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5-[5-R-FURFURYLIDENE]-2,2-DIMETHYL-1,3-DIOXANE-4,6-DIONES

6.* SYNTHESIS, STRUCTURE, AND PROPERTIES OF SUBSTITUTED FURYLIMINO- AND FURFURYLIDENEPHOSPHORANES. MOLECULAR AND CRYSTAL STRUCTURE OF N-[5-(2,2-DIMETHYL-4,6-DIOXO-1,3-DIOXAN-5-YLIDENE)METHYL-2-FURYL]IMINO(TRIPHENYL)PHOSPHORANE

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Furylimino- and furfurylidenephosphoranes have been synthesized by sequential conversions of 5-unsubstituted and 5-methylfurfurylidenedioxanediones. The ylide fragment linked directly with the furfurylidenedioxanedione residue displays strong electron-donating properties, as a result of which resonance occurs in the system of conjugated bonds. The molecular and crystal structure of the iminophosphorane was studied by x-ray structural analysis and the resonance of the bonds in the molecule was confirmed.

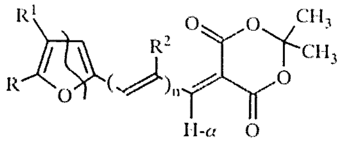
Phosphoranes and iminophosphoranes are used widely in various areas of organic synthesis, consequently an accurate understanding of the reasons for the stability and chemical properties of the reasons for the stability and chemical properties of these compounds is extremely important for the correct interpretation of reaction mechanisms involving tetra-coordinated phosphorus [2]. It was noted in a review [3] that two aspects were of particular interest when studying the structure of phosphoranes. These are the clarification of the nature of the phosphorus–ylide carbon (or nitrogen) bond and the determination of the geometry of the ylide fragment of the molecule.

Information in the literature on phosphorus ylides in which a furan ring is linked directly with the ylide nitrogen or carbon is extremely scarce. Nevertheless, an analysis of the literature data shows that the stability of this series of ylides is determined by the character of the substituent at position 5 of the furan ring. When strong electron acceptors [NO_2, $CH{=}CH(CN)_2$] are present the phosphoranes are fairly stable [4]. In other cases labile ylides are formed which are even difficult to isolate from solution [5].

Methods are described in the present work for obtaining stable phosphoranes and iminophosphoranes, which in principle may be used in various complex-forming reactions and as synthons for introducing furfurylidene or furylimino fragments.

The sequence of conversions of furfurylidenedioxanediones and their vinylogs (I)-(VII) is shown in Scheme 1.

Scheme 1



I–VII

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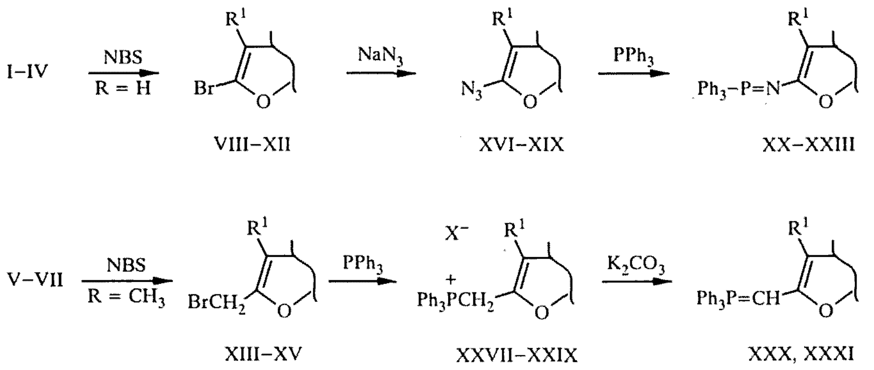


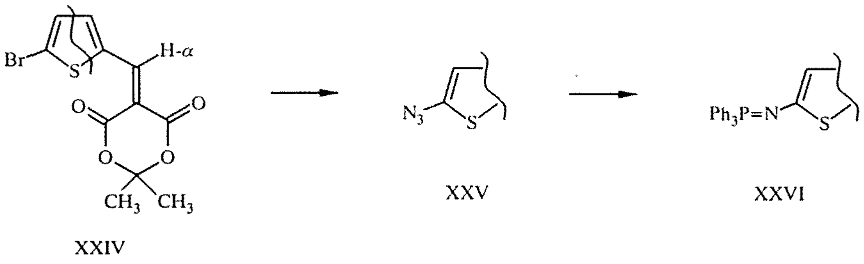
I—IV, VIII—XI, XIII, XV, XVI, XVIII—XX, XXIII, XXX, XXXI $R = R^1 = H$; V, VII, XXII, XXVII—XXIX $R^1 = H$; V—VII $R = CH_3$; VI, XIV $R^1 = CH_3$; XII, XVII, XXVI $R^1 = Br$; II, III, VII, IX, X, XII, XV, XVIII, XXXI $R^2 = H$; IV, IX, XIX, XXIII $R^2 = CH_3$; XXVII, XXIX $X = Br$; XXVIII $X = ClO_4$; I, V, VI, VIII, XII—XIV, XVI, XVII, XX, XXVI—XXVIII, XXX $n = 0$; II, IV, VII, IX, XI, XV, XVIII, XIX, XXII, XXIII, XXIX, XXI $n = 1$; III, X $n = 2$

The 5-bromofuran (VIII)-(XII) and 5-bromomethylfuran derivatives (XIII)-(XV) were obtained in fairly high yield (Table 1) by brominating the starting compounds (I)-(VII) with N-bromosuccinimide. This was effected under classical conditions by boiling in carbon tetrachloride in the presence of various initiators (azodiisobutyronitrile, benzoyl peroxide) or on irradiation with an incandescent lamp. It was established that the presence of a methyl group at position 4 of the furan ring or in the exocyclic system of conjugated multiple bonds did not change the direction of the bromination reaction. It occurred strictly selectively at position 5 of the furan ring. Best results were obtained at molar ratios of substrate:NBS:azodiisobutyronitrile of 1.0:1.1:0.001. Irradiation with an ordinary incandescent lamp reduces the reaction time by about half and almost completely prevents resinification of the reaction mixture. As a result the isolation process is improved and the yield of the desired product is increased to 75-87%.

The reaction of the 5-bromofuran derivatives (VIII), (IX), (XI), and (XII) with sodium azide in acetone at room temperature leads to the formation of the corresponding azides (XVI)-(XIX) (Table 1 and [1]). These are crystalline compounds of various shades of yellow, unstable on storage, and having a characteristic absorption band at 2140-2150 cm^{-1} in the IR spectra.

Reaction of equimolar quantities of the azides (XVI)-(XIX) with triphenylphosphine in dry benzene at room temperature is accompanied by elimination of nitrogen and leads to the formation of the iminophosphoranes (XX)-(XXIII), which are extremely stable deeply colored (from violet to blue) crystalline compounds with a characteristic metallic luster.

The iminophosphorane (XXVI) (Table 1) was obtained in a similar manner from 5-bromothienylmethylidenedioxanedione (XXIV) via the corresponding derivative (XXV).



The 5-bromomethyl derivatives (XIII) and (XV) readily form salts on reaction with equimolar quantities of triphenylphosphine in benzene solution. The phosphonium bromide (XXVII) obtained in this way is extremely unstable and is sensitive to the moisture of the air. Treatment of an alcohol solution of the salt (XXVII) with a small excess of 70% perchloric acid leads to the preparation of the corresponding perchlorate (XXVIII), which is stable even in aqueous solution. The phosphonium bromide (XXIX), a vinylog of compound (XXVII), is less sensitive to moisture and is more stable on storage (Table 1).

The phosphoranes (XXX) and (XXXI) are formed on reacting the salts (XXVII)-(XXIX) with a small excess of potassium (or sodium) hydrogen carbonate in aqueous solution. These are crystalline, deeply colored (red or blue) substances

TABLE 1. Physicochemical Characteristics of Compounds (II)-(IV), (VI), (VII), (IX)-(XI), (XIII)-(XV), and (XVII)-(XXXI)

Compound	Empirical formula	Mp, °C	UV spectrum (ethanol), λ_{max}, nm (log ε)	IR spectrum, ν, cm^{-1}	Yield, %
II	$C_{13}H_{12}O_5$	153...154	212 (3,98); 238 (3,91); 408 (4,60)	1716, 1750	87
III	$C_{15}H_{14}O_5$	134...136	228 (4,05); 280 (3,84); 440 (4,74)	1730, 1760	83
IV	$C_{14}H_{14}O_5$	124...125	263 (3,89); 308 (3,59); 402 (4,51)	1720, 1750	84
VI	$C_{13}H_{14}O_5$	123...125	232 (3,70); 415 (4,50)	1710, 1725	84
VII	$C_{14}H_{14}O_5$	154...155	218 (4,04); 238 (3,97); 431 (4,52)	1720, 1750	75
IX	$C_{13}H_{11}BrO_5$	157...160	249 (3,89); 417 (4,48)	1703, 1753	86
X	$C_{15}H_{13}BrO_5$	189...190	404 (4,30); 471 (4,50)	1712, 1752	80
XI	$C_{14}H_{13}BrO_5$	140...142	263 (4,13); 414 (4,13)	1700, 1740	83
XIII	$C_{12}H_{11}BrO_5$	134...135	212 (3,71); 250 (3,62); 374 (4,37)	1730, 1760	87
XIV	$C_{13}H_{13}BrO_5$	135...136	378 (4,04)	1700, 1720	86
XV	$C_{14}H_{13}BrO_5$	167...168	417 (4,51)	1694, 1725	81
XVII	$C_{11}H_8BrN_3O_5$	106	260 (4,13); 427 (4,15)	1720, 1750	79
XVIII	$C_{13}H_{11}N_3O_5$	130 (decomp.)	282 (4,24); 416 (4,36)	1715, 1735	76
XIX	$C_{14}H_{13}N_3O_5$	125 (decomp.)	286 (4,29); 408 (4,40)	1710, 1740	78
XX	$C_{29}H_{24}NO_5P$	190 (decomp.)	229 (4,08); 270 (3,63); 460sh (4,65); 486 (4,95)	1680, 1720	88
XXI	$C_{29}H_{23}BrNO_5P$	175 (decomp.)	228 (4,43); 267 (3,97); 468sh (4,57); 493 (4,93)	1650, 1696	89
XXII	$C_{31}H_{26}NO_5P$	230 (decomp.)	275 (4,04); 292 (4,32); 568sh (4,32); 610 (4,52)	1700, 1730	87
XXIII	$C_{32}H_{28}NO_5P$	200 (decomp.)	551sh (4,15); 598 (4,31)	1710, 1730	85
XXIV	$C_{11}H_8BrO_4S$	130...131	207 (4,32); 259 (4,10); 376 (4,66)	1720, 1755	92
XXV	$C_{11}H_9N_3O_4S$	100...101	214 (4,05); 255 (3,93); 291 (3,55); 419 (4,49)	1700, 1740	78
XXVI	$C_{29}H_{24}NO_4SP$	230 (decomp.)	207 (4,78); 267 (4,47); 481 (5,01)	1680, 1700	84
XXVII*	$C_{30}H_{26}BrO_5P$	215...216	371 (4,40)	1706, 1756	91
XXVIII*	$C_{30}H_{26}ClO_9P$	214...215	369 (4,52)	1713, 1756	83
XXIX*	$C_{32}H_{28}BrO_5P$	185 (decomp.)	414 (4,52)	1690, 1715	83
XXX**	$C_{30}H_{25}O_5P$	200 (decomp.)	512sh (4,46); 543 (4,88)	1653, 1703	86
XXXI	$C_{32}H_{27}O_5P$	182 (decomp.)	416 (4,40); 565 (4,35)	1635, 1710	85

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*The UV spectrum was drawn in acetic acid.

**The UV spectrum was drawn in heptane.

(Table 1). The phosphoranes (XXX) and (XXXI), like the iminophosphoranes (XX)-(XXIII) described above, are far less reactive and do not enter into any reactions characteristic of this class of compound (Wittig type reactions).

The structures of the compounds synthesized were confirmed by data of their IR, UV (Table 1), and PMR spectra (Table 2). There were two bands in the IR spectra for the stretching vibrations of the carbonyl groups of the dioxanedione ring. The high frequency band corresponds to the asymmetric and the low frequency to the symmetric vibration, the latter has approximately twice the intensity of the former.

On the basis of a comparative analysis of the PMR spectra of the furan and thiophene derivatives of Meldrum acid it was shown in previous communications [6-8] that the furfurylidene derivatives have the s-cis conformation while the thienylmethylidene derivative has the s-trans form for the mutual disposition of the five-membered heterocycle and the exocyclic multiple bond. The conclusions drawn previously were confirmed in the present case, primarily by the presence of long-range coupling between the α-H and the 4-H proton of the furan ring, confirming the W-shaped disposition of the bonds between these nuclei, and secondly by the strong paramagnetic displacement of the furan 3-H proton signal and its absence in the case of the thiophene derivatives (Table 2).

TABLE 2. PMR Spectra (in acetone-D_6) of Compounds (II)-(IV), (VI), (VII), (IX)-(XV), (XX), (XXI), and (XXX)

Compound	$C(CH_3)_2$	α-H	3-H	4-H	$J_{3,4}$	Other signals and coupling constants
II*	1,76	7,16	6,87	6,57	3,5	8,15 (1H, Hβ, $J\alpha\beta$ = 11,0); 9,06 (1H, Hγ, $J\alpha\gamma$ = 11,0, $J\beta\gamma$ = 12,5); 7,63 (1H, 5-H, $J_{4\text{-}5}$ = 2,0)
III	1,75	8,07	6,62	6,52	3,5	7,53 (1H, 5-H, $J_{4\text{-}5}$ = 2,0); 7,83 (1H, Hβ, $J\alpha\beta$ = 12,0); 7,18 (1H, Hγ, $J\beta\gamma$ = 13,8); 6,99 (1H, Hδ, $J\delta\varepsilon$ = 14,8; $J\gamma\delta$ = 11,0); 6,82 (1H, Hε)
IV	1,80	8,02	6,89	6,59	3,65	2,32 (3H, CH_3); 7,12 (1H, Hγ, $J\gamma_{\text{-}4}$ = 0,6); 7,66 (1H, 5-H, $J_{4\text{-}5}$ = 2,0)
VI	1,63	7,95	8,18			2,00 (3H, 4-CH_3); 2,32 (3H, 5-CH_3)
VII	1,63	7,31	6,88	6,25	3,5	2,35 (3H, CH_3); J_4-γ = 0,8; 7,80 (1H, Hβ, $J\alpha\beta$ = 9,0); 8,07 (1H, Hγ, $J\beta\gamma$ = 11,6; $J\alpha\gamma$ = 5,8)
IX*	1,67	7.98	6,83	6,50	3,8	8,13 (1H, Hβ, $J\alpha\beta$ = 11,6; $J\alpha\gamma$ = =-3,7); 7,13 (1H, Hγ, $J\beta\gamma$ = 7,7)
X**	1,35	7,83	5,98	6,08	3,5	5,93...6,53 (4H, Hβ, Hγ, Hδ, Hε); $J\alpha\beta$ = 12,0
XI	1,67	7,93	6,67	6,93	4,0	2,17 (3H, CH_3); 7,15 (1H, Hγ)
XII	1,68	7,97	8,28			$J\alpha_{\text{-}3}$ = 0,4
XIII*	1,65	8,15	8,29	6,61	4,0	4,40 (2H, CH_2Br)
XIV	1,68	7,98	8,13			2,10 (3H, 4-CH_3); 4,67 (2H, CH_2Br)
XV	1,67	8,13	6,96	6,53	3,5	7,98 (1H, Hβ, $J\alpha\beta$ = 11,6; $J\alpha\gamma$ = = -7,8); 7,36 (1H, Hγ, $J\beta\gamma$ = 7,2); 4,63 (2H, CH_2Br)
XX*	1,68		8,98	5,97		7,60...7,80 (16H, 3×C_6H_5, Hα)
XXI	1,52	7,22	8,88			7,60...7,80 (15H, 3×C_6H_5)
XXX*	1,68	7,05	8,76	6,25		4,09 (1H, CH)

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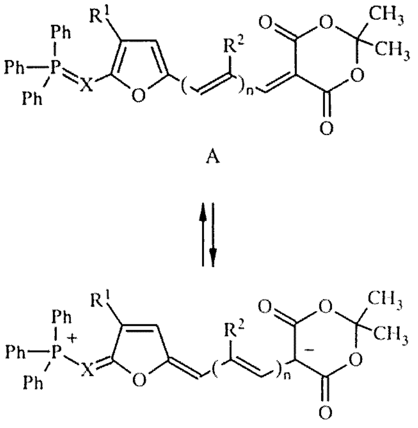
*In $CDCl_3$.

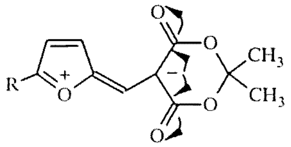
**In CF_3COOD.

Analysis of the shape of the long-wave absorption in the electronic spectra of the furan and thiophene derivatives carried out in [1, 8] enabled all the compounds synthesized to be subdivided into two groups. Substances with smooth, symmetrical, and broad ($\Delta\nu_{1/2}$ ~4000 cm^{-1}) bands, possessing positive solvatochromia, belong to the first group. Substances with narrow ($\Delta\nu_{1/2}$ ~ 1600 cm^{-1}), asymmetric (often having an inflexion on one side) bands, with a negative solvatochromia, belong to the second. The phosphoranes and iminophosphoranes (XX)-(XXIII), (XXVI), (XXX), and (XXXI) are typical representatives of the second group in this spectral characteristic. They have narrow asymmetric long-wave absorption bands, displaced bathochromically by 70-140 nm compared with the absorption of the corresponding phosphonium salts and azides, which have broad symmetrical bands. The introduction of a vinyl link between the furan and dioxanedione fragments in the phosphorane and iminophosphorane molecules leads to a bathochromic shift of the long-wave absorption of 120-140 nm. The same shift in the corresponding bromo derivatives, salts, and azides is approximately 40 nm. The phosphorane (XXX) and the iminophosphorane (XX) possess marked negative solvatochromia. The maximum of the long-wave absorption of phosphorane (XXX) is shifted from 543 to 526 nm on changing from heptane to acetonitrile. An even more clearly defined displacement of the long-wave absorption maximum was observed for the phosphorane (XXXI), viz. in cyclohexane 656, acetone 635, and ethanol 565 nm. All this indicates the significant contribution of the resonance structure B containing charge separation to the ground state of these molecules.



A

B



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On the other hand the resonance structure A, with no charge separation, makes a significant contribution to the ground state of the bromo derivatives, salts, and azides, typical representatives of compounds of the first group. The presence of a normal alternation of multiple bonds in the conjugation system of a representative of this group of compounds, viz. 5-(5-methylfurfurylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione, was proved by x-ray structural analysis in [6].

An X-ray structural investigation of the iminophosphorane (XX) was carried out to confirm the possible resonance of multiple bonds in molecules of compounds of the second group. The atomic coordinates, interatomic distances, and sizes of valence angles are given in Tables 3-5.

The iminophosphorane molecule (XX) (see Fig. 1) has the s-cis conformation with an intramolecular hydrogen bond at $H_{(9)}...O_{(3)}$. The parameters of the hydrogen bond are: distances $H_{(9)}...O_{(3)}$ and $C_{(9)}...O_{(3)}$ equal to 2.199 and 2.865 Å respectively, angles $C_{(9)}-H_{(9)}...O_{(3)}$ and $H_{(9)}...O_{(3)}-C_{(6)}$ equal to 127.1 and 123.0° respectively. The internal stresses in the exocyclic double bond are mainly displayed in the increase of the valence angle $C_{(5)}-C_{(7)}-C_{(8)}$ to 134.3°.

The furfurylidene fragment of the molecule together with the nitrogen and phosphorus atoms is practically planar and is turned (as a result of the intramolecular $H_{(9)}...O_{(3)}$ contact) about the $C_{(7)}-C_{(8)}$ bond so that the angle between the planes of the furan ring and the "side of the bath" $C_{(4)}-C_{(5)}-C_{(6)}$ is 10.8°. In its turn the "side of the bath" $C_{(4)}-C_{(5)}-C_{(6)}$ is inclined at only 4.5° to the base of the bath.

Nevertheless none of this disturbs the efficiency of the conjugation in the molecule. Transfer of the unshared electron pair from the nitrogen atom in the direction of the oxygen atoms of the carbonyl groups leads to a strong distortion of the interatomic distances in the conjugated system. Thus the formally single $C_{(7)}-C_{(8)}$, $C_{(9)}-C_{(10)}$, and $C_{(11)}-N$ bonds are shorter than the formally double $C_{(5)}-C_{(7)}$, $C_{(8)}-C_{(9)}$, and $C_{(10)}-C_{(11)}$ bonds, i.e., in this case there is a real system of resonating bonds.

The unshared electron pair of the furan ring oxygen atom is included in the conjugation and is heavily displaced in the direction of the $C_{(11)}$ atom to such an extent that the $O_{(5)}-C_{(11)}$ bond becomes a multiple bond in the furan ring. This indicates the significant contribution of structure (C) having a positive charge on the furan oxygen to the overall resonance of the molecule.

The P–N bond is significantly shorter than a standard single P–N bond (1.77 Å [9]) and only insignificantly longer than a standard double bond (1.57 Å [10]). The phosphorus atom is in the sp^3 hybridized state since the mean value of its valence angle is 109.4°. The doubly coordinated nitrogen atom is in fact linked by double bonds with the phosphorus atom and with the $C_{(11)}$ carbon atom. The length of the $N-C_{(11)}$ bond is practically equal to the length of a C=N bond in a conjugated system (1.31 Å [11]) but nevertheless the nitrogen atom has the sp^2 (but not sp.) hybrid state. This is indicated by the size of the $C_{(11)}-N-P$ valence angle (130.9°). The increase in the valence angle at the nitrogen atom is evidently linked with the mutual repulsion of the furan and benzene rings, which in turn leads to an increase in the $N-P-C_{(12)}$ valence angle to 117.1°.

The valence angle at the nitrogen atom and the P–N and $N-C_{(11)}$ interatomic distances indicate an overlap of the $2p_z$ atomic orbital (AO) of the unshared electron pair of the nitrogen atom with the $2p_z$ AO of the $C_{(11)}$ atom released as a result

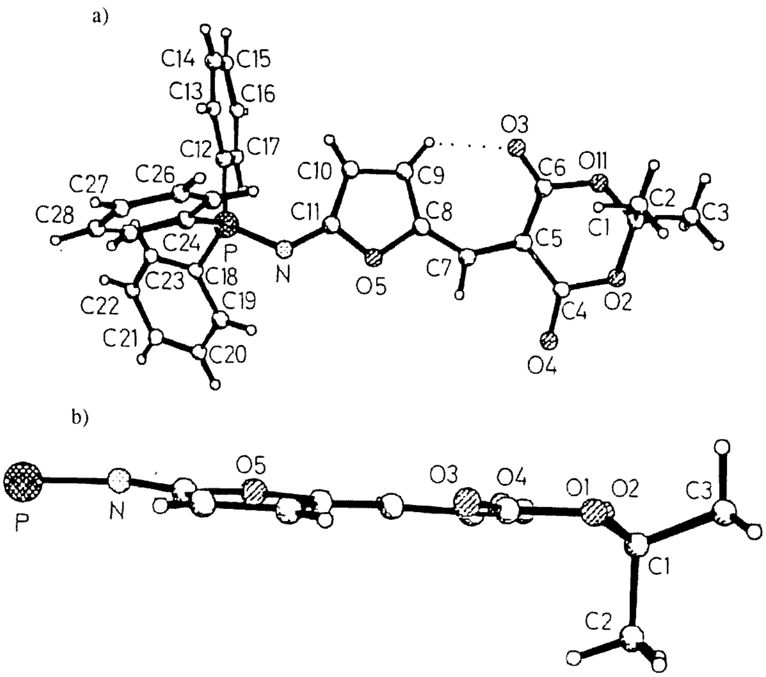

Fig. 1. Projection of spatial models of compound (XX) on the plane of (a) the base of the bath and (b) the plane of symmetry of the dioxane ring.

of the strong acceptor action of the substituent in position 2 of the furan ring. Evidently the $O_{(5)}-C_{(11)}$ interatomic distance is sharply reduced as a result of a similar displacement of the unshared pair of electrons of the oxygen atom towards the $C_{(11)}$ atom.

It may be assumed that the second unshared pair of the nitrogen atom in a $2sp^2$ atomic orbital lying in the $P-N-C_{(11)}$ plane is capable of reacting with the vacant $3d_{x^2-y^2}$ atomic orbital of phosphorus forming a coordinated π-bond orientated in this plane.

Comparison of the data on the structure of compound (XX) and of 2,2-dimethyl-5-(5-methylfurfurylidene)-1,3-dioxane-4,6-dione [6] confirms the reality of the change in alternation of the bonds in the conjugated system on changing the character of the substituent in position 5 of the furan ring. In the presence of a strong electron donor in position 5 of the furan ring resonance (dynamic alternation) is accompanied by a change in many of the spectral properties of the compounds. The simplest criteria of the difference of the two systems of conjugation are the shape and solvatochromic behavior of the long-wave absorption band in the electronic spectra, and the character of the shift of this band on increasing or reducing the conjugated chain length. The size of the coupling constant between the furan ring β-protons (an increase of coupling constant from 3-4 to 5-5.5 Hz) may serve as the criterion of resonance in the furan compounds.

In conclusion we noted that the phosphorane and iminophosphorane fragments in position 5 of the furan ring in furfurylidenedioxanediones are exceptionally strong electron-donating substituents, as a result of which these compounds are similar to the merocyanine dyes in depth and purity of color. It is remarkable that these properties are displayed most clearly by the thienylidene derivative (XXVI) which possesses a high absorption intensity, a very narrow (less than 1500 cm^{-1}) long-wave absorption band, and high photostability.

EXPERIMENTAL

The electronic spectra were described on a Specord M 40 spectrophotometer, the IR spectra on Specord IR 75 and M 80 spectrometers in Nujol mulls, and the PMR spectra on Tesla BS 467A (60 MHz) and Bruker WM 250 (250 MHz) spectrometers, the internal standard being TMS. A check on the progress of reactions and the purity of products was effected by TLC on Silufol UV 254 plates in the system toluene–ethanol, 20:3.

The composition of the compounds obtained was confirmed by data of elemental analysis for C, H, and N.

TABLE 3. Atomic Coordinates in the (XX) Molecule, Å ($\times 10^4$ for P, O, N, and C atoms; $\times 10^3$ for H atoms)

Atom	x	y	z	Atom	x	y	z
P	3090(0)	3355(0)	581(1)	$C_{(24)}$	3580(1)	2832(1)	1236(3)
$O_{(1)}$	782(1)	5535(1)	8659(2)	$C_{(25)}$	3460(2)	2549(2)	2728(3)
$O_{(2)}$	1984(1)	6573(1)	9268(2)	$C_{(26)}$	3816(2)	1982(2)	3263(3)
$O_{(3)}$	682(1)	4684(1)	6732(2)	$C_{(27)}$	4302(2)	1713(2)	2326(4)
$O_{(4)}$	3091(1)	6763(1)	7990(2)	$C_{(28)}$	4435(2)	2002(2)	869(3)
$O_{(5)}$	2844(1)	4874(1)	3940(2)	$C_{(29)}$	4074(1)	2551(1)	309(3)
N	3125(1)	4216(1)	1883(2)	$H_{(21)}$	181(2)	567(2)	1171(3)
$C_{(1)}$	1270(1)	5978(1)	9871(3)	$H_{(22)}$	178(1)	505(2)	1038(3)
$C_{(2)}$	1477(2)	5379(2)	10924(3)	$H_{(23)}$	100(2)	500(2)	1136(3)
$C_{(3)}$	803(2)	6472(2)	10626(3)	$H_{(31)}$	113(2)	683(2)	1143(3)
$C_{(4)}$	2403(1)	6330(1)	8181(3)	$H_{(32)}$	33(2)	611(2)	1102(3)
$C_{(5)}$	1971(1)	5609(1)	7284(2)	$H_{(33)}$	69(2)	685(2)	986(3)
$C_{(6)}$	1128(1)	5227(1)	7503(3)	$H_{(7)}$	293(1)	574(1)	622(2)
$C_{(7)}$	2399(1)	5410(1)	6087(3)	$H_{(9)}$	111(1)	395(1)	506(3)
$C_{(8)}$	2217(1)	4818(1)	4964(3)	$H_{(10)}$	152(1)	330(1)	277(3)
$C_{(9)}$	1592(2)	4122(2)	5425(3)	$H_{(13)}$	203(1)	186(1)	100(2)
$C_{(10)}$	1820(2)	3767(2)	3288(3)	$H_{(14)}$	77(2)	117(2)	20(3)
$C_{(11)}$	2600(1)	4239(1)	2934(2)	$H_{(15)}$	7(2)	182(1)	-146(3)
$C_{(12)}$	2118(1)	2958(1)	-109(3)	$H_{(16)}$	68(2)	316(1)	-226(3)
$C_{(13)}$	1747(2)	2139(1)	351(3)	$H_{(17)}$	196(1)	389(1)	-142(3)
$C_{(14)}$	977(2)	1715(2)	-132(3)	$H_{(19)}$	407(1)	522(1)	17(3)
$C_{(15)}$	590(2)	2092(2)	-1087(3)	$H_{(20)}$	468(2)	603(1)	-198(3)
$C_{(16)}$	950(2)	2901(2)	-1568(3)	$H_{(21)}$	462(1)	539(1)	-435(3)
$C_{(17)}$	1706(2)	3329(2)	-1079(3)	$H_{(22)}$	390(1)	401(1)	-460(3)
$C_{(18)}$	3614(1)	4140(1)	-1016(3)	$H_{(23)}$	330(1)	322(1)	-256(2)
$C_{(19)}$	4032(1)	4983(1)	-836(3)	$H_{(25)}$	312(1)	276(1)	335(3)
$C_{(20)}$	4399(2)	5442(2)	-2085(4)	$H_{(26)}$	372(1)	178(2)	428(3)
$C_{(21)}$	4363(2)	5075(2)	-3479(3)	$H_{(27)}$	454(2)	131(2)	271(3)
$C_{(22)}$	3952(2)	4247(2)	-3666(3)	$H_{(28)}$	480(1)	183(1)	25(3)
$C_{(23)}$	3574(1)	3777(1)	-2445(3)	$H_{(29)}$	418(1)	274(1)	-68(2)
$C_{(24)}$	3580(1)	2832(1)	1236(3)				

TABLE 4. Bond Lengths in the (XX) Molecule*

Bond	d, Å	Bond	d, Å
P—N	1,588(2)	$C_{(5)}$—$C_{(6)}$	1,434(3)
P—$C_{(12)}$	1,798(2)	$C_{(5)}$—$C_{(7)}$	1,397(3)
P—$C_{(18)}$	1,795(2)	$C_{(7)}$—$C_{(8)}$	1,371(3)
P—$C_{(24)}$	1,802(3)	$C_{(8)}$—$C_{(9)}$	1,888(3)
$O_{(1)}$—$C_{(1)}$	1,424(3)	$C_{(9)}$—$C_{(10)}$	1,363(4)
$O_{(1)}$—$C_{(6)}$	1,370(3)	$C_{(10)}$—$C_{(11)}$	1,391(3)
$O_{(2)}$—$C_{(1)}$	1,432(2)	$C_{(11)}$—N	1,317(3)
$O_{(2)}$—$C_{(4)}$	1,368(3)	$O_{(5)}$—$C_{(8)}$	1,407(3)
$O_{(3)}$—$C_{(6)}$	1,211(3)	$O_{(5)}$—$C_{(11)}$	1,352(2)
$O_{(4)}$—$C_{(4)}$	1,216(3)	$C_{(7)}$—$H_{(7)}$	0,93(2)
$C_{(1)}$—$C_{(2)}$	1,501(4)	$C_{(9)}$—$H_{(9)}$	0,92(2)
$C_{(1)}$—$C_{(3)}$	1,502(3)	$O_{(3)}$...$H_{(9)}$	2,199(3)
$C_{(4)}$—$C_{(5)}$	1,450(3)	$O_{(3)}$...$C_{(9)}$	2,865(3)

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*Interatomic distances are not given for the benzene ring.

Clear red crystals of compound (XX) of composition $C_{29}H_{24}NO_5P$ were monoclinic with unit cell parameters a = 17.650(3), b = 16.939(3), c = 8.799(1) Å; γ = 108.49(1)°, V = 2489.2(8) Å^3. The space group was P $2_{1/b}$, Z = 4. The experimental data were obtained on a Syntex PT automatic diffractometer (MoKα radiation, β filter, $\theta/2\theta$ scanning to $2\theta_{max}$ =

TABLE 5. Valence Angles in the (XX) Molecule

Valence angle	ω, deg	Valence angle	ω, deg
$NPC_{(12)}$	117,1(1)	$O_{(4)}C_{(4)}C_{(5)}$	126,3(2)
$NPC_{(18)}$	106,0(1)	$C_{(6)}C_{(5)}C_{(7)}$	123,8(2)
$NPC_{(24)}$	109,3(1)	$C_{(5)}C_{(7)}C_{(8)}$	134,3(2)
$C_{(12)}PC_{(24)}$	107,6(1)	$C_{(7)}C_{(8)}C_{(9)}$	139,4(2)
$C_{(12)}PC_{(18)}$	106,3(1)	$C_{(8)}C_{(9)}C_{(10)}$	109,2(2)
$C_{(18)}PC_{(24)}$	110,5(1)	$C_{(9)}C_{(10)}C_{(11)}$	107,6(2)
$PNC_{(11)}$	130,9(1)	$C_{(9)}C_{(8)}O_{(5)}$	106,1(2)
$C_{(2)}C_{(1)}C_{(3)}$	113,5(2)	$C_{(8)}O_{(5)}C_{(11)}$	108,5(1)
$O_{(1)}C_{(1)}O_{(2)}$	111,0(2)	$O_{(5)}C_{(11)}C_{(10)}$	108,6(1)
$C_{(1)}C_{(2)}C_{(4)}$	118,6(2)	$C_{(10)}C_{(11)}N$	135,8(2)
$C_{(1)}O_{(1)}C_{(6)}$	119,1(2)	$C_{(8)}C_{(9)}H_{(9)}$	122(1)
$O_{(1)}C_{(6)}C_{(5)}$	116,8(2)	$C_{(9)}H_{(9)}O_{(3)}$	127,1(5)
$C_{(5)}C_{(6)}O_{(3)}$	126,8(2)	$C_{(11)}C_{(10)}H_{(10)}$	125(2)
$C_{(4)}C_{(5)}C_{(6)}$	120,0(2)		

48°) using 2539 reflections with $I > 3\sigma(1)$. The structure was solved by the direct method with the SHELXTL set of programs [12] and refined by an anisotropic approach (isotropic for H atoms) to divergence factors $R = 0.032$ and $R_w = 0.036$.* The dimensions of the crystal investigated were 0.22 × 0.28 × 0.35 mm.

5-(5-Bromofurfurylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (VIII). N-Bromosuccinimide (2.14 g, 11 mmole) and benzoyl peroxide (0.18 g, 1 mmole) were added to a solution of 5-(2-furfurylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (I) in carbon tetrachloride (20 ml). The reaction mixture was boiled for 2 h, cooled to room temperature, the succinimide filtered off, and the solution cooled to −5°C. The precipitated crystals were filtered off and purified by recrystallization from ethanol.

Compounds (IX)-(XV) and (XXIV) were obtained analogously.

Compounds (XVI)-(XIX) and (XXV) were obtained according to [1].

N-[5-(2,2-Dimethyl-4,6-dioxo-1,3-dioxan-5-ylidene)methyl-2-furyl]imino(triphenyl)phosphorane (XX). A solution of triphenylphosphine (10 mmole) in benzene (50 ml) was added to a solution of the azide (XVI) in benzene (50 ml). The reaction mixture was stirred for 2 h (until evolution of nitrogen had ceased), the solvent evaporated to a volume of 20-30 ml, the precipitated crystals were filtered off, washed with benzene, and air dried.

The iminophosphoranes (XXI)-(XXIII) and (XXVI) were obtained analogously.

2,2-Dimethyl-5-(5-triphenylphosphoniomethyl-2-furfurylidene)-1,3-dioxane-4,6-dione Bromide (XXVII). A solution of triphenylphosphine (2.62 g, 10 mmole) in dry benzene (20 ml) was added to a solution of the bromide (XIII) (3.15 g, 10 mmole) in dry benzene (30 ml). The reaction mixture was left for 2 h. The precipitated crystals were filtered off and dried under vacuum.

The salt (XXIX) was obtained analogously.

2,2-Dimethyl-5-(5-triphenylphosphoniomethyl-2-furfurylidene)-1,3-dioxane-4,6-dione Perchlorate (XXVIII). A solution of salt (XXVII) (5.77 g, 10 mmole) in ethanol (50 ml) was treated with 70% $HClO_4$ (3 ml, 30 mmole) with stirring. The precipitated solid was filtered off, washed with dry ether, and dried in the air.

5-(2,2-Dimethyl-4,6-dioxo-1,3-dioxan-5-ylidene)methyl-furfurylidenetriphenylphosphorane (XXX). A solution of $KHCO_3$ (0.6 g, 6.1 mmole) in water (100 ml) was added to a solution of the phosphonium salt (XXVIII) (3.2 g, 5.5 mmole) in alcohol (100 ml). The reaction mixture was stirred for 2 h, the precipitated red solid was filtered off, and recrystallized from alcohol.

The phosphonium ylide (XXXI) was prepared analogously.

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*Values of the anisotropic temperature factors for nonhydrogen atoms may be obtained from the authors.

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