dried over phosphorus pentoxide in a desiccator. Carbon tetrachloride and benzene were purified chromatographically by using Molecular Sieve Type 4 Å and basic aluminium oxide. Carbon disulfide (Merck Uvasol) was used without further purification. The phosphonates and dioxaphosphorinanes, not commercially available, were prepared by literature methods.[2] The proton acceptors were redistilled or recrystallized immediately before use, and the purity was checked by IR and mass spectroscopy.

Infrared measurements. All measurements were carried out with a Perkin-Elmer 225 or a UNICAM SP 200 G spectrophotometer. The ground state stretching vibration of the proton donor O–H band was used for the determination of the association constants. Quartz absorption cells (Hellma No. 110, QI) of 10.00 mm path length were used. The spectra were run at temperatures of 25, 35 and 50 °C immediately after preparing the solutions. The concentration of phenol was kept at about 0.0025 M and the concentration range of the proton acceptors was 0.0020 – 0.0100 M. The solutions were made up by weighing, and the molarity of each solution was calculated at various temperatures from the change in density with temperature of carbon tetrachloride or of benzene. The details of the measurements have been published previously.[3,4] The K_{ass}, ΔH, $\Delta\nu_{OH}$ and $\nu_{\frac{1}{2}}$ values of the complexes between phenol and the phosphorinanes and the phosphonates tabulated in Tables 1 and 2 are the mean value of five separate determinations and have been corrected for the change in density of the solvent with temperature. The $\Delta\nu_{OH}$ values are estimated to be accurate within $\pm 3-5$ cm^{-1}, ΔH values within ± 2 kJ and K_{ass} values within 10 %.

Table 1. Spectral data for 1:1 hydrogen-bonded complexes between phenol and various 5,5-dimethyl-2-oxo-1,3,2-dioxaphosphorinanes (1) in carbon tetrachloride.



R	$\Delta\nu_{OH}$/ cm^{-1}	K_{ass}/ M^{-1}	$-\Delta H$/ kJ mol^{-1}	$-\Delta S$/ J K^{-1} mol^{-1}	$\nu_{\frac{1}{2}}$/ cm^{-1}	Temp/ °C
Cl	182	33.0 26.5 16.5	23.4	49.4	122	25 35 50
CCl_3	220	40.4 26.6 18.8	24.7	50.6	145	25 35 50
OC_6H_5	245	80.9 54.5 34.5	26.8	53.1	158	25 35 50
SCH_3	257	79.2 57.7 34.2	26.8	53.1	168	25 35 50
H	259	75.2 52.6 32.5	26.8	54.0	169	25 35 50
OCH_3	277	135.5 89.0 55.0	28.5	55.2	176	25 35 50
$C(C_6H_5)_3$	332	206.2 143.0 75.3	31.4	57.7	214	25 35 50
C_6H_5	333	240.1 149.4 92.7	30.1	55.2	213	25 35 50
CH_3	336	295.4 205.0 112.5	31.4	57.3	215	25 35 50
$CH_2C_6H_5$	337	317.8 211.8 121.2	31.0	55.7	217	25 35 50
$N(CH_3)_2$	356	352.6 233.0 131.0	31.8	57.3	221	25 35 50
$C(CH_3)_3$	359	322.6 232.1 128.5	32.2	59.0	222	25 35 50

Dipole moment measurements. The dipole moment measurements were carried out in carbon tetrachloride or in benzene at 20 ± 0.05 °C. The dielectric constants were measured with an internally thermostated, heterodyne-beat dipolmeter, type DMO 1, manufactured by Wissenschaftlich-Technische Werkstätten, GmbH, Germany. The thermostated dielectric cell, type DFL, of 20 ml capacity, had gold-coated interior plates. The refractive indices were measured at 20 °C with a Bausch & Lomb Precision Refractometer, 33-45-02-01. The den-

Table 2. Infrared data for the interaction of phenol with various diethylphosphonates, $(C_2H_5O)_2P(O)R$. Comparison of hydrogen bond data, dipole moments and electron densities. Solvent carbon tetrachloride.

R	ν_{PO}/cm^{-1} in CS_2	μ_a/D in CCl_4	Δq/ electrons [a]	ν_{OH}/ cm^{-1}	K_{ass}/ M^{-1}	$-\Delta H$/ kJ mol^{-1}	$-\Delta S$/ J K^{-1} mol^{-1}	$\nu_{\frac{1}{2}}$/ cm^{-1}	Temp/ °C
					71.9		51.5		25
CCl_3	1279	3.26	−0.5218	244	51.0	25.9		157	35
					32.3				50
					141.0		53.1		25
SCH_3	1262	2.67		294	98.0	28.0		183	35
					58.6				50
					130.1		54.0		25
H	1260	3.11	−0.3625	298	95.3	28.5		184	35
					54.1				50
					296.1		54.8		25
$C(C_6H_5)_3$	1247	2.86		338	178.3	30.1		218	35
					105.2				50
					380.4		57.3		25
CH_3	1243	2.74	−0.4008	357	249.5	31.8		223	35
					141.1				50
					455.9		57.7		25
$N(CH_3)_2$	1253			367	294.6	32.6		234	35
					170.3				50

[a] Δq, Calculated excess charge density on the P=O oxygen by the CNDO/2 method (details will be published elsewhere).

sity of carbon tetrachloride, benzene and of the solutions was determined by using a 20 ml capacity pycnometer. All solutions were prepared by weighing and they were handled in a dry-box. For the dipole moment measurements the weight fraction range of phenol was $4\times10^{-4}-30\times10^{-4}$ and of proton acceptor $8\times10^{-4}-60\times10^{-4}$.

The experimentally observed dielectric constants, ε_2, the specific volumes, v_2, and the square of the refractive indices, n_2^2, of the carbon tetrachloride and benzene solutions of proton donor and of acceptor were found to be lineary dependent on their weight fractions, w_2. The equations employed were:

$$\varepsilon_2=\varepsilon_1+\alpha w_2 \quad (1)$$

$$v_2=v_1+\beta w_2 \quad (2)$$

$$n_2^2=n_1^2+\gamma w_2 \quad (3)$$

The dielectric constant, ε_1, the specific volume, v_1, and the square of the refractive index, n_1^2, correspond to the values of pure carbon tetrachloride or of pure benzene at 20 °C. The α, β and γ values were obtained by the method at least squares. The total polarization, $P_{2\infty}$, and the molar refraction, R_D, at infinite dilution were calculated by using the method of Sharpe and Walker.[5] The dipole moment, μ, was calculated [5] from eqn. (4).

$$\mu=0{,}01281\ (P_0T)^{\frac{1}{2}} \quad (4)$$

P_0 is the orientation polarization derived from $P_0=P_{2\infty}-R_D$ (it is assumed that $R_D=P_E+P_A$). The probable error in the dipole moment, μ, was estimated not to exceed 0.05 D for each compound examined. The μ_a values for the phosphorinanes are tabulated in Table 3 (for details see Ref. 2), and for the phosphonates in Table 2.

To evaluate the dipole moment of the hydrogen bonded complex we need to know the concentration of the free proton donor, and the concentration of the free acceptor and of the hydrogen bonded complex in the reaction mixture (see eqn. 5).

$$C_6H_5OH+O=P\lessgtr \rightleftharpoons C_6H_5OH\cdots O=P\lessgtr \quad (5)$$

By using the K_{ass} values obtained by IR measurements (see Table 4), the weight fraction of

Table 3. Experimental P=O stretching frequency, ν_{PO}, and dipole moment, μ_a, and CNDO/2 calculated P=O bond moment, μ_{PO}, and excess charge density, Δq, on the P=O oxygen for various 5,5-dimethyl-2-oxo-1,3,2-dioxaphosphorinanes, *1*.

R	ν_{PO}/cm^{-1} in CS_2	in KBr	$\mu_{a/D}$ in C_6H_6	$\mu_{PO/D}$ ax	eq[b]	Δq/electrons [d]
Cl	1321 1296	1287	6.49	10.40	10.72	−0.3492 (eq)
CCl_3	1310 1286	1286	6.18	10.44	10.74	−0.4196 (eq)
OC_6H_5	1322 1297	1285	5.71 [a]	9.24 (ga)[c]	9.32	−0.3289 (eq/ga)
SCH_3	1286 1268	1273	5.65	10.77 (ga)	10.46	−0.4173 (eq/ga)
H	1310 1281		5.94	9.74	9.68	−0.3333 (eq)
OCH_3	1306 1273	1287	5.41	10.04 (ga)	9.96	−0.3541 (eq/ga)
$C(C_6H_5)_3$	1254	–	–	–	–	–
C_6H_5	1285 1259	1275	5.73	10.57	10.66	−0.3763 (ax)
CH_3	1252	1244	4.91	10.78	–	−0.3790 (ax)
$CH_2C_6H_5$	1275 1255	1246	5.25	–	–	–
$N(CH_3)_2$	1259	1238	4.24	10.75	–	−0.3923 (ax/ga)
$C(CH_3)_3$	1250	1247	4.13	10.88	–	−0.3988 (ax)

[a] From ref. 35. [b] ax and eq. mean P=O in axial or in equatorial position (for details see Ref. 2). [c] ga means *gauche* conformation (see Ref. 2). [d] Calculated charge density on P=O oxygen in the more stable (lowest energy) conformation (see Ref. 2).

Table 4. Total polarization, $P_{x\infty}$, molar refraction, R_D, parameters α_x, β_x, γ_x, and dipole moments, μ_x, and additional dipole moments $\vec{\Delta\mu}$ ($\vec{\Delta\mu}=\vec{\mu_x}-\vec{\mu_d}-\vec{\mu_a}$) of the complex formed between phenol and various phosphoryl compounds at 20 °C.[a] The dipole moment increment due to charge transfer, $\vec{\Delta\mu}_{CT}$, and to electrostatic attraction $\vec{\Delta\mu}_{ind}$ ($\vec{\Delta\mu}=\vec{\Delta\mu}_{ind}+\vec{\Delta\mu}_{CT}$).

Proton acceptor	Solvent	K_{ass}/M^{-1}	α_x	β_x	γ_x	$P_{x\infty}$/cm^3	R_D/cm^3	$\vec{\mu_x}$/D	$\vec{\Delta\mu}$/D	$\vec{\Delta\mu}_{ind}$/D	$\vec{\Delta\mu}_{CT}$/D
1, R=CCl_3	C_6H_6	19	16.754	−0.9363	0.0593	1141.98	25.31	7.33	0.19	0.07	0.12
1, R=CH_3	C_6H_6	140	17.944	−0.6834	−0.1661	903.58	27.53	6.51	0.33	0.12	0.21
$(C_2H_5O)_2P(O)CCl_3$	CCl_4	85	9.091	0.1316	0.1400	410.71	78.02	3.99	0.23	0.09	0.14
$(C_2H_5O)_2P(O)H$	CCl_4	153	15.294	0.2780	0.0682	433.80	59.41	3.98	0.28	0.11	0.17
$(C_2H_5O)_2P(O)CH_3$	CCl_4	423	13.710	0.5600	0.1276	440.03	83.62	4.14	0.37	0.14	0.23

[a] Weight fraction range of phenol, $4\times10^{-4}-30\times10^{-4}$; and of acceptor, $8\times10^{-4}-60\times10^{-4}$. K_{ass} measured at 20 °C.

the different species in the mixture could be calculated. To obtain the dielectric constant, ε_x, of the hydrogen-bonded complex, the contribution due to free phenol, ε_d, and that of the free proton acceptor, ε_a, have to be subtracted from the observed value, *i.e.*, $\varepsilon_x = \varepsilon_{obs} - (\varepsilon_d + \varepsilon_a)$. The ε_d and ε_a values could easily be obtained from the curves $(\varepsilon_d - \varepsilon_l)$ *vs.* w_d and $(\varepsilon_a - \varepsilon_l)$ *vs.* w_a, respectively (w_d = weight fraction of phenol, w_a = weight fraction of proton acceptor). Similarly, the v_x and n_x^2 values could be obtained. It was found, just as for the proton donor and the acceptors in CCl_4 or in C_6H_6, that the plots of dielectric constant, ε_x, specific volume, v_x, and square of the refractive index, n_x^2, of the hydrogen-bonded complex against the weight fraction showed no deviation from linearity. The dipole moments, μ_x, of the following hydrogen bonded complexes phenol/dioxaphosphorinanes (R = CCl_3, CH_3, see Table 4) in benzene and phenol/diethylphosphonates (R = CCl_3, H, CH_3) in carbon tetrachloride have been determined experimentally at 20 °C. The polarization data α_x, β_x, γ_x, $P_{x\infty}$, R_D and $\vec{\mu}_x$ of the hydrogen-bonded complexes are given in Table 4.

Calculations of μ_{PO}. CNDO/2 calculations of the P=O bond moments were carried out and by using the method of Santry and Segal.[6] The calculated μ_{PO} values when P=O is in the axial or in the equatorial position, and the R group (R = $-OC_6H_5$, $-SCH_3$, $-OCH_3$ or $-N(CH_3)_2$ is in the *gauche* conformation (see Ref. 2), are tabulated in Table 3. Calculations of the total energy of the various conformations of the phosphoryl compounds have been published elsewhere.[2]

Calculations of $\vec{\Delta\mu}$. The formation of a hydrogen bond, $X-H+B \rightleftharpoons X-H\cdots B$, brings about displacements of the electrons and the nuclei which results in a difference between the dipole moment of the hydrogen bonded complex and the vector sum of the individual moments of the components. This difference can be expressed in terms of a dipole increment, $\Delta\mu$, defined by the vector equation (6).

$$\vec{\Delta\mu} = \vec{\mu}_x - \vec{\mu}_d - \vec{\mu}_a \qquad (6)$$

where $\vec{\mu}_x$, $\vec{\mu}_d$ and $\vec{\mu}_a$ are the dipole moment of the hydrogen bonded complex, of phenol (1.47 D in benzene and 1.502 in carbon tetrachloride [8] at 20 °C) and of the phosphoryl compounds, respectively. The value of $\vec{\Delta\mu}$ can only be computed from experimental values of μ_x, μ_d and μ_a if the angles between these vectors are given, *i.e.*, we have to assume a geometrical configuration of the complex. In the calculation of the $\vec{\Delta\mu}$ value from experimental data [9,10] one neglects the change of dipole moment which can appear in the outside parts of the $-H\cdots B$ bridge. This may be questionable, in particular for groups like $\ddot{N}-P=O$ and $\ddot{O}-P=O$ where unshared electron pairs may operate. However, IR as well as ^1H NMR measurements show that the changes observed outside the H-bond are negligible compared to the changes observed in the $-H\cdots B$ part.[9] Nevertheless, by comparing a series of hydrogen bonded complexes with similar structural characteristics, the evolution of $\vec{\Delta\mu}$ values corresponding to the various spatial structures allow us to predict the most probable structures.[11,12] The evaluation of the additional dipole moment, $\vec{\Delta\mu}$, acting along the hydrogen bond, is based on the following equation, $\vec{\mu}_x = \vec{\mu}_a + \vec{\mu}_d + \vec{\Delta\mu}$ which when squared, on introducing an azimuthal angle ϕ yields:

$$(\mu_x^2)_\phi = \mu_a^2 + \mu_d^2 + \Delta\mu^2 + 2\Delta\mu\mu_d \cos\beta_d + 2\Delta\mu\mu_a \cos\beta_a + 2\mu_d\mu_a \cos\beta_d \cos\beta_a + 2\mu_d\mu_a \sin\beta_d \sin\beta_a \cos\phi$$

Since the phenol part of the complex can rotate around the O−H bond, the average value of $\cos\phi \approx 0$. This yields $\mu_x^2 = \mu_d^2 + \mu_a^2 + \Delta\mu^2 + 2\Delta\mu\mu_d \cos\beta_d + 2\Delta\mu\mu_a \cos\beta_a + 2\mu_d\mu_a \cos\beta_d$

The value of $\Delta\mu$ from the above equation becomes:

$$\Delta\mu = \sqrt{\mu_x^2 - \mu_d^2 \sin^2\beta_d - \mu_a^2 \sin^2\beta_a} - \mu_d \cos\beta_d - \mu_d \cos\beta_a$$

The value of the angle β_d between the resultant dipole moment and the O−H direction in the phenol molecule (see Fig. 1) has been calculated [10] to be 27°. The angle β_a between the P=O vector and the resultant dipole moment of the phosphoryl acceptors has been estimated in the following way. The equation of the P=O vector is tabulated from a COORD program devised by Dewar.[13] The direction of the total dipole moment, β_a, of the various phosphoryl compounds is known from the CNDO/2 calculation.[2] Simple mathematics are then used to calculate the angle β_a between the two vectors. The results of the calculated β_a values of the

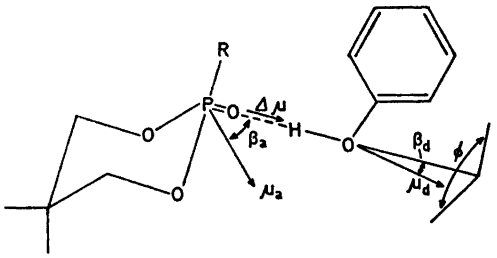


Fig. 1. Hydrogen bonding between phenol and 1,3,2-dioxaphosphorinane showing the various angles used to calculate $\vec{\Delta\mu}$.

hydrogen bonded complexes phenol/dioxaphosphorinanes are 46.2 and 19.9° for R = CCl_3 and CH_3, and the angles of the phenol/diethylphosphonates are 71.0, 46.3 and 66.7° for R = CCl_3, CH_3 and H, respectively. The $\Delta\mu$ values for the various hydrogen-bonded complexes are tabulated in Table 4.

Charge-transfer in H-bonds. Following Ratajczak [14,15] it is to be expected that the observed enhancement of the dipole moment of hydrogen bonded complexes might be due to two main contributions, (a) to an induced dipole moment due to mutual electrostatic attraction,

$$X^{\delta-}-H^{\delta+}\cdots{}^{\delta-}B,$$

and (b) to a dipole moment due to charge transfer (electron delocalization),

$$X^{\delta-}-H\cdots B^{\delta+}$$

Therefore, it can be written,

$$\vec{\Delta\mu} = \vec{\Delta\mu}_{ind} + \vec{\Delta\mu}_{CT}$$

An approximate estimate of $\vec{\Delta\mu}_{ind}$ can be evaluated according to the method of Frank,[16] hence the dipole moment, $\Delta\mu_{CT}$, due to electron delocalization can be obtained. The method of Frank leads to the following relationship [9]

$$\Delta\mu_{ind} = 2\alpha\mu_b(\varepsilon+2)/3\varepsilon r^3$$

where ε is the dielectric constant of the solvent,[17] α is taken to be the polarizability of the O–H bond of phenol,[18] μ_b is the inducing dipole moment approximated by the dipole moment of the lone-pair orbital of the oxygen atom ($\mu_b = 2$ D), and r is the distance between the dipole and the polarizable center. This was taken to be the distance between the O atom and the center of the O–H bond. The distance r was estimated from an empirical correlation between this quantity and $\Delta\nu_{OH}$.[19,20] The $\vec{\Delta\mu}_{ind}$ and $\vec{\Delta\mu}_{CT}$ values thus obtained are given in Table 4. The $\Delta\mu_{ind}$ values are between 0.07–0.14 D and values of $\Delta\mu_{CT}$ between 0.12–0.23 D, depending upon the system. A linear plot of ΔH against $\Delta\mu^2$, predicted theoretically,[9] can be shown to exist by using the values in Tables 1 and 4.

RESULTS AND DISCUSSION

As can be seen from Tables 1–3, the measured values for 2-oxo-1,3,2-dioxaphosphorinanes and diethylphosphonates fall onto the same straight line correlating K_{ass} with $\Delta\mu_{OH}$, and ΔH with $\Delta\nu_{OH}$, *i.e.*, there is no marked difference in hydrogen bonding ability between the phosphorinanes and the phosphonates in relation to $\Delta\nu_{OH}$. In both cases the equations correlating log K_{ass} with $\Delta\nu_{OH}$ are given by,

$$\log K_{ass}^{25} = 0.0062\ \Delta\nu_{OH} + 0.378 \text{ (at 25 °C)}$$

$$\log K_{ass}^{35} = 0.066\ \Delta\nu_{OH} + 0.084 \text{ (at 35 °C)}$$

$$\log K_{ass}^{50} = 0.056\ \Delta\nu_{OH} + 0.174 \text{ (at 50 °C)}$$

If comparison is made, however, between 2-oxo-1,3,2-dioxaphosphorinanes and diethylphosphonates containing the same P–R group, we see that the phosphonates, in general, have a lower P=O stretching frequency shift, larger K_{ass} and $\Delta\nu_{OH}$ values with phenol than the phosphorinanes, *e.g.*, the phosphorinane containing the P-CCl_3 group (ν_{PO}, 1310, 1286; K_{ass}[28], 40; ν_{OH}, 220) should be compared with $(C_2H_5O)_2POCCl_3$ (ν_{OH}, 1279 cm^{-1}; K_{ass}[25], 72 M^{-1}; ν_{OH}, 224 cm^{-1}). The main reason for this might be that the O-P-O angle is found to be smaller in the diethylphosphonates [21] than in the 1,3,2-dioxaphosphorinanes.[22,23] As a consequence, different hybridization may occur on the phosphorus atom and thus cause a lower electron density on the P=O oxygen in the latter compound (see Δq in Tables 2 and 3).

A conformational study of the 5,5-dimethyl-2-oxo-1,3,2-dioxaphosphorinanes by means of dipole moments, ionization potentials and

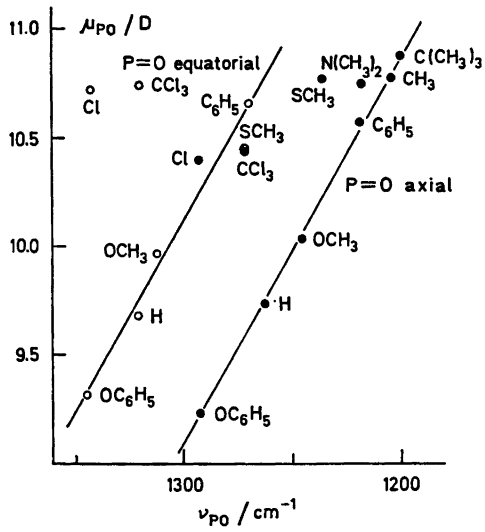


Fig. 2. Correlation of the P=O bond moment, μ_{PO}, calculated by the CNDO/2 method with IR frequency ν_{PO} in axial (●) and equatorial (○) position of the various phosphorinanes.

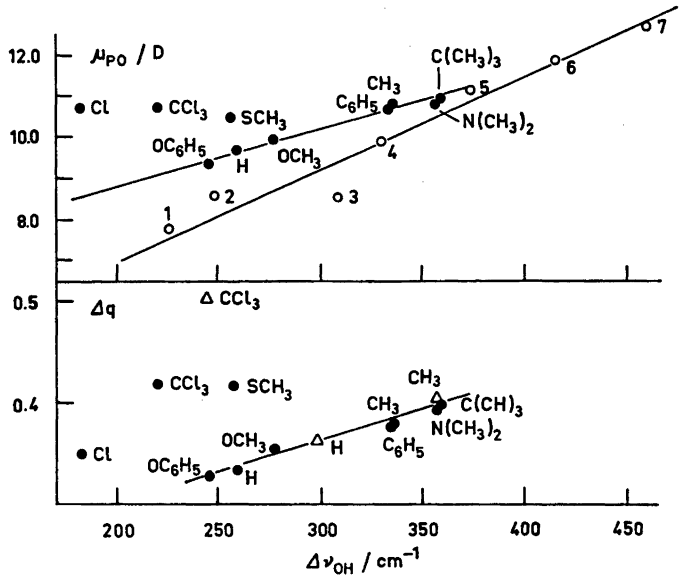


Fig. 3. CNDO/2 calculated P=O bond moment, μ_{PO}, and excess charge density, Δq, on P=O oxygen *vs.* $\Delta\nu_{OH}$ for the association of phenol with 1,3,2-dioxaphosphorinanes (●) and diethylphosphonates (△). Open circles are μ_{PO} data calculated from IR intensity measurements of the P=O band,[24]

(1) $(C_6H_5O)_3PO$,
(2) $(C_6H_5O)_2(CH_3O)PO$,
(3) $(CH_3O)_3PO$,
(4) $(C_2H_5O)_3PO$,
(5) $(C_2H_5O)_2(CH_3)_2NPO$,
(6) $(C_6H_5)_3PO$,
(7) $[(CH_3)_2N]_3PO$.

CNDO/2 calculations has been published.[2] In this work we have calculated by the CNDO/2 method the P=O bond moments, μ_{PO}^{ax} and μ_{PO}^{eq} (P=O in the axial or equatorial position) and found that they form, with the exception of R=Cl or CCl_3, a fairly good linear relationship when plotted against observed P=O stretching frequencies in the axial and equatorial positions (Fig. 2). Following Majoral [23] we have associated the band with the lowest μ_{PO} value with a conformer with the P=O group in the axial position. Since we have found that the CNDO/2 calculated μ_{PO}^{ax} and μ_{PO}^{eq} correlate with the two bands which appear in the region 1320 – 1250 cm^{-1}, our findings substantiate the conclusion drawn by Majoral that the two bands may be assigned to P=O stretching frequencies.

We have also found, as shown in Fig. 3, that the P=O bond moments, μ_{PO}, calculated by the CNDO/2 method (μ_{PO}^{eq} values for R=Cl, CCl_3, OC_6H_5, SCH_3, H, OCH_3 and C_6H_5, and μ_{PO}^{ax} for R=$N(CH_3)_2$, $C(CH_3)_3$ and CH_3) give, with the exception of R=Cl, CCl_3 or SCH_3, a linear relation with $\Delta\nu_{OH}$. A similar relationship has also been found to exist by using the μ_{PO} values reported by Schulze and Müller [24] as shown in Fig. 3. Our CNDO/2 calculated P=O bond moments are in fairly good agreement with those calculated from infrared P=O bond

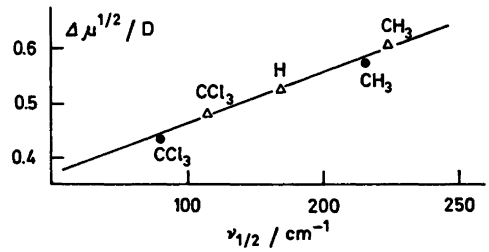


Fig. 4. Half band width, $\nu_{\frac{1}{2}}$, of the O–H band *vs.* the square root of the dipole moment, $\mu^{\frac{1}{2}}$, for the association of phenol with phosphorinanes (●) and diethylphosphonates (△).

intensities of Schulze and Müller. In contrast, however, Mauret and Fayel[25] have reported μ_{PO} values of order 3 – 4 D for similar phosphoryl compounds. The great deviation of 2-oxo-1,3,2-dioxaphosphorinanes and diethylphosphonates containing the groups R = Cl, CCl_3 or SCH_3 from the straight line correlating μ_{PO} with $\Delta\nu_{OH}$ and ν_{PO} (see Figs. 2 and 3), may be due to the fact that the parameters in the CNDO/2 program do not satisfactorily account for the interaction of the *d*-orbitals.[26] It is well known,[6,26] that the atomic parameters of the CNDO/2 method have been found to be unsatisfactory for charge density and dipole moment calculations for the second row atoms. To our knowledge there have not previously been reported any systematic CNDO/2 calculations of the charge density, Δq, on phosphoryl oxygen. Wagner[27] has, however, by using the internally consistent LCAO-MO method, reported Δq values which are not consistent with our results. It is also interesting to note that we have found a linear correlation between Δq and $\Delta\nu_{OH}$ for the association of the phosphoryl compounds with phenol. The Δq values of 2-oxo-1,3,2-dioxaphosphorinanes and diethylphosphonates fall onto the same straight line (Fig. 3). No linear correlation has been found between Δq and the Taft inductive substituent constant σ^* for the group R. This should imply that the electron density on the phosphoryl oxygen is not entirely controlled by the inductive effects of the substituents groups. In this connection it should be mentioned that alkaline hydrolysis of a series of organohalophosphorus compounds indicates that the electron density on the phosphorus atom is influenced by mesomeric effects, *e.g.*, there is an increase in the activation energy of approximately 16.7 and 25.1 kJ mol^{-1} in passing from dialkyl to dialkoxy and from dialkyl to bisdialkylamino groups,[28–30] respectively. Consequently, it is reasonable to assume that the unshared electron pair on the nitrogen, and to a smaller extent that on the oxygen atom, is conjugated with a 3*d* orbital of the phosphorus atom and hence reduces its fractional positive charge. This observation is also in accordance with the data obtained from bond lengths[31] and spectroscopic studies.[32,33] What may be questionable is to what extent the mesomeric effects are transmitted through the

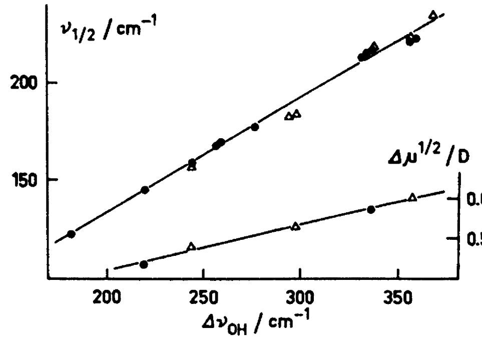


Fig. 5. Half band width, $\nu_{\frac{1}{2}}$, of the O – H band and the square root of the additional dipole moment, $\Delta\mu^{\frac{1}{2}}$, *vs.* $\Delta\nu_{OH}$ for the association of phenol with phosphorinanes (●) and diethylphosphonates (△).

P = O group and hence affect the electron density on phosphoryl oxygen. Lack of linearity between Δq and σ^*, however, indicates strongly that the resonance effect plays an important part.

The $\vec{\Delta\mu}$ values have been determined by using experimentally obtained μ_x, μ_d, μ_a values and a CNDO/2 calculated β_a value (see Fig. 1). In Fig. 4 we have shown that there exists a linear relationship between the square root of the additional dipole moment $\Delta\mu^{\frac{1}{2}}$ and half band width $\nu_{\frac{1}{2}}$. This finding is very important and demonstrates clearly that the greater the half band width the greater is the enhancement of the dipole moment. We have also found, as shown in Fig. 5, a linear correlation between $\Delta\mu^{\frac{1}{2}}$ and $\Delta\nu_{OH}$ (or ΔH). This indicates, since the extent of the proton transfer reaction in this system is negligible,[34] that the dipole increment is mainly determined by the strength of the H-bond formed. If the method of Frank[16] with included modifications[9] gives reliable $\vec{\Delta\mu}_{ind}$ values, we can see from Table 4 that the main factor responsible for the enhancement of polarity observed in the $>P = O \cdots H - OC_6H_5$ system is the change of electron distribution due to an electron-transfer effect. As can be seen from Tables 1 and 4 this electron delocalization effect is linearly related to the H-bond strength, *i.e.*, the stronger the H-bond the greater is the electron delocalization effect.

REFERENCES

1. Gramstad, T. and Simonsen, O. R. *Spectrochim. Acta A 32* (1976) 723.
2. Fægri, K., Gramstad, T. and Tjessem, K. *J. Mol. Struct. 32* (1976) 37.
3. Gramstad, T. *Acta Chem. Scand. 15* (1961) 1337.
4. Gramstad, T. and Sandström, J. *Spectrochim. Acta A 25* (1969) 31.
5. Sharpe, A. N. and Walker, S. *J. Chem. Soc.* (1961) 2974.
6. Santry, D. P. and Segal, G. A. *J. Chem. Phys. 47* (1967) 158.
7. Foubert, A. F. and Huyskens, P. L. *Can. J. Chem. 54* (1976) 610.
8. Nagakura, S. and Baba, H. *J. Am. Chem. Soc. 74* (1952) 5693.
9. Ratajczak, H. and Orville-Thomas, W. J. *J. Chem. Phys. 58* (1973) 911.
10. Ratajczak, H. and Sobczyk, L. *J. Chem. Phys. 50* (1969) 556.
11. Debecker, G. and Huyskens, P. *J. Chim. Phys. 68* (1971) 287.
12. Nouwen, R. and Huyskens, P. *J. Mol. Struct. 16* (1973) 459.
13. Program 136, Quantum Chemistry Program Exchange, Indiana University, Bloomington, Indiana, Indiana, USA.
14. Ratajczak, H. *J. Phys. Chem. 76* (1972) 3991.
15. Ratajczak, H. *J. Phys. Chem. 76* (1972) 3000.
16. Frank, F. C. *Proc. R. Soc. London A 152* (1936) 171.
17. Weissberger, A. and Proskainer, E. S., Eds., *Organic Solvents*, Interscience, New York 1955, Vol. 77.
18. Moelwyn-Hughes, E. A. *Physical Chemistry*, Pergamon, New York 1961, p. 385.
19. Nakamoto, K., Margoshes, M. and Rundle, R. E. *J. Am. Chem. Soc. 77* (1955) 6480.
20. Ratajczak, H. and Orville-Thomas, W. J. *J. Mol. Struct. 1* (1968) 449.
21. Kyogoku, Y. and Iitaka, Y. *Acta Crystallogr. 21* (1966) 49.
22. Kainosho, M., Nakamura, A. and Tsubi, M. *Bull. Chem. Soc. Jpn. 42* (1969) 1713.
23. Majoral, J. P. and Navech, J. *Spectrochim. Acta A 28* (1972) 2247.
24. Schulze, H. and Müller, A. *Z. Naturforsch. Teil B 25* (1970) 148.
25. Mauret, P. and Fayet, J. P. *Bull. Soc. Chim. Fr.* (1969) 2363.
26. Santry, D. P. *J. Am. Chem. Soc. 90* (1968) 3309.
27. Wagner, E. L. *J. Am. Chem. Soc. 85* (1963) 161.
28. Larsson, L. *Sven. Kem. Tidsskr. 70* (1968) 405.
29. Hudson, R. F. and Keay, L. J. *J. Chem. Soc.* (1956) 2463; *Ibid.* (1960) 1859.
30. Aksnes, G. *Acta Chem. Scand. 14* (1960) 1515.
31. Cruickshank, D. N. J. *J. Chem. Soc.* (1961) 5486.
32. Gramstad, T. *Spectrochim. Acta 19* (1963) 497.
33. Blindheim, U. and Gramstad, T. *Spectrochim. Acta A 25* (1969) 1105.
34. Gramstad, T. and Vikane, O. *Spectrochim. Acta A 28* (1972) 2131.
35. Kainosho, M. and Shimozawa, T. *Tetrahedron Lett.* (1969) 865.

Received December 3, 1976.