

Synthesis and Spectroscopic Characterization of Two New Thiosaccharinate Salts. Molecular Structure of Bis(triphenylphosphine)iminium thiosaccharinate, *PNP(tsac)*

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Summary. We report the synthesis, FTIR, Raman and NMR spectroscopic features of bis(triphenylphosphine)iminium and tetrabutylammonium thiosaccharinates, *PNP(tsac)* and *NBu₄(tsac)* (*tsac*: thiosaccharinate anion, *PNP*: bis(triphenylphosphine)iminium). The molecular structure of the former compound was determined by X-ray diffraction methods. The salt crystallizes in the monoclinic $P2_1/n$ space group with $a = 9.6481(9)$, $b = 29.258(3)$, $c = 13.177(2)$ Å, $\beta = 97.53(1)^\circ$, and $Z = 4$ molecules per unit cell. Slight but significant changes in the bonding structure of the thiosaccharinate anion as compared with those reported for the neutral molecule are observed.

Keywords. Thiosaccharin; Bis(triphenylphosphine)iminium; IR spectroscopy; NMR spectroscopy; X-Ray structure determination.

Introduction

The use of bulky counter-ions to isolate heavy anions in crystal lattices to reduce the strength of specific interactions with their environment is a well-known technique. Usually, literature reports on the chemistry of thiosaccharin ($C_7H_5NO_2S_2$), the thione

form of saccharin, deal with the synthesis and structural characterization of ionic salts involving small cations, namely $K(tsac)$ [1], $Na(tsac)$ [2] and $NH_4(tsac)$ [3] (*tsac*: deprotonated form of thiosaccharin). In these salts the thiosaccharinate anions show preferential interactions with the cations generally through the iminic nitrogen atom and less frequently through the exocyclic sulfur and oxygen atoms, because they are negatively charged, as has been demonstrated by theoretical calculations [4–6]. Moreover, the thiosaccharinate anion binds soft metals, like Cd(II), Tl(I), Pd(II), Ag(I) or Cu(I), acting as η^1 -S monodentate [7–9], η^2 -S,N bidentate chelate [7, 10] or μ^2 -S-(η^3 -S,N) bridging tridentate [9] ligands.

In this paper we focus on the isolation of new ionic thiosaccharinates in an attempt to reduce the interactions between the anion and their surroundings. To this purpose, we selected bulky and single-charged counter-ions. We present here the X-ray diffraction structure and spectroscopic properties of bis(triphenylphosphine)iminium thiosaccharinate, (*PNP*)*tsac* (**1**) and also the spectroscopic characterization of the tetrabutylammonium salt of thiosaccharinate, (*NBu₄*)*tsac* (**2**).

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Results and Discussions

Solid State Vibrational Spectra

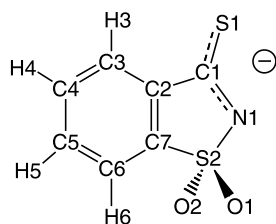
The FTIR spectra of powdered samples of **1** and **2** dispersed as Nujol mulls gave the same information

as with KBr dispersions. The infrared and Raman spectra of the compounds show the characteristic bands of PNP^+ [11, 12] and NBu_4^+ [13] cations, with minor overlapping by the thiosaccharinate bands [14]. The wavenumbers and tentative assign-

Table 1. FTIR and Raman bands wavenumbers/cm⁻¹ and approximate assignments of $PNP(tsac)$ (**1**) and $NBu_4(tsac)$ (**2**)

Htsac [14]		K(tsac) · H ₂ O [15]	NH ₄ (tsac) · H ₂ O [3]	$PNP(tsac)$ (1)		$NBu_4(tsac)$ (2)		Assignments ^b
IR ^a	Raman	IR	IR	IR	Raman	IR	Raman	
		3578m	3579w					ν OH (H ₂ O)
3341vs								ν (NH)
	3084w	3074vw						ν (CH)
	3060w	3064vw		3057w	3062vs	3062md	3063m	ν (CH), ν (CH) PNP^+
				3045w	3052vs			ν (CH) PNP^+
						2962vs	2966m	ν (CH ₂ /CH ₃) NBu_4^+
						2934s	2931s	ν (CH ₂ /CH ₃) NBu_4^+
						2874s	2873s	ν (CH ₂ /CH ₃) NBu_4^+
		1625w	1628w					δ (H ₂ O)
1590w	1590vs			1589w	1589vs		1588m	ν (CC), ν (CC) PNP^+
				1482m				ν (CC) PNP^+
						1471s	1470w	δ (CNC) NBu_4^+
1455s	1460m	1455s	1454s	1455m	1455w	1454s	1453m	ν (CC) δ (CH)
				1438s	1439vw			ν (CC) PNP^+
				1381m	1380vw			ν s(PNP) PNP^+
1247m	1248s	1338m	1340m	1365s	1366w	1356vs	1360w	ν (CN) δ (φ S)
1318s								δ (NH)
1283m	1282s	1307m	1317m	c	1314vw	1319m	1320w	ν (CC) δ (CH)
				1288s	1290vw			δ (CH) PNP^+
				1256vs, br	1255vvw			ν as(PNP) PNP^+
1376vs	1375m, br	1251vs	1248vs	c		1279s	1279vw	ν as(SO ₂)
1218s	1222s	1234s	1236vs	1226s	1227s	1223s	1223vs	δ (CH) ν (CC)
1156vs	1155m	1153m	1155vs	1147vs	1147m	1148s	1141m	ν s(SO ₂) ν (CC)
1120m	1126vw	1113s	1111s	1116vs		1118m	1110w	ν s(SO ₂) δ (φ SN)
				c	1109m			ν (PC) PNP^+
1039m	1038vw	1016s	1014s	1010s	1010w	1010vs	1009m	ν (CS) δ (φ SN)
				997m	1001vs			ν s(CC) PNP^+
817vs	820vw	851s	845s	826s	825w	832s	831vw	ν (NS) δ (CCC)
769s	770vw	769m	769s	775m		770s	767vw	γ (CH) γ (CCC)
				755s				γ (CH) PNP^+
				724vs				γ (PNP) PNP^+
700vw	701m		698w	694s	698w	696vw	696m	δ (CCC), δ (CCC) PNP^+
591s	582vw	594d	592m	589m	588vw	595m	592w	γ (SO ₂) γ (CCC)
		557m	555s	551vs	550vw	553m	552w	δ w(SO ₂) δ (CS)
				533vs				δ (PNP) PNP^+
527s	530w	521w	524m	c	517vw	516w	516w	γ (φ SN)
				499s	494vw			δ (CPC) PNP^+
	436vw	436m	434s	438m	437vw	436m	435w	γ (CCC)
	368s	383w			373s		372vs	γ (iso)
	274w	282m			266m		270m	γ (iso)
	101vs				111s		115s	τ (SO ₂) γ (iso)

^a vs Very strong, s strong, m medium, w weak, vw very weak, br broad; ^b ν stretching, δ in plane bending, γ out of plane bending, φ benzene ring, as asymmetric, s symmetric, PNP^+ bis(triphenylphosphine)iminium cation, NBu_4^+ tetrabutylammonium cation, iso isoindole ring; ^c overlapped with an intense band



Scheme 1

ments of the principal IR and *Raman* bands are reported in Table 1 together with vibrational data of related compounds.

Three intense IR bands due to the thiosaccharinate hetero-cycle vibrations (see Scheme 1 for atoms numbering) are clearly identified for both salts. The C1–N, C1–S1 and N–S2 bond stretching modes mainly contribute to the IR bands appearing at 1365 (**1**) and 1356 (**2**), 1010 (**1** and **2**) and 826 (**1**) and 832 (**2**) cm^{-1} . The first and third bands are blue-shifted and the second bands red-shifted with respect to the corresponding thiosaccharin bands (at 1283, 1039 and 817 cm^{-1}) [14]. In solid α -thiosaccharin the acidic proton is bonded to the nitrogen atom (thione tautomeric form) [16] and therefore the C1–N and C1–S1 bonds have single and double bond character. Upon deprotonation, the negative electronic charge delocalizes over the thioamide functional group, and also over the SO₂ group and the benzenic ring, as demonstrated by *ab initio* theoretical calculations [5, 6]. Then, the C1–N bond order increases and both the C1–S1 and N–S2 bond orders decrease causing the observed displacements of the associated vibrational bands. As can be seen from Table 1, the corresponding band positions observed for potassium or ammonium thiosaccharinates are in the range between thiosaccharin and the salts reported here. The existence of short contacts between the cations and the N thiosaccharinate atoms in K(*tsac*) [1] and NH₄(*tsac*) [3], localizes more negative electronic charge on the iminic nitrogen. As expected, there are no significant differences between **1** and **2** concerning the bands due to vibrations of the thiosaccharinate benzene rings.

The FTIR and *Raman* spectra of compounds **1** and **2** show the strong and medium intensity bands expected for the stretching and bending modes of the bulky cations. The PNP⁺ and NBu₄⁺ vibration modes were assigned by comparison to published data [11–13].

NMR Spectra

The thiosaccharin H1 chemical shift in DMSO-d₆ ($\delta = 6.02$ ppm) [17] shows that its thiol (C–SH) tautomeric form is more stable than the thione (C=S) form in polar solvents, and the last form is dominant in weakly or non-polar solvents as CDCl₃ ($\delta = 10.30$ – 8.10 ppm, broad and flat signal). This is also clearly reflected by the ¹³C chemical shifts of the C1 atoms, measured at 161.53 ppm in DMSO-d₆ [17] and at 187.70 ppm in CDCl₃. The opposite relationships between tautomeric forms and polarity of the solvents has been observed for other cyclic thioamides like pyridine, and pyrimidine-2-thione, thiazoline, and benzthiazoline-2-thione [18, 19]. Then the presence of the polar SO₂ group in thiosaccharin must be responsible of its particular behavior in solution. To gain more insight on these facts, we are now performing theoretical calculations of solvent effects on thiosaccharin and its anion.

Principal features of the PNP⁺ and NBu₄⁺ cations in DMSO-d₆ solutions have been observed and assigned. In the ¹H and ¹³C NMR spectra of compound **1**, both the proton and carbon resonances of thiosaccharinate and PNP⁺ appear superimposed. The ¹H chemical shifts of the PNP⁺ benzene rings and of three of the aromatic thiosaccharinate protons are observed as an unresolved multiplet between 7.94 and 7.36 ppm. Similarly, the ¹³C resonances of the PNP⁺ cation and of C4 and C5 atoms of the thiosaccharinate anion are assigned tentatively. The ¹³C chemical shift of the C1 atom shows the largest downfield displacement for a thiosaccharin compound observed until now.

The quite different NMR spectra signature of the anion and cation species in NBu₄(*tsac*) facilitated the assignment of the thiosaccharinate ¹H and ¹³C chemical shifts. The ¹H chemical shift of three of the thiosaccharinate protons appear as an unresolved multiplet between 7.94 and 7.65 ppm, in contrast with the behavior of H*tsac* [17]. Moreover, the ¹³C chemical shift of the C1 atom shows the same downfield displacement already discussed for **1**. These observations, along with other small chemical shift changes, reflect an efficient delocalization of the electronic charge over the thioamide functional group [5, 17].

X-Ray Structural Analysis of **1**

Crystal data and structure refinement results for compound **1** are summarized in Table 2. Figure 1 shows an ORTEP [20] drawing of the molecule.

Table 2. Crystal data and structure solution methods and refinement results for bis(triphenylphosphine)iminium thiosaccharinate (1)

Chemical formula	C ₄₃ H ₃₄ N ₂ O ₂ P ₂ S ₂
Formula weight	736.78
Temperature/K	296(2)
Crystal system	Monoclinic
Space group	P2 ₁ /n (No. 14)
Cell constants ^a	
<i>a</i> /Å	9.6481(9)
<i>b</i> /Å	29.258(3)
<i>c</i> /Å	13.177(2)
β /°	97.53(1)
Volume/Å ³	3687.6(8)
<i>Z</i> , <i>D</i> _{calc} /Mg/m ³	4, 1.327
Absorption coefficient, μ /mm ⁻¹	2.445
<i>F</i> (000)	1536
Crystal size/mm ³	0.36 × 0.36 × 0.36
Crystal color/shape	Yellow/spherical
Radiation	Graph. monochr. CuK α , λ = 1.54184 Å
Theta range for data collection/°	3.02 to 67.98
Limiting indices	-11 ≤ <i>h</i> ≤ 11, -35 ≤ <i>k</i> ≤ 1, -15 ≤ <i>l</i> ≤ 0
Reflections collected/unique	7225/6650 [<i>R</i> (int) = 0.020]
Completeness/%	98.9 (to = 67.98°)
Observed reflections [<i>I</i> > 2 σ (<i>I</i>)]	5765
Maximum and min. transmission	0.5476 and 0.4126
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	6650/0/461
Goodness-of-fit on <i>F</i> ²	1.044
Weights, <i>w</i>	[$\sigma^2(F_o^2) + (0.0677P)^2 + 1.63P$] ⁻¹ <i>P</i> = [Max(<i>F_o</i> ² , 0) + 2 <i>F_c</i> ²]/3
Final <i>R</i> indices ^b [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> 1 = 0.0428, <i>wR</i> 2 = 0.1162
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0496, <i>wR</i> 2 = 0.1235
Extinction coefficient	0.0015(1)
Largest diff. peak and hole/e · Å ⁻³	0.460 and -0.349

^a The unit cell dimensions were obtained by least squares refinement of [(sin θ)/ λ]² values for 23 reflections in the 16.27 < θ < 44.97° range

^b *R*-indices defined as: *R*₁ = $\Sigma||F_o| - |F_c||/\Sigma|F_o|$; *wR*₂ = [$\Sigma w(|F_o|^2 - |F_c|^2)^2/\Sigma w(|F_o|^2)^2$]^{1/2}

As expected, the thiosaccharinate (*tsac*) C₆SNC(S) molecular skeleton is nearly planar (rms distance of atoms from the least-squares plane equal to 0.042 Å). By comparing with the neutral thiosaccharin (*Htsac*) molecule [14], it can be appreciated that the major bonding changes in the charged moiety occur at the thioamidic functional group. This is shown by the shortening observed in both the N1–C1 bond length (from 1.384 Å in neutral *Htsac* to 1.324(3) Å in *tsac*) and the N1–S2 distance (from 1.664 Å to 1.624(2) Å), and also by the lengthening of the C1–S1 bond (from 1.622 Å in *Htsac* to 1.678(2) Å in *tsac*). Smaller lengthening is also observed in the C1–C2 bond distance (from 1.472 to 1.494(3) Å) and S2–C7 distance (from 1.750 to 1.759(2) Å). In contrast, no signifi-

cant changes are observed for C(2)–C(7) and sulfonyl S–O bond distances when comparing the neutral and charged molecules.

The bond distances and angles agree well with those reported for the potassium, sodium, and ammonium thiosaccharinate salts [1–3]. Notwithstanding, compared with the values observed for NH₄(*tsac*), slight but significant shortening in N1–C1 bond distance (from 1.334(5) to 1.324(3) Å) is observed. At the same time, a lengthening in the N1–S2 distance (from 1.616(3) to 1.624(2) Å) and C1–S1 bond length (from 1.666(4) to 1.678(2) Å) occurs. In the crystal structure of NH₄(*tsac*) a strong and almost linear thiosaccharinate-ammonium contact (N(*tsac*) ··· H–NH₃⁺) was observed (*d*(N ··· H) =

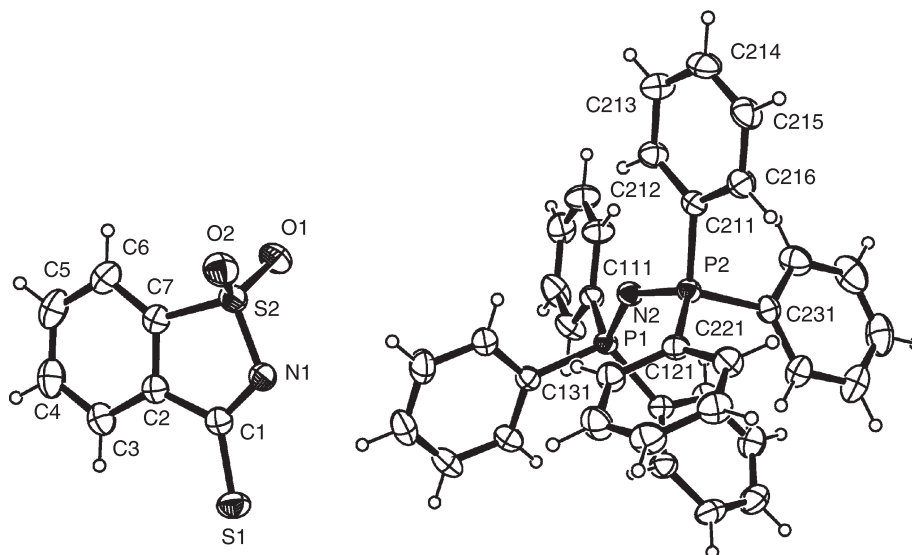


Fig. 1. Molecular plot of the bis(triphenylphosphine)iminium thiosaccharinate salt showing the labeling of the non-H atoms and their displacement ellipsoids at the 30% probability level. For simplicity, only one phenyl ring of the triphenylphosphine groups was fully labeled

2.900 Å and $\angle(\text{N}\cdots\text{H}-\text{N}) = 173.7^\circ$ [3]. In the *PNP(tsac)* molecular structure specific intermolecular short contacts are absent. Then, the last compound can be considered as a reference of a solid state “free” thiosaccharinate anion.

The bis(triphenylphosphine)iminium cation shows the expected molecular conformation with the two triphenylphosphine ($=\text{PPh}_3$) groups linked by the nitrogen atom (N–P bond distances of 1.584(2) and 1.581(2) Å) in a characteristic bent arrangement ($\angle(\text{P}-\text{N}-\text{P}) = 136.7(1)^\circ$). Within each $=\text{PPh}_3$ group the phosphorus atom is in a tetrahedral coordination with three phenyl groups (P–C distances in the range from 1.794(2) to 1.802(2) Å and C–P–C angles from 105.54(9) to 109.0(1)°) and the bridging N-atom (N–P–C angles from 106.90(9) to 113.3(1)°). The P–N bond distances and P–N–P angle are very similar to that observed for other bis(triphenylphosphine)iminium compounds with bulky or little charged anions [11, 21, 22]. *Guzei et al.* have reported an average P–N distance of 1.576 Å and a P–N–P angle of 143°, calculated over 562 structures of PNP^+ compounds reported in the CSD [22].

Experimental

Analytical reagent grade bis(triphenylphosphine)iminium chloride and tetrabutylammonium tetrafluoroborate were purchased from Aldrich Chemical Co. and used as received. The

solvents were of analytical reagent grade and dried by commonly used techniques [23]. Elemental analyses for C, H, N, and S were carried out with a Carlo Erba EA model 1108 elemental analyzer at INQUIMAE (FCEyN-UBA, Argentina), and the results were found to be in good agreement ($\pm 0.4\%$) with the calculated values. Conductivity measurements of the compounds in solution were performed with an OAKTON digital conductimeter calibrated with aqueous solutions of twice re-crystallized KCl (744.7 ppm, 1413 μS). The infrared spectra between 4000 and 400 cm^{-1} of the solid compounds, dispersed in KBr discs and Nujol mulls, were obtained with a Nicolet Nexus FTIR instrument. The Raman dispersion spectra of the solid substances in the region between 3500 and 100 cm^{-1} were obtained with a FRA 106 accessory mounted on a Bruker IFS 66 FTIR instrument, employing the 1064 nm excitation line from an Nd-YAG laser. The ^1H , ^{13}C and ^{31}P -NMR spectra of *DMSO-d*₆ solutions, at 300 K, were recorded on a Multinuclear Bruker ARX-300 equipment. The chemical shift data were measured by the replacement methods and are given relative to external H_3PO_4 and *TMS*. UV-visible spectra of the solid compounds dispersed in KBr and in solutions were collected on a Cecil 2021 spectrophotometer.

Thiosaccharin (1,2-benzisothiazol-3-(2H)-thione-1,1-dioxide), in its solid α -form, was prepared following the technique published by *Schibye et al.* [24]. Mp: 178–180°C (Ref. [24] 179°C). FTIR and ^1H and ^{13}C NMR (in *DMSO-d*₆) spectra were found to be identical with the one described in Refs. [14] and [17]. ^1H NMR (300 MHz, CDCl_3): $\delta = 10.3$ – 8.10 (broad, H1), 8.14 (d, $^3J(\text{H},\text{H}) = 7.7$ Hz, H6), 7.80 (t, $^3J(\text{H},\text{H}) = 7.3$ Hz, H3), 7.72 (t, $^3J(\text{H},\text{H}) = 7.3$ Hz, H5), 7.21 (d, $^3J(\text{H},\text{H}) = 7.7$ Hz, H4) ppm; ^{13}C NMR (75 MHz, CDCl_3): $\delta = 187.70$ (C1), 135.40 (C7), 135.34 (C5), 133.80 (C4), 130.45 (C2), 127.02 (C3), 120.85 (C6) ppm.

Bis(triphenylphosphoranylidene)ammonium{1,2-benzisothiazol-3-(2H)-thionate-1,1-dioxide}, PNP(tsac)

(**1**, C₄₃H₃₄N₂O₂P₂S₂)

To 20 cm³ of an aqueous solution of 286 mg bis(triphenylphosphine)iminium chloride (0.50 mmol) was slowly added 20 cm³ of an aqueous solution of 99.0 mg thiosaccharin (0.50 mmol) under continuous mechanical stirring. The light yellow polycrystalline precipitate was filtered off, washed several times with cold H₂O. Yellow single crystals, some of them suitable for X-ray structural analysis, were obtained by slow evaporation of saturated solutions of the salt in absolute ethanol. Yield: 261 mg (71%). Molar conductance (1.0 × 10⁻³ M, in acetone): 127 Ω⁻¹ mol⁻¹ cm⁻¹. ¹H NMR (300 MHz, DMSO-d₆): δ = 8.08 (d, ³J(H,H) = 7.6 Hz, H₆), 7.94–7.36 (m, PNP⁺ and tsac) ppm; ¹³C NMR (75 MHz, DMSO-d₆): for tsac, δ = 192.98 (C1), 138.28 (C7), 136.92 (C2), 132.00 (C5), 130.98 (C4), 125.42 (C3), 119.00 (C6) ppm; for phenyl groups of PNP⁺, δ = 133.82 (C1), 129.71 (C2 and C6), 127.74 (C3 and C5), 126.30 (C4) ppm; ³¹P{¹H} NMR (121 MHz, DMSO-d₆): δ = 76.5 (¹J(³¹P,¹³C) = 99.2 Hz, PNP⁺) ppm; UV-Vis (CHCl₃, c = 1 × 10⁻⁴ mol dm⁻³): λ_{max} (ε) = 242 (17100), 267 (10600), 344 (5850) nm (mol⁻¹ dm³ cm⁻¹); (KBr disks) λ_{max} = 205 (vs), 235 (s), 266 (m), 344 (sh), 357 (m) nm.

*Tetrabutylammonium{1,2-benzisothiazol-3-(2H)-thionate-1,1-dioxide}, NBu₄(tsac) (**2**, C₂₃H₄₀N₂O₂S₂)*

To 12 cm³ of an aqueous solution of 32.9 mg tetrabutylammonium tetrafluoroborate (0.10 mmol) another 4 cm³ of an aqueous solution of 19.9 mg thiosaccharin (0.10 mmol) was slowly added at room temperature under continuous mechanical stirring. The yellow polycrystalline precipitate formed was filtered off and then washed with cold H₂O. It was re-crystallized from saturated aqueous solutions by slow evaporation of the solvent. Yield: 27.0 mg (61.0%). Molar conductance (1.0 × 10⁻⁴ M, in H₂O): 143 Ω⁻¹ mol⁻¹ cm⁻¹. ¹H NMR (300 MHz, DMSO-d₆): for tsac, δ = 8.07 (d, ³J(H,H) = 7.7 Hz, H₆), 7.94–7.65 (m, 3H) ppm; for NBu₄⁺, δ = 3.02–2.89 (m, H_α), 1.44–1.29 (m, H_β), 1.09 (sex, ³J(H,H) = 7.4 Hz, H_γ), 0.72 (t, ³J(H,H) = 7.4 Hz, H_δ) ppm; ¹³C NMR (75 MHz, DMSO-d₆): for tsac, δ = 192.16 (C1), 138.48 (C7), 137.11 (C2), 132.21 (C5), 130.97 (C4), 125.40 (C3), 119.20 (C6) ppm; for NBu₄⁺, δ = 58.00 (C_α), 23.46 (C_β), 19.57 (C_γ), 13.81 (C_δ) ppm; UV-Vis (water, c = 1 × 10⁻⁴ mol dm⁻³): λ_{max} (ε) = 205 (15600), 281 (4750), 330 (5040) nm (mol⁻¹ dm³ cm⁻¹); (KBr disks, λ_{max}): 207 (vs), 258 (m), 346 (m, broad).

X-Ray Diffraction Data

Diffraction data were collected on an Enraf-Nonius CAD4 diffractometer with EXPRESS [25] and reduced by Lorentz and polarization effects with XCAD4 [26]. The data were corrected numerically for absorption with PLATON [27]. The structure was solved by direct and Fourier methods with SHELXS [28] and its non-H atom refined by full-matrix least-squares with SHELXL [29]. The hydrogen atoms were positioned stereo-chemically and refined with the riding model. The structural data has been de-

posited with the Cambridge Crystallographic Data Center (No. CCDC-629368).

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