Phosphorylation of 3-hydroxy- and 5,7-dihydroxyflavones with hexaethylphosphorous triamide

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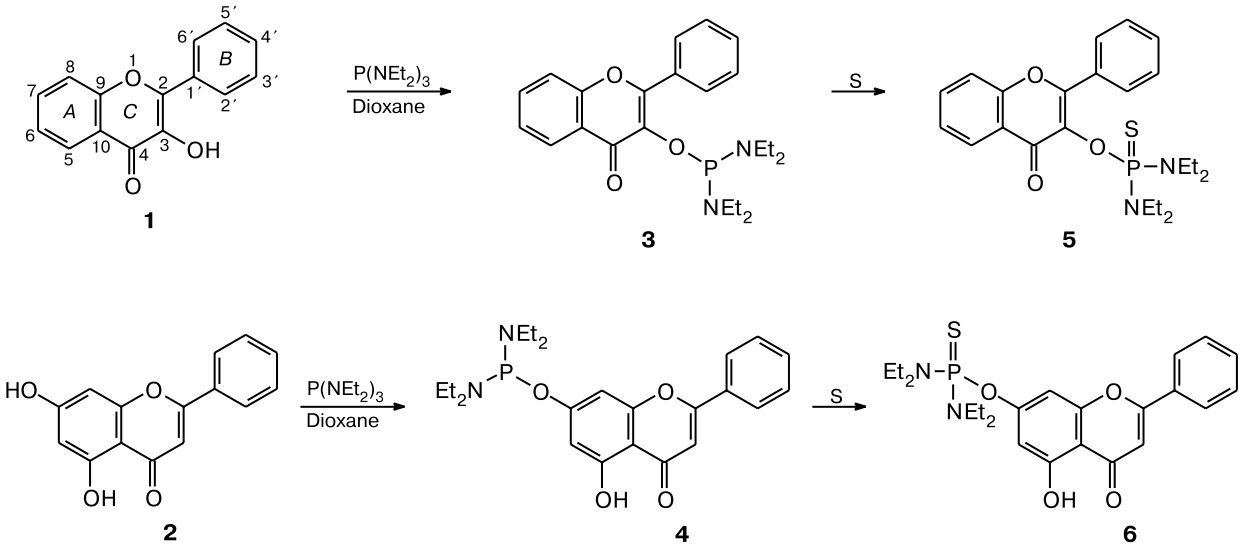
The reactions of 3-hydroxy- and 5,7-dihydroxyflavones with hexaethylphosphorous triamide proceed according to a classical scheme, but the reaction of 5,7-dihydroxyflavone occurs regioselectively. Dismutation of phosphites, which has been studied earlier only for the simplest aryl systems, is extended to flavonoids.

Key words: flavonoids, 3-hydroxyflavone, 5,7-dihydroxyflavone, phosphorylation, dismutation.

Recently,[1,2] our laboratory has begun to study phosphorylation of known flavonoids, *viz.*, quercetine and dihydroquercetine, with trivalent phosphorus compounds. This field of investigation is of interest, on the one hand, from the viewpoint of the characteristic features of the chemistry of these compounds, which are determined by their multifunctionality, and, on the other hand, in the design of new biologically active compounds based on accessible natural products.

In continuation of our studies, we examined phosphorylation of new flavonoids, *viz.*, 3-hydroxy- (**1**) and 5,7-dihydroxyflavones (**2**). The reactions of compounds **1** and **2** with an equimolar amount of hexaethylphosphorous triamide (HEPTA) at room temperature afforded the corresponding diamidophosphites **3** and **4**. The reaction was monitored by TLC and ^{31}P NMR spectroscopy (δ_P 142.8 and 131.5 for compounds **3** and **4**, respectively). The yields of the reaction products, which were calculated from the integral intensities of the corresponding signals in the ^{31}P NMR spectra, were ~95%. Diamidophosphites **3** and **4** were used without additional purification in the reaction with elemental sulfur at 60 °C to prepare thiono-

Scheme 1



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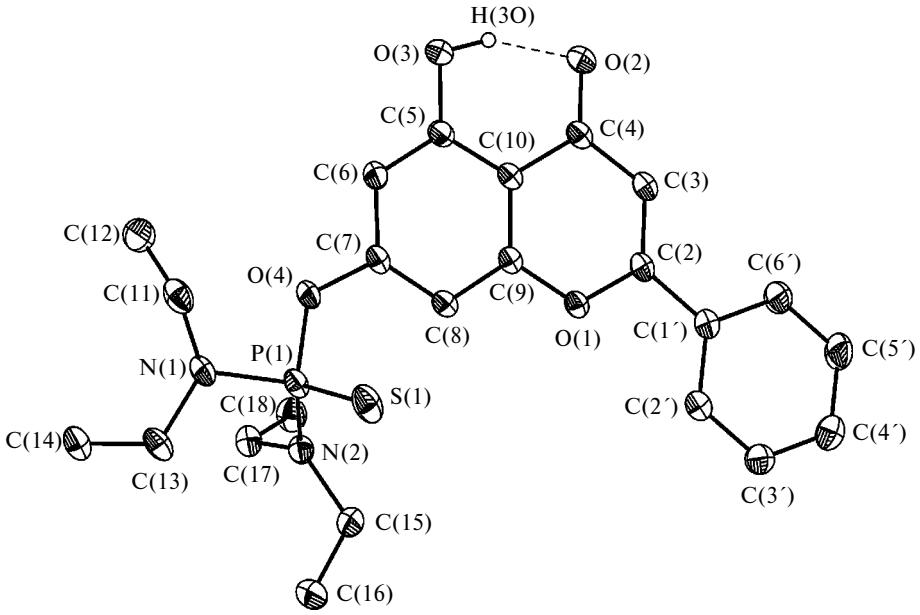


Fig. 1. Structure of thionophosphate **6**.

phosphates **5** (δ_P 80.6) and **6** (δ_P 75.8), which were isolated in the individual state by column chromatography (Scheme 1).

Study by ^{1}H NMR spectroscopy demonstrated that compound **6** is a monosubstitution product of the flavonoid moiety at position 7. This reaction proceeds regioselectively due to the presence of the strong intramolecular C(4)=O...H—O—C(5) hydrogen bond, which substantially decreases the reactivity of the C(5)OH group in this transformation. Compound **6** is characterized by magnetic nonequivalence of the methylene protons of the diethylamide fragments (^{1}H NMR spectroscopic data). The geminal proton-proton coupling constant $^2J_{H,H}$ is 26.0 Hz, and the vicinal proton-phosphorus coupling constants $^3J_{H,P}$ are 13.7 and 14.3 Hz. In the NMR spectrum of compound **5**, the methylene protons are magnetically equivalent, and the coupling constant $^3J_{H,P}$ is somewhat smaller (12.5 Hz).

The structure of compound **6** was additionally studied by X-ray diffraction. The overall view of the molecule is shown in Fig. 1. The selected geometric parameters are given in Table 1.

Analysis of the bond lengths and bond angles in the flavonoid fragment demonstrated that they are virtually identical to the corresponding parameters of the 5-hydroxy-7-methoxyflavone (HMF) molecule.[3] The O(2)...O(3) distance, which characterizes the strength of the intramolecular O—H...O hydrogen bond, is 2.589(2) and 2.582 Å in compound **6** and HMF, respectively. Slight differences in the geometry, in particular, in the twist angle of the ring *B* (C(2′)—C(1′)—C(2)—O(1) torsion angles are 3.8 and 23°, respectively), are determined by the crystal packing effects. Analysis of intermolecular con-

Table 1. Bond lengths (*d*) and bond angles (ω) in compound **6** determined by X-ray diffraction analysis and in the TEDAMTP molecule based on the results of B3PW91/6-311G* calculations

Parameter	**6**	TEDAMTP
Bond	*d*/Å	
P(1)—S(1)	1.9323(5)	1.967
P(1)—N(1)	1.650(1)	1.706
P(1)—N(2)	1.631(1)	1.686
P(1)—O(4)	1.627(1)	1.656
O(1)—C(2)	1.360(2)	—
O(1)—C(9)	1.368(1)	—
O(2)—C(4)	1.251(2)	—
O(3)—C(5)	1.346(2)	—
C(2)—C(3)	1.352(2)	—
C(3)—C(4)	1.436(2)	—
C(5)—C(6)	1.382(2)	—
C(5)—C(10)	1.412(2)	—
C(4)—C(10)	1.449(2)	—
C(9)—C(10)	1.393(2)	—
Angle	ω/deg	
O(4)—P(1)—N(2)	106.72(6)	106.9
O(4)—P(1)—N(1)	95.30(6)	95.8
N(2)—P(1)—N(1)	105.93(6)	104.9
O(4)—P(1)—S(1)	113.07(4)	114.5
N(2)—P(1)—S(1)	114.39(5)	113.5
N(1)—P(1)—S(1)	119.27(5)	119.2
C(13)—N(1)—C(11)	115.4(1)	114.4
C(13)—N(1)—P(1)	116.5(1)	116.0
C(11)—N(1)—P(1)	118.06(9)	115.1
C(15)—N(2)—C(17)	116.1(1)	117.2
C(15)—N(2)—P(1)	124.3(1)	122.6
C(17)—N(2)—P(1)	119.48(9)	119.9
C(2)—O(1)—C(9)	120.0(1)	—

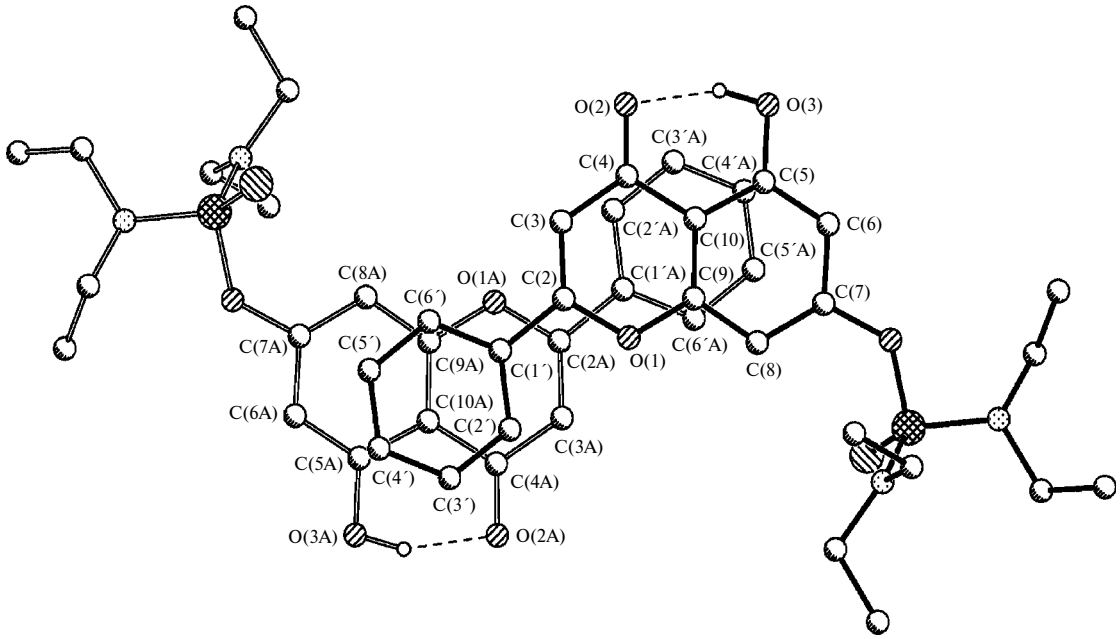


Fig. 2. Stacked-bonded dimer **6**.

tacts demonstrated that, although stacking interactions occur in both compounds, the distance between the rings and their mutual arrangement are somewhat different. In HMF, there is an interaction between the rings *A* and *C* with the shortest intermolecular C(4)...C(9) contact (3.33 Å), whereas stacking interactions between all rings occur in compound **6** (Fig. 2) with the shortest C(4´)...C(5A) and C(2´)...C(4A) distances (3.34 and 3.40 Å). Apparently, these differences in the character of stacking interactions are responsible for a substantial shortening of the O(1)—C(9) bond in molecule **6** (1.368(1) Å) compared to that in HMF (1.381 Å).

The diethylamido groups in the thionophosphate fragment are noticeably different. The sums of the angles at the N(1) and N(2) atoms are 350.1(1) and 359.9(1)°, respectively. In addition, the differences in the configuration lead also to variations in the P—N bond lengths. Shortening of the P(1)—N(2) bond in the planar NEt_2 group by 0.02 Å suggests the presence of the conjugation between the P=S bond and the lone electron pair of the N(1) atom. Actually, the P=S bond lies in the C(17)—N(2)—C(18) plane (the C(15)—N(2)—P(1)—S(1) torsion angle is 3.9°). The lone electron pair of the N(1) atom is antiperiplanar with respect to the P(1)—S(1) bond (the C(13)—N(1)—P(1)—S(1) torsion angle is 74.3°), which is favorable for an anomeric interaction, *viz.*, the charge transfer from the lone electron pair of the N(1) atom to the antibonding σ orbital of the P—S bond.

However, this nonequivalence of the NEt_2 groups in the thionophosphate fragment is not unique for compound **6**. Analysis of the data retrieved from the Cambridge Structural Database (CSD)[4] demonstrated that one $NAlk_2$ group is planar in almost all structures containing the $OP(=S)(NAlk_2)_2$ fragment, whereas another $NAlk_2$ group has a pyramidal configuration. The P=S bond in these compounds, like that in molecule **6**, is coplanar with the flattened $NAlk_2$ group. It should be noted that if the P atom is bound to only one $NAlk_2$ group, the latter is virtually always flattened. As an example we refer to the crystal structure of 1,6-bis-*O*-(*N*,*N*-tetraethyldiamidothionophosphoryl)galactitol 2,3:4,5-bis-(*N*-diethylamidocyclothionophosphate), whose molecule contains two $OP(=S)(NEt_2)_2$ groups and the $O_2P(=S)NEt_2$ group.[5] In this compound, the amino group in the $O_2P(=S)(NEt_2)_2$ fragment has a planar configuration (the sum of the angles at the nitrogen atom is 359.8°). By contrast, only one NEt_2 group in $OP(=S)(NEt_2)_2$ is planar (the sums of the angles at the nitrogen atoms are in a range of 359.6—360°), whereas the second NEt_2 group is pyramidal (the sums of the angles at the nitrogen atoms are in a range of 348.1—354.7°).

To estimate whether the difference in the P—N bond lengths is a consequence of conjugation with the P=S bond and to examine the possibility of existence of the above-mentioned anomeric interaction, we carried out quantum-chemical calculations for the model compound methyl *N*,*N*-tetraethyldiamidothionophosphate $MeOP(S)(NEt_2)_2$ (TEDAMTP). The calculations were performed with full geometry optimization by the B3PW91/6-311G* method using the GAUSSIAN-98 program package.[6] In spite of the fact that calculations at this level of theory give slightly overestimated bond lengths with the P atom, the main characteristic features revealed for **6** are observed also for the isolated TEDAMTP mol-

ecule (see Table 1). The sums of the angles at the N(1) and N(2) atoms are 345.5 and 359.8°, respectively. The difference between the P(1)—N(1) and P(1)—N(2) bond lengths (1.686 and 1.706 Å, respectively) is equal to that observed in the crystal ((0.02 Å).

Topological analysis of the electron density function for the TEDAMTP compound demonstrated that, in spite of shortening of the P(1)—N(2) bond compared to the P(1)—N(1) bond, the electron densities (1.208 and 1.216 e Å^{-3}) at the corresponding critical points (3, −1) are virtually identical. Moreover, the P(1)—N(1) and P(1)—N(2) bonds are characterized by similar ellipticities (ε) (0.187 and 0.197 Å, respectively; for comparison, ε for the P(1)—O(4) bond is 0.075 Å), which serve as a measure of the deviation of the electron density distribution from cylindrical symmetry and, consequently, show the contribution of the π component.

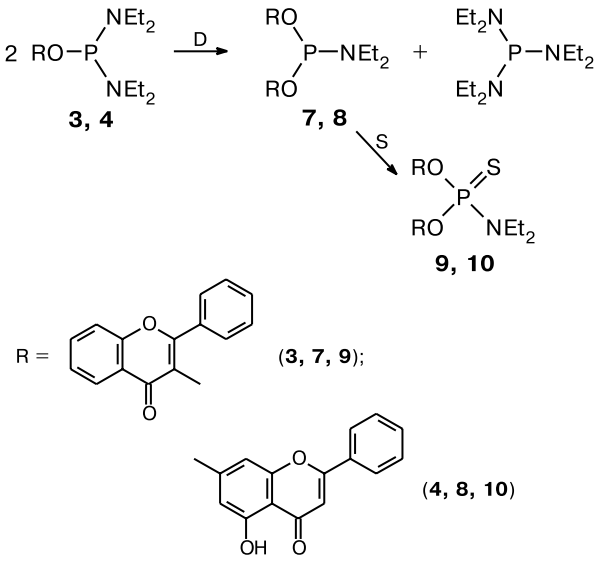
The NBO analysis demonstrated that the high ellipticity of the P(1)—N(1) bond results from an interaction between the lone electron pair of the N atom and the antibonding orbital of the P—S bond with an energy of 8.97 kcal mol^{-1}. The low energy of this anomeric interaction and the similar populations of the orbitals corresponding to the lone electron pairs of the N(1) and N(2) atoms (1.85 and 1.82) suggest that the conjugation of the N(2)Et$_2$ group with the P=S bond is rather weak.

Storage of crude phosphites **3** and **4** for two days afforded phosphites of another type, but the conversion (which was determined from the integral intensity ratio in the ^{31}P NMR spectrum) was no higher than 20%. Heating of phosphites **3** and **4** at 60 °C for 8 h led (^{31}P NMR spectroscopic data) to the transformation of diamidophosphite **3** (δ_P 131.5) into monoamidophosphite **7** (δ_P 139.2) and the transformation of phosphite **4** (δ_P 142.8) into monoamidophosphite **8** (δ_P 147.1). The yields of the products increased to 50%. The resulting mixtures of phosphites were subjected to sulfurization. Column chromatography afforded thionophosphates **9** (δ_P 64.7) and **10** (δ_P 71.9), which contain two flavonoid fragments linked through the P atom. The constants $^3J_{H,P}$ for these compounds are analogous to those for the monomeric products. This reaction pathway can be attributable to dismutation (Scheme 2).

Unfortunately, because of high hygroscopicity of dioxane used as the solvent, we failed to detect the second reaction product, *viz.*, HEPTA, in the free state. Nevertheless, we observed accumulation of its hydrolysis product, *viz.*, tetraethylphosphorous diamide, in the reaction mixture. In addition, dismutation afforded free flavonoids, which were isolated in trace amounts by column chromatography. Analogous dismutation has been studied in detail earlier[7] for other aryl diamidophosphites, which were prepared starting from certain phenols and naphthols.

To summarize, phosphorylation of flavones with hexaethylphosphorous triamide occurs regioselectively

Scheme 2



and gives the target products in high yields. Phosphite based on 5,7-dihydroxyflavone contains the pseudochiral P atom. This complex spatial organization is retained in solution, as evidenced by the magnetic nonequivalence of the methylene protons of the diethylamido groups observed in ^{1}H NMR spectra. Dismutation of phosphites of 3-hydroxy- and 5,7-dihydroxyflavones was investigated.

Experimental

All experiments with trivalent phosphorus compounds were carried out under dry nitrogen in dry solvents, which were purified according to standard procedures. The ^{1}H NMR spectra were recorded on a Bruker WP-250 instrument in $CDCl_3$ with Me_4Si as the internal standard. The ^{31}P NMR spectra were measured on a Bruker WP-80 instrument (32.4 MHz) with H_3PO_4 as the external standard. The reactions were monitored and the purity of the products was checked by TLC on Silufol UV-254 plates using a 3 : 1 hexane—dioxane mixture as the eluent. The chromatograms were visualized in an iodine chamber or by heating. Adsorption chromatography was carried out on silica gel L 40/60 μm (Merck). Commercial reagents were purchased from Aldrich, and HEPTA was prepared according to a known procedure.[8]

Flavon-3-yl *N,N,N′,N′*-tetraethyldiamidothionophosphate (5). Hexaethylphosphorous triamide (0.27 g, 1.1 mmol) was added dropwise to a suspension containing 3-hydroxyflavone **1** (0.26 g, 1.1 mmol) and dry dioxane (5 mL). The reaction was monitored by TLC and ^{31}P NMR spectroscopy. The reaction mixture was kept at room temperature for 4 h. The solvent was distilled off *in vacuo*. The resulting oily compound, flavon-3-yl *N,N,N′,N′*-tetraethyldiamidophosphite, (**3**) (δ_P 142.8) was dissolved in anhydrous benzene, and then sulfur (0.04 g, 1.25 mmol) was added. To accelerate sulfurization, 1—2 drops of triethylamine were added and the reaction mixture was heated at 60 °C for 3 h. The solvent was distilled off *in vacuo*. Thionophosphate **5**

was isolated by column chromatography in a yield of 0.29 g (62%), m.p. 109—111 °C, R_f 0.6. Found (%): C, 62.10; H, 6.61; N, 6.34; P, 7.01; S, 7.18. $C_{23}H_{29}N_2O_3PS$. Calculated (%): C, 62.14; H, 6.58; N, 6.30; P, 6.97; S, 7.21. ^{31}P NMR (C_6H_6), δ: 80.6. ^{1}H NMR, δ: 8.27 (dd, 1 H, H(5), ^3J = 7.9 Hz, ^4J = 1.8 Hz); 7.37 (ddd, 1 H, H(6), ^3J = 8.1 Hz, ^3J = 7.3 Hz, ^4J = 1.6 Hz); 7.64 (ddd, 1 H, H(7), ^3J = 8.4 Hz, ^3J = 7.0 Hz, ^4J = 1.6 Hz); 7.45 (dd, 1 H, H(8), ^3J = 8.1 Hz, ^4J = 1.6 Hz); 7.79 (dd, 2 H, H(2′), H(6′), ^3J = 7.3 Hz, ^4J = 1.6 Hz); 7.45—7.50 (m, 3 H, H(3′), H(4′), H(5′)); 3.07 (m, 8 H, NC$\underline{H}_2$Me); 1.04 (t, 12 H, NCH$_2$C$\underline{H}_3$, ^3J = 7.1 Hz).

5-Hydroxyflavon-7-yl *N,N,N′,N′*-tetraethyldiamidothionophosphate (6) was prepared by the reaction of 5,7-dihydroxyflavone (0.33 g, 1.29 mmol), HEPTA (0.32 g, 0.129 mmol), and sulfur (0.05 g, 1.56 mmol) analogously to the synthesis of product **5**. Intermediate 5-hydroxyflavon-7-yl *N,N,N′,N′*-tetraethyldiamidophosphite (**4**) (δ_P 142.8) was used without additional purification. The yield was 0.44 g (71%), m.p. 123—125 °C, R_f 0.5. Found (%): C, 59.81; H, 6.38; N, 6.04; P, 6.71; S, 7.02. $C_{23}H_{29}N_2O_4PS$. Calculated (%) C, 59.87; H, 6.35; N, 6.08; P, 6.73; S, 6.96. ^{31}P NMR (C_6H_6), δ: 75.8. ^{1}H NMR, δ: 6.70 (s, 1 H, H(3)); 6.58 (dd, 1 H, H(6), ^4J = 2.2 Hz, $^4J_{H(6),P}$ = 1.1 Hz); 6.99 (dd, 1 H, H(8), ^4J = 2.2 Hz, $^4J_{H(8),P}$ = 1.2 Hz); 7.89 (dd, 2 H, H(2′), H(6′), ^3J = 7.4 Hz, ^4J = 1.5 Hz); 7.53—7.54 (m, 3 H, H(3′), H(4′), H(5′)); 12.69 (s, 1 H, OH); 3.25 (m, 8 H, NC$\underline{H}_2$Me); 1.18 (t, 12 H, NCH$_2$C$\underline{H}_3$, ^3J = 7.0 Hz).

Bis(flavon-3-yl) *N,N*-diethylamidothionophosphate (9). Product **3** was synthesized according to the above-described procedure from 3-hydroxyflavone (0.5 g, 2.13 mmol) and HEPTA (0.52 g, 0.23 mmol). A dioxane solution containing this product was heated at 60 °C for 8 h. The reaction was monitored by TLC and ^{31}P NMR spectroscopy. Sulfur (0.08 g, 2.5 mmol) and 1—2 drops of triethylamine (as the catalyst) were added to the resulting mixture of phosphite **3** (δ_P 142.8) and bis(flavon-3-yl) *N,N*-diethylamidophosphite (**7**) (δ_P 147.1) characterized by the integral intensity ratio of 1 : 1. The reaction mixture was heated at 60 °C for 3 h. The solvent was distilled off *in vacuo*, and thionophosphate **9** was isolated by column chromatography. The yield was 0.55 g (43%), m.p. 218—220 °C, R_f 0.3. Found (%): C, 67.03; H, 4.66; N, 2.33; P, 5.10; S, 5.21. $C_{34}H_{28}NO_6PS$. Calculated (%): C, 66.99; H, 4.63; N, 2.30; P, 5.08; S, 5.26. ^{31}P NMR (C_6H_6) δ: 70.1. ^{1}H NMR, δ: 8.19 (dd, 2 H, H(5), ^3J = 8.0 Hz, ^4J = 1.5 Hz); 7.37 (ddd, 2 H, H(6), ^3J = 8.1 Hz, ^3J = 7.3 Hz, ^4J = 1.6 Hz); 7.65 (ddd, 2 H, H(7), ^3J = 8.4 Hz, ^3J = 7.0 Hz, ^4J = 1.6 Hz); 7.47 (dd, 2 H, H(8), ^3J = 8.1 Hz, ^4J = 2.2 Hz); 7.83 (dd, 4 H, H(2′), H(6′), ^3J = 7.6 Hz, ^4J = 1.2 Hz); 7.28—7.37 (m, 6 H, H(3′), H(4′), H(5′)); 3.41 (m, 4 H, NC$\underline{H}_2$Me); 1.05 (t, 6 H, NCH$_2$C$\underline{H}_3$, ^3J = 7.1 Hz).

Bis(5-hydroxyflavon-7-yl) *N,N*-diethylamidothionophosphate (10) was prepared by the reaction of 5,7-hydroxyflavone (0.5 g, 1.96 mmol), HEPTA (0.49 g, 1.96 mmol), and sulfur (0.08 g, 2.5 mol) analogously to the synthesis of product **9**. The resulting bis(5-hydroxyflavon-7-yl) *N,N*-diethylamidophosphite (**8**) (δ_P 139.2) was used without isolation. The yield was 0.49 g (38%), m.p. 210—212 °C, R_f 0.4. Found (%): C, 63.68; H, 4.44; N, 2.16; P, 4.79; S, 5.05. $C_{34}H_{28}NO_8PS$. Calculated (%): C, 63.65; H, 4.40; N, 2.18; P, 4.83; S, 5.00. ^{31}P NMR (C_6H_6), δ: 64.7. ^{1}H NMR, δ: 6.73 (s, 2 H, H(3)); 6.71 (dd, 2 H, H(6), ^4J = 2.3 Hz, $^4J_{H(6),P}$ = 1.2 Hz); 6.99 (dd, 2 H, H(8), ^4J = 2.2 Hz, $^4J_{H(8),P}$ = 1.2 Hz); 7.90 (dd, 4 H, H(2′), H(6′), ^3J = 7.4 Hz, ^4J = 1.5 Hz); 7.55 (m, 6 H, H(3′), H(4′), H(5′)); 12.77 (s, 1 H, OH); 3.49 (m, 4 H, NC$\underline{H}_2$Me); 1.22 (t, 6 H, NCH$_2$C$\underline{H}_3$, ^3J = 7.0 Hz).

Table 2. Selected crystallographic data and details of the structure refinement of compound **6**

Parameter	Characteristic
Molecular formula	$C_{23}H_{29}N_2O_4PS$
Molecular weight	460.51
Crystal system	Triclinic
Space group	*P*1
T/K	120
Diffractometer	«SMART CCD»
Z (*Z′*)	2 (1)
a/Å	7.7412(5)
b/Å	11.5874(8)
c/Å	13.8553(9)
α/deg	101.356(1)
β/deg	105.212(1)
γ/deg	103.009(1)
V/Å^3	1124.4(1)
d_{calc}/g cm^{-3}	1.360
μ/cm^{-1}	2.48
F(000)	488
Scan mode	ω
$2\theta_{max}$/deg	60
Number of measured reflections	13366
Number of independent reflections	6475
Number of reflections with $I > 2\sigma(I)$	5620
R_{int}	0.0439
Number of parameters in refinement	288
GOF	1.047
R_1	0.0439
wR_2	0.0995
Residual electron density/e Å^{-3}, ρ_{min}/ρ_{max}	0.526/−0.345

Single crystals of compound **6** were prepared by crystallization from a hexane—dioxane mixture. **X-ray diffraction study** was carried out at 120 K on an automated SMART CCD diffractometer. The structure was solved by direct methods and refined against F^2_{hkl} by the least-squares method with anisotropic displacement parameters for all nonhydrogen atoms. The H atoms were located from difference Fourier maps and refined isotropically. The principal crystallographic characteristics and details of the structure refinement are given in Table 2. All calculations were carried out on an IBM-PC/AT using the SHELXTL PLUS program package.[9]

Quantum-chemical calculations were carried out by the B3PW91/6-311G* method with full geometry optimization using the GAUSSIAN-98 program package.[6] The electronic structure was studied in the localized orbital approximation using NBO analysis[10] and in terms of the topological theory of Atoms in Molecules.[11]

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