The structure and properties of 3-(triphenylphosphoranylidene)naphthalene-1,2,4(3*H*)-trione

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The structure of 3-(triphenylphosphoranylidene)naphthalene-1,2,4(3*H*)-trione was established with the use of IR and ^{13}C NMR spectroscopy and quantum-chemical calculations. Reactions of this compound with NH_2OH and $RNHNH_2$ involve the carbonyl group in position 1 and a reaction with *o*-phenylenediamine involves the carbonyl groups in positions 1 and 2.

Key words: 2,3-dichloronaphthoquinone, triphenylphosphine, triphenylphosphoranylidenenaphthalenetrione, oxime, hydrazones, benzophenazinone.

Among naphthoquinone derivatives, nitrogen-,[1] sulfur-,[2,3] and phosphorus-containing[4,5] ylides are known, whose stability is due to the electron-acceptor effect of the naphthoquinone skeleton. However, these compounds have been studied insufficiently; in particular, no spectral characteristics that could confirm their structures have been obtained. The goal of the present work is to confirm spectrally and chemically the structure of 3-(triphenylphosphoranylidene)naphthalene-1,2,4(3*H*)-trione (**1**), whose derivatives are biologically active.[5]

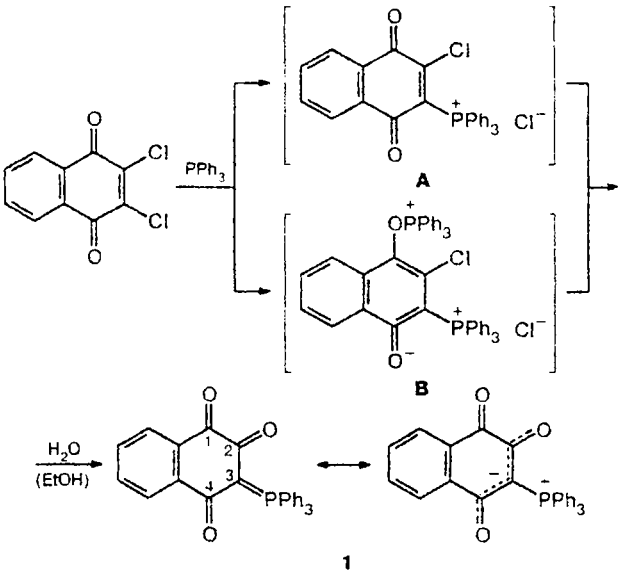
Phosphorane **1** is formed upon heating (100—120 °C) equimolar amounts of 2,3-dichloronaphthoquinone (DCN) and triphenylphosphine in ethanol (see Ref. 7). We found that a nearly twofold excess of Ph_3P is necessary for carrying out this reaction at room temperature in chloroform or ethanol.[5]

It is known that tertiary phosphines react with benzoquinone derivatives to form hydrolyzable adducts where the phosphorus atom may be bonded to the oxygen (or carbon) atoms.[6] Apparently, the reaction of DCN with Ph_3P proceeds in a similar way *via* intermediate monosubstituted adduct **A** (on heating)[4] or disubstituted adduct **B** (at room temperature),[5] which further react with water or ethanol to give phosphorane **1** (Scheme 1). Indeed, 4 min after mixing the reagents in a *ca.* 1 : 2 ratio at 20 °C, the ^{31}P NMR spectrum (DMSO) exhibited three signals at δ −4.1, 15.6, and 28.6, which correspond to Ph_3P, phosphorane **1**, and $Ph_3P{=}O$, respectively. The NMR spectrum of the mixture recorded after 6 h showed only two low-field signals (ratio of integral intensities ~1 : 1). The NMR study of this reaction at a reagent ratio of 1 : 1 (in CH_2Cl_2) reveals, along with the above-mentioned signals, two other signals at δ 17—19, which probably correspond to adduct **B**. The participation of water (or ethanol) in the formation of **1** is confirmed by the virtual absence of phosphorane **1** (TLC data) when the reaction was carried out in chloroform purified from hydroxyl-containing admixtures.

Using commercial chloroform, containing ethanol for stabilization, as a solvent gives phosphorane **1** in 68% yield over the same period (48 h).

The data of the ^1H, ^{31}P, and ^{13}C NMR spectra of

Scheme 1



Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 2, pp. 373—376, February, 1999.

Table 1. ^{1}H, ^{31}P, and ^{13}C NMR spectral data of compounds **1**—**3**

Compound	δ (*J*/Hz)		
	^{1}H	^{31}P	^{13}C
1	7.40—7.80 (m, 17 H, H(6), H(7), 3 Ph); 8.02, 8.12 (m, 2 H, H(5), H(8))	14.2	87.78 (C(3), $^{1}J_{C,P}$ = 98.4); 123.42 (C_i, $^{1}J_{C,P}$ = 92.1); 126.23, 127.00 (C(5), C(8)); 128.76 (C_m, $^{3}J_{C,P}$ = 12.8); 131.73, 133.94 (C(6), C(7)); 132.20 (C(8a)); 132.50 (C_p); 133.53 (C_o, $^{2}J_{C,P}$ = 10.3); 135.65 (C(4a), $^{3}J_{C,P}$ = 10.4); 176.17 (C(1)); 181.88 (C(2)); 182.60 (C(4), $^{2}J_{C,P}$ = 10.8)
2a	7.30—7.80 (m, 17 H, H(6), H(7), 3 Ph); 8.01, 8.21 (m, 2 H, H(5), H(8)); 17.49 (s, 1 H, OH)	14.4	85.81 (C(3), $^{1}J_{C,P}$ = 102.2); 122.36 (C(5)); 123.30 (C_i, $^{1}J_{C,P}$ = 85.9); 125.60 (C(8)); 128.16 (C(8a)); 128.56 (C(6)); 128.80 (C_m, $^{3}J_{C,P}$ = 12.6); 130.78 (C(4a) , $^{3}J_{C,P}$ = 8.9); 131.58 (C(7)); 132.60 (C_p, $^{4}J_{C,P}$ = 2.2); 133.46 (C_o, $^{2}J_{C,P}$ = 10.4); 143.48 (C(1), $^{3}J_{C,P}$ = $^{3}J_{C,H}$ = 9.0); 180.60 (C(2), $^{2}J_{C,P}$ = 6.0); 182.26 (C(4), $^{2}J_{C,P}$ = $^{3}J_{C,H}$ = 4.5)
2b	7.20—8.10 (m, Ar, NH_2)	14.7	—
2c	7.20—8.40 (m, 24 H, Ar); 14.80 (s, 1 H, NH)	14.5	—
2e	7.20—8.10 (m, 21 H, Ar, NH_2); 13.63 (s, 1 H, NH)	14.8	—
2f	7.20—8.10 (m, 21 H, Ar, NH_2); 14.73 (s, 1 H, NH)	14.7	—
3	6.94 (m, 1 H, H(8)); 7.35 (m, 2 H, H(9), H(10)); 7.46 (m, 2 H, H_m); 7.54 (m, 3 H, H_p); 7.67 (m, 1 H, H(3)); 7.76 (m, 1 H, H(2)); 7.81 (m, 6 H, H_o); 8.02 (m, 1 H, H(11)); 8.44 (dd, 1 H, H(4), ^{3}J = 8.0, ^{4}J = 2.0); 9.14 (dd, 1 H, H(1), ^{3}J = 8.0, ^{4}J = 2.0)	14.7	79.96 (C(6), $^{3}J_{C,P}$ = 108.0); 124.75, 125.09, 126.34, 130.01, 129.56, 128.94, 128.48, 128.17 (C(1), C(2), C(3), C(4), C(8), C(9), C(10), C(11)); 125.50 (C(12b), $^{4}J_{C,P}$ = 2.0); 125.82 (C_i, $^{1}J_{C,P}$ = 93.6); 128.43 (C_m, $^{3}J_{C,P}$ = 13.0); 131.78 (C_p, $^{4}J_{C,P}$ = 2.5); 133.66 (C_o, $^{2}J_{C,P}$ = 11.0); 134.90 (C(4a), $^{3}J_{C,P}$ = 11.0); 137.85, 140.96 (C(7a), C(11a)); 140.34 (C(12a), $^{3}J_{C,P}$ = 9.0); 149.76 (C(6a), $^{2}J_{C,P}$ = 6.0); 178.67 (C(5), $^{2}J_{C,P}$ = 5.0)

compound **1** are given in Table 1. The difference in the chemical shifts of protons in *peri*-positions with respect to the carbonyl groups, which had made it possible to elucidate the structure of sulfur-containing ylides,[3] was smaller for phosphorane **1** (Δδ 0.1). The ^{13}C NMR spectrum is the most informative, showing that the chemical shifts of the junction and α- and β-C atoms have values typical of naphthoquinone derivatives, while the signal for C(3) is characteristically (for phosphorus ylides) shifted upfield and lies at δ 87.78 (*cf.* Ref. 7). Three signals at δ 182.60, 181.88, and 176.17 are observed in the region of resonance of the carbonyl C atoms, which attests to the presence of three carbonyl groups in compound **1**, one of them differing from the two others. In accordance with this, the carbonyl group (in position 1) in the IR spectrum of compound **1** absorbs at 1700 cm^{-1}, *i.e.*, in the region characteristic of aryl ketones rather than quinones.[8] In addition, the presence of an intense absorption band at 1570 cm^{-1} inherent in enolizable β-diketones (see Ref. 9) suggests that the negative charge is delocalized between the carbonyl groups in positions 2 and 4 adjacent to the ylide fragment, which corroborates the ylide structure of compound **1**. The results of quantum-chemical calculations (Table 2) performed by us do not contradict this conclusion. These show that the C(1)—O bond in ylide **1** is identical with that in DCN, while the multiplicity of the C(2)—O and C(4)—O bonds are lower than two. Moreover, the C(1)—C(2), C(2)—C(3), and C(3)—C(4) bond orders and lengths differ significantly.

Table 2. Bond orders (*p*) and lengths (*d*/Å) in compound **1** and 2,3-dichloronaphthoquinone (DCN) calculated by the MNDO, PM3, and AM1 methods

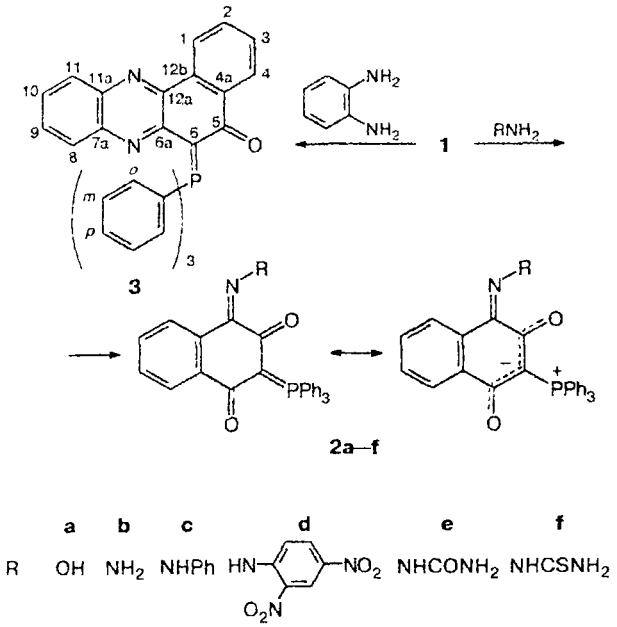
Compound	Bond	MNDO		PM3		AM1,
		p	*d*	*p*	*d*	*d*
DCN	C(1)—O	1.94	1.225	1.91	1.217	1.235
1	C(1)—O	1.94	1.224	1.92	1.214	1.233
1	C(2)—O	1.83	1.231	1.82	1.224	1.241
1	C(4)—O	1.78	1.239	1.74	1.236	1.253
1	C(1)—C(2)	0.84	1.541	0.86	1.529	1.521
1	C(2)—C(3)	1.06	1.449	1.05	1.447	1.440
1	C(3)—C(4)	1.07	1.457	1.10	1.444	1.443

Ylide **1** is soluble in hydrochloric acid and does not react with carbonyl and nitroxo compounds. In the reaction with NH_2OH, compound **1** behaves as a typi-

cal ketone to give oxime **2a**, a product of condensation at the carbonyl group in position 1. The direction of the nucleophile attack was determined from the ^{13}C NMR spectrum of compound **2a** (see Table 1), where signals for the ylide C atom (δ 85.81) and the C(1) atom bonded to the hydroxyimino group (δ 143.48) are observed. In contrast to ylide **1**, the region of resonance of the carbonyl C atoms exhibits only two signals for C(2)—O and C(4)—O, whose chemical shifts are close to those in ylide **1**. The signals for C(1) and C(4) atoms are multiplets because of spin-spin coupling with the P atom and the H atoms in the *peri*-positions, whereas the signal for the C(2) atom is a doublet (*cf.* Ref. 10).

Ylide **1** reacts with hydrazine and its derivatives (phenylhydrazine, 2,4-dinitrophenylhydrazine, semicarbazide, and thiosemicarbazide) in a similar way to give hydrazones, semicarbazones, and thiosemicarbazones (**2b—f**), while its reaction with *o*-phenylenediamine yields benzophenazinone **3** (Scheme 2).

Scheme 2



The structures of compounds **2** and **3** were confirmed by spectral and analytical data (Tables 1 and 3). The IR spectra of these compounds exhibit absorption bands at 1620 (ν(C=N)), 1600 (ν(C=C)), 1520—1560 (ν(C—O)), and 1440 cm^{-1} (ν(C—P)). The band of the C=O stretching vibrations (1700 cm^{-1}) is observed only in the spectrum of semicarbazone **2e**, which correlates with the zwitterionic structure of the compounds. In the ^1H NMR spectra of phosphoranes **2a,c,e**, a signal at δ 13—17 corresponds to the OH or NH protons linked by a hydrogen bond with the O atom of the carbonyl group. The ^1H chemical shifts of the protons at C(11) and C(8) in phenazinone **3** differ (δ 8.02 and 6.94, respectively) because of magnetic shielding of the H(8) atom by the phenyl groups at the phosphorus atom. The ^{31}P NMR spectra of compounds **1—3** are characterized by a signal at δ 14.5.

Table 3. Characteristics of compounds **2** and **3**

Compound	Yield	M.p./°C (cloroform—methanol)	Molecular mass Found / Calculated	Molecular formula
2a	73	204—206.5	449.1146 / 449.1180	$C_{28}H_{20}NO_3P$ [a]
2b	67	228.5—232	448.1273 / 448.1339	$C_{28}H_{21}N_2O_2P$
2c	73	232—234	524.1708 / 524.1653	$C_{34}H_{25}N_2O_2P$
2d	75	306—309	614.1421 / 614.1354	$C_{34}H_{23}N_4O_6P$
2e	80	249—252	491.1358 / 491.1398	$C_{29}H_{22}N_3O_3P$
2f	80	263—266	507.1212 / 507.1170	$C_{29}H_{22}N_3O_2PS$ [b]
3	34	273—277	506.1544 / 506.1548	$C_{34}H_{23}N_2OP$ [c]

[a] Found (%): C, 74.91; H, 4.21; N, 3.31; calculated (%): C, 74.83; H, 4.45; N, 3.11.
[b] Found (%): C, 68.57; H, 4.22; N, 8.17; S, 6.86; calculated (%): C, 68.64; H, 4.34; N, 8.28; S, 6.31.
[c] Found (%): C, 80.80; H, 4.51; N, 5.41; P, 6.15; calculated (%): C, 80.63; H, 4.54; N, 5.53; P, 6.12.

Experimental

IR spectra were recorded on a UR-20 instrument (KBr). ^1H NMR spectra were recorded on Bruker AC-200 (compounds **1**, **2a**, and **3**) and Varian A-56/60A (compounds **2b—f**) spectrometers in $CDCl_3$. ^{31}P NMR spectra were recorded on a Bruker HX-90 instrument in DMSO and $CHCl_3$ with H_3PO_4 as the external standard. ^{13}C NMR spectra were recorded on Bruker AM-400 (compound **2a**) and Bruker AC-200 (compound **1**) spectrometers in $CDCl_3$. The molecular masses and the elemental composition of the compounds synthesized were determined on a Finnigan MAT-8200 GC/MS instrument from the precise value of the mass number of molecular ions. Quantum-chemical calculations and full optimization of molecular geometry were performed with the MOPAC (version 5.0)[11] and MNDO-89 programs.[12] Products were chromatographed on silica gel and Silufol UV-254 plates with chloroform as the eluent.

3-(Triphenylphosphoranylidene)naphthalene-1,2,4(3*H*)-trione (1). A mixture of DCN (5.0 g, 22 mmol) and Ph_3P (10.0 g, 38 mmol) in chloroform (400 mL) was heated to dissolution, cooled, and kept at room temperature for 48 h. The resulting solution was concentrated to 30—50 mL, and the residue was chromatographed and recrystallized from benzene with addition of chloroform. Yield 4.3 g, m.p. 237.5—239.5 °C. Found (%): C, 76.81; H, 4.38; P, 7.15. $C_{28}H_{19}O_3P$. Calculated (%): C, 77.40; H, 4.38; P, 7.14. Molecular mass, found/calculated: 434.1022/434.1071. Dilution of the mother liquor with methanol gave an additional 2.2 g of phosphorane **1**, m.p. 234.5—237.5 °C (*cf.* Ref. 4; m.p. 230 °C). Total yield 6.5 g (68%). The ^1H, ^{31}P, and ^{13}C NMR spectral data of compound **1** are listed in Table 1.

1-Hydroxyimino-3-(triphenylphosphoranylidene)-1,3-dihydronaphthalene-2,4-dione (2a). A mixture of ylide **1** (1.0 g, 2.3 mmol) and $NH_2OH \cdot HCl$ (0.5 g, 7 mmol) in 25 mL of ethanol was refluxed for 4 h and cooled. The precipitate that formed was filtered off and recrystallized from ethanol with addition of chloroform to give compound **2a** (0.76 g).

Hydrazone **2b** and semicarbazone **2e** were obtained in a similar manner (reaction time 2 and 0.5 h, respectively). Compound **2e** was purified by chromatography.

3-(Triphenylphosphoranylidene)-1-phenylhydrazono-1,3-dihydronaphthalene-2,4-dione (2c). A mixture of ylide **1** (1.0 g, 2.3 mmol) and $PhNHNH_2$ (0.3 mL, 3 mmol) in 20 mL of ethanol and 0.05 mL of conc. H_2SO_4 was refluxed for 0.5 h and cooled. The precipitate that formed was filtered off and recrystallized from ethanol to give compound **2c** (0.88 g).

Dinitrophenylhydrazone **2d** and thiosemicarbazone **2f** were obtained in a similar manner.

6-(Triphenylphosphoranylidene)benzo[*a*]phenazin-5-one (3). A mixture of ylide **1** (0.43 g, 1 mmol) and *o*-phenylenediamine (0.1 g, 1 mmol) in 10 mL of 50% AcOH was refluxed for 1 h and cooled. The precipitate that formed was separated, dissolved in CH_2Cl_2, filtered through a layer of Al_2O_3, and recrystallized from a 2 : 1 benzene—light petroleum mixture to give compound **3** (0.17 g).

The ^1H, ^{31}P, and ^{13}C NMR spectral data of compounds **2** and **3** are given in Table 1. The yields, melting points, and elemental analysis data are listed in Table 3.

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Received January 21, 1998;
in revised form July 16, 1998