Phosphorus Containing Polymethine Dyes

III. Electronic Structure and Solvatochromism of some Phosphorus Containing Polymethine Dyes[*]

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Résumé

Certains aspects de la structure électronique d'une mérophosphinine dérivée du cyclopentadiénylène-triphényl-phosphorane, ainsi que d'une série de phosphacyanines dérivées de méthylène-triphényl-phosphoranes dont le groupement méthylénique porte un substituant électrocapteur, sont commentés à la lumière de données expérimentales relatives à la solvatochromie et au spectre infra-rouge de ces matières colorantes.

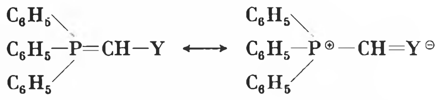
In part I of this series some new phosphorus containing polymethine dyes were described, which were divided into the following groups:

1. Phosphinine and phosphacyanine dyes derived from cyclopentadienylenetriphenylphosphorane.
2. Phosphacyanine dyes derived either from methylenetriphenylphosphoranes or from methylene-tris(2-cyanoethyl)-phosphoranes having an electron-captor group attached to the methylene group of the phosphorane.
3. Merophosphinine dyes derived from cyclopentadienylenetriphenylphosphorane.

The dyes of the latter two classes show a solvent displacement of their absorption maximum. An attempt is made, in this paper, to gain some insight into the electronic structure of these dyes from their solvatochromic behaviour. Hereby some use is also made of infra-red spectral data.

I. Solvatochromism and electronic structure of the phosphacyanine dyes I

In this section we shall deal in detail with the dyes of general formula I which are derived from the methylenetriphenylphosphoranes of formula II.



$$(C_6H_5)_3P{=}CH{-}Y \longleftrightarrow (C_6H_5)_3P^{\oplus}{-}CH{=}Y^{\ominus}$$

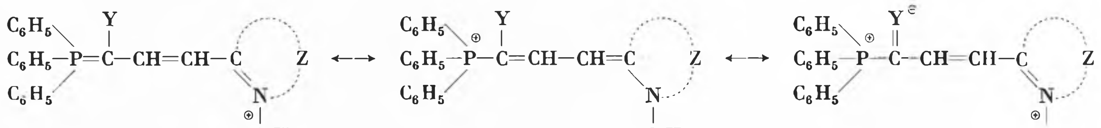
IIa IIb

Phosphoranes II (Y = $COCH_3$, COC_6H_5, $COOC_2H_5$, CN)

In these formulae, Y stands for an electron-acceptor group, such as acetyl, benzoyl, carbethoxy or cyano, while Z represents the remaining atoms of a five- or six-membered azole ring.

The electronic structure of these dyes is ultimately determined by the competition between three auxochromophoric systems present in the molecule: the phosphacyanine system (Ia ⟷ Ib), the merocyanine system (Ib ⟷ Ic) and the merophosphinine system (Ia ⟷ Ic).

There is some analogy, therefore, between the phosphacyanines I and the so-called "Holopolar Trinuclear Cyanine Dyes", independently discovered by *Eastman Kodak Cie.*[1] and by *Gevaert Photo-Producten N. V.*[2], and whose electronic structure as been discussed in terms of interfering auxochromophoric systems, some years ago, by Brooker *et al.*[3] and by two of the present authors[4].



Ia Ib Ic

Phosphacyanines I (Y = $COCH_3$, COC_6H_5, $COOC_2H_5$, CN)

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[*] Part I: *Bull. Soc. Chim. Belges 73* (1964) 921.
Part II, *ibid. 74* (1965) 12.

[**] Contribution from the Chemical Research Laboratories of the Gevaert-Agfa N.V., Mortsel-Antwerp (Belgium).

[1] Kodak S.A., Belg. Pat. 519147 (April 11, 1953), prior. U.S.A. April 16, 1952.

[2] Gevaert Photo-Producten N.V., Belg.Pat. 521309 (July 9, 1953).

[3] a) L.G.S. Brooker, F.L. White, D.W. Heseltine, G.H. Keyes, S.G. Dent jr. and E.V. Van Lare, *J. Phot. Sci. 1* (1953) 183. b) L.G.S. Brooker, *Experientia, Suppl. II* (1955) 254.

[4] a) A. Van Dormael, 27e Congrès Int. Chim. Ind., Brussels, September 1954, Compte rendu, vol. III *(Belg. Chem. Ind. XX*, special edition) p. 658. b) A. Van Dormael and J. Nys, 31e Congrès Int. Chim. Ind., Liège 1958, Compte rendu *(Belg. Chem. Ind.*, Vol. II special edition) p. 512.

There is one important difference, however, between the holopolar trinuclear cyanines and the phosphacyanines considered here: the former are intra-ionic dyes whereas the latter contain a net positive charge and are essentially cationic dyes with gegen-ions in the bulk of the solution. Their electronic structure will nevertheless be determined—as it was in the afore-mentioned trinuclear cyanine dyes—by the acidity/basicity relationships between the various chromophoric groups, as well as by eventual steric effects.

The importance of the contribution of these two factors is in turn largely determined by the kind of hybridization of the orbitals at the phosphorus atom. According to the current views about the electronic structure of phosphorus derivatives[5] it seems most likely that in the present case the four σ-bonds originating at the phosphorus atom are essentially sp^3-hybrids, the π-bonding between the phosphorus atom and the polymethine chain resulting from the interaction between a phosphorus d-orbital and the p_z-orbital of the adjacent carbon atom.

In that eventuality, the bond geometry at the phosphorus atom would be akin to that encountered in phosphorus oxychloride[6a] or in tri-alkylphosphine oxide[6b]; i.e., the bond structure at the P-atom would belong to the C_{3v}-symmetry group, the three phosphorus-benzene links being included in three planes of symmetry inclined at 120° to each other. Furthermore, owing to the very low electron-affinity of a d-orbital compared with that of a sp^3-orbital, a high heteropolarity of the P–C bond might be anticipated, resulting in a high π-basicity of the phosphorus atom, and, consequently, in a low π-electron concentration at the $\rangle P{=}\overset{|}{C}-$ chromophore.

In addition, a scale drawing (Fig. 1) shows that steric hindrance probably doesn't play an important role.

An attempt is made here, to elucidate some features of the electronic structure of the phosphacyanine dyes I by means of an analysis of their infra-red spectra and of their solvatochromic behaviour.

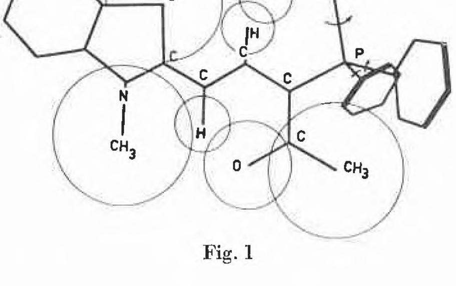


Fig. 1

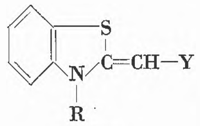
A. Infra-red spectra of the phosphacyanines I

Valuable information about the electronic structure of the phosphacyanines I in their ground state can be obtained from a study of the position of the C=O bands (when $Y = COCH_3$, COC_6H_5, $COOC_2H_5$) or C≡N bands (when Y = CN) in their infra-red absorption spectra.

A good starting point for the evaluation of carbonyl- or cyano-vibration frequencies is the study of the I.R.-spectra of the corresponding acyl-, carbethoxy- or cyano-methylene triphenylphosphoranes II. Infra-red data for most of these derivatives are known[7]. The C=O, resp. C≡N vibration frequencies in these molecules are strikingly low: the observed frequencies (Table I) lie far outside the range of the corresponding frequencies in aliphatic α,β-unsaturated esters, ketones or nitriles.

These low frequencies indicate a considerable electromeric displacement of π-electrons from the phosphorus atom towards the carbonyl resp. cyano group, and are consistent with the sp^3-hybridization of the σ-bonds originating at the phosphorus atom, accompanied by a d_π–p_π-bonding between P and the adjacent carbon atom.

Methylenetriphenylphosphoranes II therefore exhibit a predominantly dipolar structure (IIb) with an appreciable positive charge on the phosphorus atom, whose π-basicity must consequently be very high. Thus, the phosphorus atom is considerably more basic than, for instance, the benzothiazole nucleus. This becomes evident when one compares the C=O frequencies in II, $Y = COOC_2H_5$ ($\nu_{C=O} = 1610$ cm^{-1}) with that in III, $R = -CH_3$, $Y = -COOC_2H_5$ ($\nu_{C=O} = 1666$ cm^{-1})[9]. The C=O frequency is much lower in the carbethoxymethylenephosphorane than in 2-carbethoxymethylene-3-methyl-2H,3H-benzothiazoline.



III

The same conclusion is reached when the C=O frequencies in II, $Y = COCH_3$ ($\nu_{C=O} = 1542$ cm^{-1}) and in 2-acetylmethylene-3-ethyl-2H,3H-benzothiazoline[10],III, $R = -C_2H_5$, $Y = COCH_3$ ($\nu_{C=O} = 1606$ cm^{-1}) are compared.

The introduction, at the α-carbon atom in the triphenylphosphoranes II, of an azolium-vinylene group to

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[5] a) D.P.Craig, A.Maccoll, R.S.Nyholm, L.E.Orgel and L.E. Sutton, *J. Chem. Soc. 1954*, 332. b) D.W.Cruickshank, *J. Chem. Soc. 1961*, 5486.

[6] a) *Tables of Interatomic Distances and Configuration in Molecules and Ions*, The Chemical Society, London 1958. b) C.I.Bränden and I.Lindqvist, *Acta Chem. Scand. 17* (1963) 353.

[7] a) G.Aksnes, *Acta Chem. Scand. 15* (1961) 692. b) S.Trippett and D.M.Walker, *J. Chem. Soc. 1959*, 3874. c) A.J.Speziale and K.W.Ratts, *J. Amer. Chem. Soc. 85* (1963) 2790. d) G.Wittig and U.Schöllkopf, *Chem. Ber. 87* (1954) 1318.

[8] L.J.Bellamy, *The Infra-red Spectra of Complex Molecules*, Methuen & Co., London; John Wiley & Sons, New York 1958.

[9] J.Nys and A.Van Dormael, *Bull. Soc. Chim. Belges 58* (1949) 491.

[10] J.Nys, 31e Congrès Int. Chim. Ind., Liège 1958, Compte rendu, vol. II *(Belg. Chem. Ind.*, special edition) p. 509.

Table I. Methylenetriphenylphosphoranes of formula II

Y	$\nu_{C=O}$ (cm^{-1})	$\lambda_{C=O}$ (μ)	$\nu_{C\equiv N}$ (cm^{-1})	$\lambda_{C\equiv N}$ (μ)
$-COOC_2H_5$	1620[7a]	6.17[7a]	–	–
	1610[7c]	6.21[7c]	–	–
	1610*	6.21*	–	–
$-CHO$	1558*	6.42*	–	–
$-COCH_3$	1542[7a]	6.48[7a]	–	–
$-COC_6H_5$	1529[7a]	6.53[7a]	–	–
$-CN$	–	–	2139[7b]	4.68[7b]
saturated ester	1750–1735[8]	5.71–5.76[8]	–	–
aliphatic α,β-unsaturated ester	1730–1717[8]	5.78–5.82[8]	–	–
saturated ketone	1706–1725[8]	5.79–5.86[8]	–	–
aliphatic α,β-unsaturated ketone	1665–1685[8]	5.93–6.00[8]	–	–
saturated nitrile	–	–	2260–2240[8]	4.42–4.46[8]
aliphatic α,β-unsaturated nitrile	–	–	2235–2215[8]	4.48–4.52[8]

* Our own results. All data refer to KBr-discs.

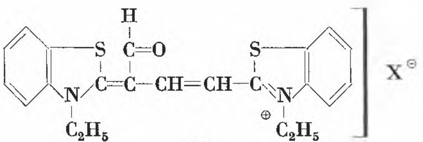
Table II. Phosphacyanines of general formula I

Y	Z = residue of:	$\nu_{C=O}$ (cm^{-1})*	$\nu_{C\equiv N}$ (cm^{-1})*
$-COOC_2H_5$	benzothiazole	1680	–
$-COOC_2H_5$	5-methylbenzoxazole	1677	–
$-COOC_2H_5$	thiazoline	1685	–
$-COCH_3$	benzothiazole	< 1600	–
$-COC_6H_5$	benzothiazole	< 1600	–
$-CN$	benzothiazole	–	2181
$-CN$	5-methylbenzoxazole	–	2181
$-CN$	thiazoline	–	2181

* In KBr-discs.

give the phosphacyanines I results in an increase of the C=O, resp. C≡N frequencies. Typical I.R.-spectra for a carbethoxy-, a benzoyl- and a cyano-substituted phosphacyanine are shown in Fig. 2; the numerical data are listed in Table II. The increase of the C=O or C≡N frequencies corresponds to a decrease of the π-electron density at the C=O, resp. C≡N groups, due to a draining of π-electrons by the electron attracting, positively charged azolium nucleus in Ia.

The C=O frequency shifts, observed on going from the phosphorane II to the phosphacyanine dyes I, although smaller, are analogous to the C=O shift that is observed on going from the formyl-methylene derivative III ($R = -C_2H_5$; $Y = -CHO$; $\nu_{C=O} = 1614$ cm^{-1}) to the formyl-substituted cyanine dye[11], IV ($\nu_{C=O} = 1634$ cm^{-1}); both shifts probably occur for the same reasons.



IV

In the case of the phosphorus containing dyes I, the various C=O frequencies and C≡N frequencies remain very low, indicating that in these dyes an appreciable π-electron density still remains on the C=O or C≡N groups.

In the acyl derivatives (I, $Y = COCH_3$ or COC_6H_5, Z = benzothiazole) the C=O frequency is so low, that it cannot be distinguished from the absorption bands in

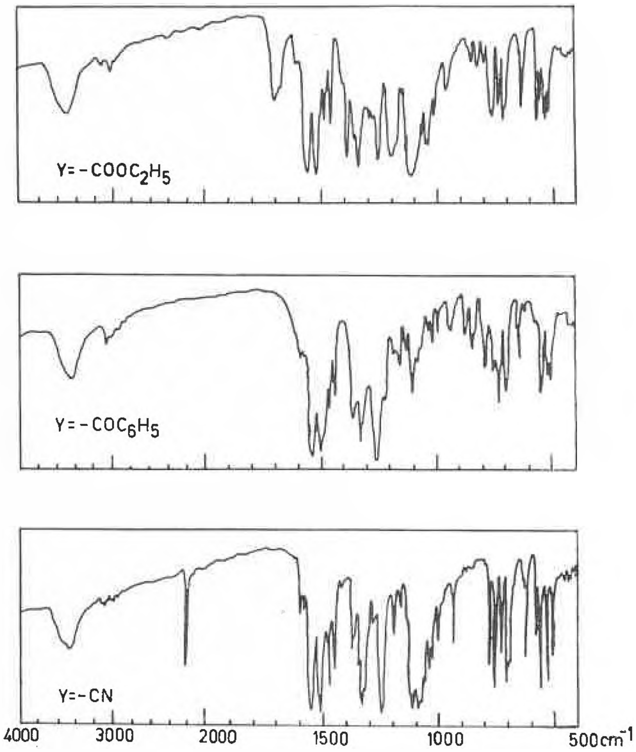


Fig. 2. Infra-red spectra of Dye I with Z = benzothiazole and Y as indicated

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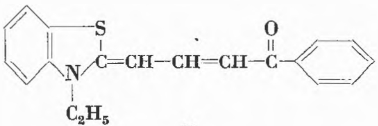
[11] J. Nys and J. Libeer, *Sci. Ind. Phot.* XXVIII (1957) 433.

the 1550 cm^{-1} region that are characteristic for conjugated polymethine chains. Only an upper limit for the C=O frequency can therefore be given: in dyes I (Z = benzothizole) Y = $COCH_3$ or COC_6H_5) the characteristic C=O frequency is lower than 1600 cm^{-1}.



V

In dye V[12], which contains the same merocyanine-like auxochromophoric system as the phosphacyanine I in which Y = COC_6H_5, the C=O frequency lies at a much higher value, i.e. 1631 cm^{-1}. It follows that the high π-electron density in the C=O (or C≡N) groups in dyes I is due to the influence of both phosphorane $\left(>P{=}C< \right)$ and azole chromophores, but predominantly of the former.

Finally, it can be seen in table II, that differences in the basicity of the azole nuclei don't notably influence either the C=O or the C≡N vibration frequencies in these dyes.

It seems therefore, that in the phosphacyanine dyes I, all three chromophoric groups are taking part in the conjugation, at least in the ground state.

The $>P{=}C<$ chromophore being largely ionized, Ib and Ic are therefore the most important extreme structures contributing to the actual distribution of electrons in these molecules, with a net predominance of Ic.

These observations suggest that, if any departure from coplanarity exists in the auxochromophoric system of the phosphacyanines I, it should be of minor importance, thereby confirming the conclusions reached on the basis of the scale drawing. This result is furthermore consistent with the experimental fact, that these dyes are spectral sensitizers for the photoconductivity in silver halide gelatine emulsions, for which planarity of the auxochromophoric system is a necessary condition.

B. Solvatochromism of the phosphacyanines

The absorption curves, in the visible range of the spectrum, of the phosphacyanine dyes listed in Table II have been determined in a variety of solvents with widely spread refractive indices and dielectric constants. The experimental results are listed in Table III.

It appears, that in all cases the transition energies (or the wave numbers of the absorption maxima) in different solvents vary linearly with the Bayliss[13] function $(n^2-1)/(2n^2+1)$ derived from the refractive indices (normal "polarization red shift" due to dispersive solute-solvent interaction). No correlation whatsoever was found between the transition energy (or the wave numbers) and the dielectric constant or Kosower's Z-value[14] of the solvents that were used (see Fig. 3, 4 and 5 for the three dyes which show the largest solvatochromic shifts).

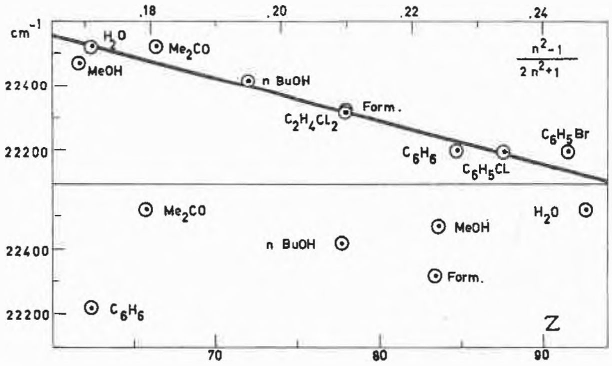


Fig. 3. Solvachromism of Dye I, Y = $-COOC_2H_5$, Z = benzothiazole

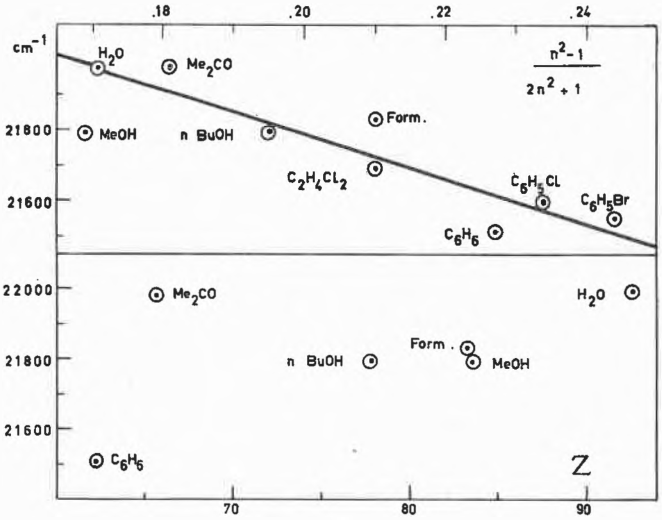


Fig. 4. Solvatochromism of Dye I, Y = $-COC_6H_5$, Z = benzothiazole

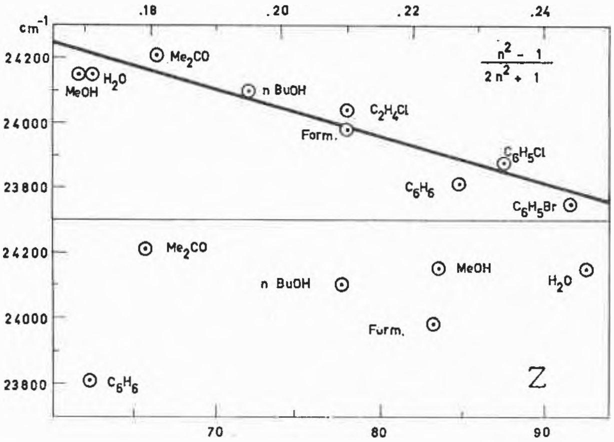


Fig. 5. Solvatochromism of Dye I, Y = $-CN$, Z = 5-methylbenzoxazole

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[12] E. B. Knott, *J. Chem. Soc. 1955*, 945.

[13] N. S. Bayliss, *J. Chem. Physics 18* (1950) 292.

[14] E. D. Kosower, *J. Amer. Chem. Soc. 80* (1958) 3253.

Table III

Solvent	Methanol	Water	Acetone	*n*-Butanol	Formamide	1,2-dichloroethane	Benzene	Chlorobenzene	Bromobenzene	
$\frac{n^2-1}{2n^2+1}$	0.169	0.171	0.181	0.195	0.210	0.210	0.227	0.234	0.244	
Z-value	83.6	94.6	65.7	77.7	83.3	–*	62.3	–*	–*	
I, Y = $-COOC_2H_5$ Z = benzothiazole	22.470 (445)	22.520 (444)	22.520 (444)	22.420 (446)	22.420 (448)	22.320 (448)	22.220 (450)	22.220 (450)	22.220 (450)	cm^{-1} (nm)
I, Y = $-COOC_2H_5$ Z = 5-methylbenzoxazole	24.210 (413)	24.270 (412)	24.270 (412)	24.150 (414)	24.100 (415)	24.150 (414)	24.040 (416)	23.910 (418)	23.870 (419)	cm^{-1} (nm)
I, Y = $-COOC_2H_5$ Z = thiazoline	25.710 (389)	25.840 (387)	25.770 (388)	25.640 (390)	25.770 (388)	25.640 (390)	25.710 (389)	25.510 (392)	25.510 (392)	cm^{-1} (nm)
I, Y = $-COCH_3$ Z = benzothiazole	22.120 (452)	22.080 (453)	22.170 (451)	22.080 (453)	22.080 (453)	22.030 (454)	21.880 (457)	–	–	cm^{-1} (nm)
I, Y = $-COC_6H_5$ Z = benzothiazole	21.790 (459)	21.980 (455)	21.980 (455)	21.790 (459)	21.830 (458)	21.690 (461)	21.510 (465)	21.600 (463)	21.550 (464)	cm^{-1} (nm)
I, Y = $-CN$ Z = benzothiazole	22.370 (447)	22.420 (446)	22.470 (445)	22.310 (448)	22.370 (447)	22.270 (449)	–**	–**	–**	cm^{-1} (nm)
I, Y = $-CN$ Z = 5-methylbenzoxazole	24.150 (414)	24.150 (414)	24.210 (413)	24.100 (415)	23.980 (417)	24.040 (416)	23.810 (420)	23.870 (419)	23.750 (421)	cm^{-1} (nm)
I, Y = $-CN$ Z = thiazoline	25.640 (390)	25.640 (390)	25.640 (390)	25.580 (391)	25.580 (391)	25.510 (392)	25.450 (393)	25.380 (394)	25.380 (394)	cm^{-1} (nm)
Dye V	20.490 (488)	19.720 (507)	21.370 (468)	20.660 (484)	20.080 (498)	21.230 (471)	21.460 (466)	–	21.050 (475)	cm^{-1} (nm)

* Z-value unknown. ** Insoluble.

This is a rather unexpected result for compounds that contain a merocyanine system. According to the theories of solvent effects in organic spectra, as developed by Bayliss[13, 15], McRae[15, 16], Ooshika[17], Lippert[18] and Liptay[19], the absence of any influence of dipole-dipole or dipole-polarisation interaction on the absorption maxima of the solvated phosphacyanines I would be explained by assuming that the dipole moments are the same in the ground state and in the excited state. Even though this is not *a priori* impossible, it seems rather difficult to visualize.

Another explanation is therefore suggested. Since the infra-red data point to a strong localization of the positive charge at the P-atom, it seems probable that the reaction field in the dielectric, around the dissolved molecule, is determined by the tripolar charge distribution on the P, O and N atoms rather than, as in a conventional merocyanine, by the static moment of the merocyanine auxochromophoric system. The reaction field will therefore no longer be parallel to the static moment of the auxochromophoric system of the dye-molecule, so that the orientation-interaction of the latter with the surrounding molecules will be lowered, leaving only a rather small dispersion-interaction to induce solvatochromic shifts.

Whatever the real situation may be, it is interesting to observe that the intra-ionic dye V (the "merocyanine" part of I, Y = COC_6H_5, Z = benzothiazole, but without the triphenyl-phosphonium substitution) displays the usual behaviour of merocyanine dyes; here the transition energies are proportional to Kosower's Z-values (Fig. 6, Table III) and not to the refractive index function.

In conclusion, it would seem that the phosphacyanines I are not purely phosphonium-substituted merocyanine dyes. All three chromophoric groups (phosphorane group, carbonyl or nitrile group and azole nucleus) appear to be involved in the absorption of light by these molecules. In this connection it is noteworthy that, in going from one solvent to another, the absorption bands are merely shifted, thereby retaining their general shape.

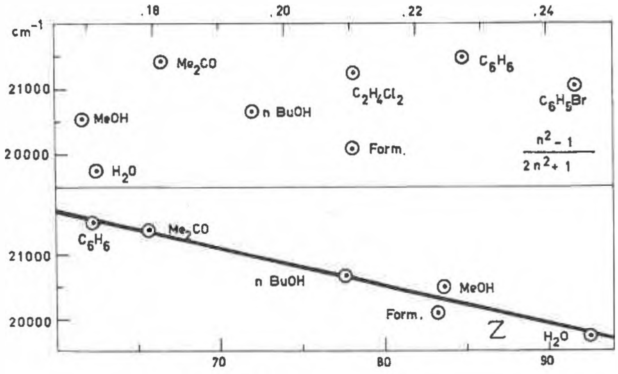

Fig. 6. Solvatochromism of Dye V

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[15] N. S. Bayliss and E. G. McRae, *J. Physic. Chem. 58* (1954) 1002.

[16] E. G. McRae, *J. Physic. Chem. 61* (1957) 562.

[17] Y. Ooshika, *J. Physic. Soc. Japan 9* (1954) 594.

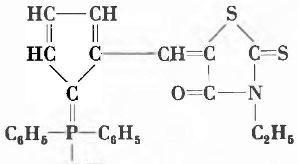
[18] E. Lippert, *Z. Elektrochem. 61* (1957) 962.

[19] W. Liptay, preprint, 2. Internationales Farbensymposium, Elmau, April 1964.

In no case were isosbestic points observed: equilibria between different tautomeric structures (eventually due to steric hindrance such as is observed in the aforementioned holopolar trinuclear cyanine dyes) are therefore excluded. This result once more suggests the existence of a coplanar structure in the auxochromophoric system of the phosphacyanine dyes.

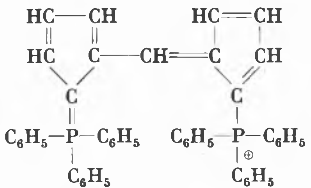
II. Solvatochromism of the merophosphinines

Contrary to the phosphacyanines, merophosphinines such as dye VI show a solvatochromic behaviour that is completely analogous to that of the merocyanine dyes: the absorption maxima of the solvated dye-molecules depend more on the polarity than on the refractive index of the solvent. In Table IV are shown the absorption data, in a variety of solvents, of the merophosphinine VI, derived from cyclopentadienylenetriphenylphosphorane and rhodanine.

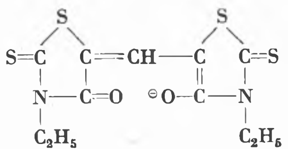


VI

Dye VI may be looked on as the structural cross between the phosphinine VII and the oxonol dye VIII.



VII



VIII

The absorption maxima of these dyes in the same series of solvents are also included in table IV. **Kosower**'s Z-value[14] has been taken as a quantitative measure for the solvent-polarities (or "ionizing power").

It may be seen that there is a trend for the absorption maximum to move towards higher wavelength values as the ionizing power of the solvent increases, i.e., "positive solvatochromism" is observed.

According to **Kosower**[20], a roughly linear relationship may be expected between the energies for π-π^* transitions in solvated molecules of merocyanine dyes, and the Z-value of the solvent that is used. The experimental results given in Table IV, and in Fig. 7 show that this same relation holds for the new merophosphinine VI, the equation being in this case

$$\Delta E = -0.036 Z + 61.70 .$$

The negative sign of the coefficient of Z in this equation is characteristic for positive solvatochromism. Its absolute value may be taken as a measure of the susceptibility,

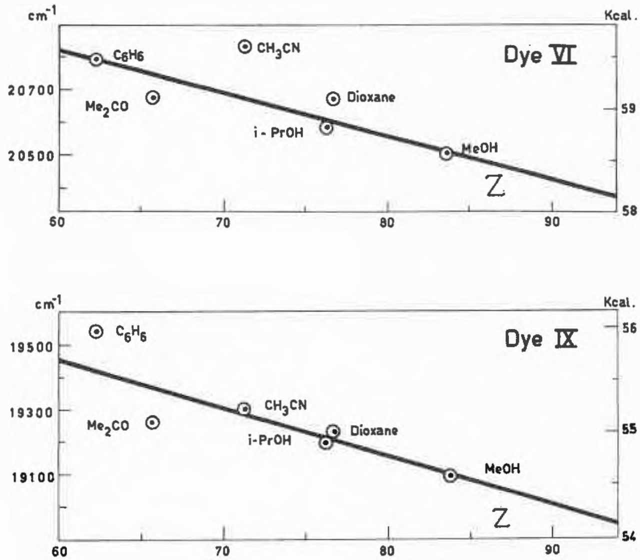


Fig. 7. Solvatochromism of Dye VI and IX

Table IV

Solvent	Z-value	λ_{max} (nm) Dye VI	$\nu_{(cm^{-1})}$ Dye VI	λ_{max} (nm) Dye VII	λ_{max} (nm) Dye VIII	$\lambda_{max}^{calc.}$ for Dye VI	"Deviation" $\lambda_{VI}^{calc.} - \lambda_{VI}^{exp.}$
Benzene	62.3	481	20.790	478	546	512	31
Acetone	65.7	482	20.670	478	546	512	30
Acetonitrile	71.3	480	20.830	477	546	512	32
Isopropanol	76.3	486	20.580	479	547	513	27
Dioxane-10% H_2O	76.7	484	20.670	480	–*	–	–
Methanol	83.6	488	20.500	475	544	510	22

* Solution is unstable.

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[20] E. D. **Kosower**, *J. Amer. Chem. Soc. 80* (1958) 3261.

Table V

Solvent	Z-value	λ_{max} (nm) Dye IX	$\nu_{(\mathrm{cm}^{-1})}$ Dye IX	λ_{max} (nm) Dye VIII	λ_{max} (nm) TMC*	$\lambda_{calc.}$ (nm) Dye IX	"Deviation" (nm) $\lambda_{\mathrm{IX}}^{calc.} - \lambda_{\mathrm{IX}}^{exp.}$
Benzene	62.3	512	19.540	546	583	564	52
Acetone	65.7	519	19.260	546	561	553	34
Acetonitrile	71.3	518	19.300	546	559	552	34
Isopropanol	76.3	521	19.200	547	564	555	34
Dioxane-10% H_2O	76.7	520	19.230	– **	566	–	–
Methanol	83.6	524	19.090	544	558	551	27

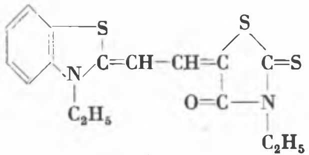
* TMC = 3-ethylbenzothiazole trimethine cyanine. ** Decomposition.

towards the polarity of the solvent, of the energy-difference between ground- and excited state in the dye molecule. In the present case, this value is rather small, which means that, in going over from a weakly polar to a highly polar solvent, only a relatively small gain in stability of the excited state over that of the ground state can be obtained.

For the corresponding benzothiazole dye IX the following relation between ΔE and Z may be calculated (cfr. Fig. 7) from the data of Table V

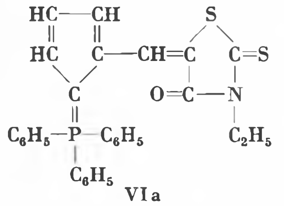
$$\Delta E = -0.05\,Z + 58.70.$$

In both dyes VI and IX, the values of the coefficients for Z do not differ very much. This may be considered as an indication of a certain similarity between the benzothiazole and the cyclopentadienylenetriphenylphosphorane nuclei regarding their influence on the polarization due to solvation, that occurs in the merocyanine, resp. merophosphinine dyes which are derived from them.

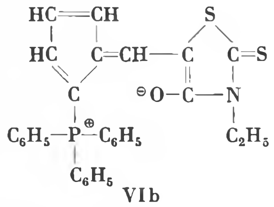


IX

In line with the interpretation of positive solvatochromism in merocyanine dyes proposed by KIPRIANOV and PETRUNKIN[21], DIMROTH[22], BROOKER[23], LONGUET-HIGGINS[24] and others, according to which the main operative factor is a smoothing of the π-electron density along the conjugation chain in the ground state, it is interesting to note (see Table IV) that no "iso-energetic point"[23] is attained over the whole range of the solvents considered, not even in the most highly polar ones. This means that, even in the solvents with the highest ionizing power, the electronic structure is still more akin to configuration VIa than to configuration VIb.



VIa



VIb

The same conclusion may be reached by another consideration. According to the "Mean Rule",[25] the wavelength corresponding to the absorption maximum of the merophosphinine VI in a given solvent should be equal to the arithmetic mean of the λ_{max} of the "parent dyes" VII and VIII in that same solvent, if the potential field of the molecule were symmetrical with respect to a plane cutting the long axis of the molecule in its middle and perpendicular to that axis.

As can be seen from the experimental data of Table IV, however, the deviation reaches appreciable values in the weakly polar solvents, as well as in the most polar solvent. As expected, the deviation gradually decreases when the polarity of the solvents increases, due to "smoothing" of the potential field within the dye molecule by the solvent-dye interaction. Even in 3 : 1 water-methanol mixtures though, the deviation still amounts to more than 5 nm, thus confirming the previous conclusion that the potential field remains asymmetrical to some extent, even in the most polar solvents that were used. This solvatochromic behaviour essentially resembles that of the dimethine merocyanine IX (table V) ob-

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[21] a) A. I. KIPRIANOV and V. E. PETRUNKIN, *J. Gen. Chem.* USSR *10* (1940) 613. b) A. I. KIPRIANOV, *Usp. Khim. 29* (1960) 1336.

[22] a) K. DIMROTH, *Angew. Chem. A 60* (1948) 70, *ibid. 72* (1960) 783. b) K. DIMROTH, *Chimia 15* (1961) 80. c) K. DIMROTH, C. REICHARDT, T. SIEPMANN and F. BOHLMANN, *Ann. Chem. 661* (1963) 1.

[23] a) L. G. S. BROOKER, G. H. KEYES and D. W. HESELTINE, *J. Amer. Chem. Soc. 73* (1951) 5351. b) L. G. S. BROOKER, *Chimia 15* (1961) 87.

[24] H. C. LONGUET-HIGGINS, *Proc. Roy. Soc.* (London) *A 255* (1960) 63.

[25] a) B. BEILENSON, N. I. FISHER and F. M. HAMER, *Proc. Roy. Soc.* (London) *A 163* (1937) 138. b) L. G. S. BROOKER, F. L. WHITE, G. H. KEYES, C. P. SMYTH and P. F. OESPER, *J. Amer. Chem. Soc. 63* (1941) 3192. c) A. I. KIPRIANOV and G. T. PILYUGIN, *Byull. Vsesoyuz. Khim. Obshchestva im D. I. Mendeleeva 1939*, No. 3–4, 60; *Chem. Abstr. 34* (1940) 4663. d) L. G. S. BROOKER, G. H. KEYES and W. W. WILLIAMS, *J. Amer. Chem. Soc. 64* (1942) 199.

tained by combining the same acidic rhodanine nucleus with the benzothiazole nucleus. The deviations are only slightly larger than in the benzothiazole-rhodanine case. This would seem to show that the "π-basicity" of benzothiazole is a little smaller than that of cyclopentadienylene triphenylphosphorane.

According to the theories developed by OOSHIKA[17], MACRAE[15, 16], BAYLISS[13, 15] and LIPTAY[19], on the other hand, orientation interaction between the solute and the solvent plays the most important role in the case of merocyanine dyes. If we accept this theory, the observed solvatochromism only indicates that the merophosphinine VI and the merocyanine IX have a relatively small dipole moment in the ground state and a larger one in the excited state.

Experimental

All absorption spectra in the visible range of the spectrum were measured with a recording Optica CF-4 grating spectrophotometer. Solvents were examined for impurities by gas chromatography. If necessary, they were carefully fractionated and dried over molecular sieves or P_2O_5.

Infra-red spectra were recorded with a Perkin-Elmer 125 spectrophotometer using KBr-discs.

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