$(Ph_4P)S_6$—A Compound Containing the Cyclic Radical Anion $S_6^{\bullet-}$**

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Dedicated to Professor Max Schmidt on the occasion of his 75th birthday

The spectroscopic evidence of the $S_3^{\bullet-}$ radical anion as the pigment of Lapis Lazuli (ultramarine) led to the unravelling of the more than 5000-year-old secret of this beautiful blue dye.[1] At the same time, the green $S_2^{\bullet-}$ ion in ultramarine green was established. On the other hand, it is still unclear which entity is at the origin of ultramarine red, for which species such as S_4 and $S_4^{\bullet-}$ have been discussed. All these radical anions are also contained in solutions of sulfur in oleum, of polysulfides in organic solvents, and in various salt melts.[2–4]

Unexpectedly, we now obtained orange-red needles of $Ph_4P^+S_6^-$ (**1**) through the reaction of sulfane and tetraphenylphosphonium azide in the presence of trimethylsilyl azide at 20 °C. In this process, **1** is formed topochemically at the surface of $Ph_4P^+N_3^-$, with the hydrogen diazide,[5] which is developed at first, acting as the oxidant of sulfane. For the formation of **1** we propose the overall reaction given in Equation (1). This is supported by the identification of all reaction products. The fact that $Ph_4P^+[H(N_3)_2]^-$ (**2**) is also involved in the formation of **1** follows from the observation that, at first, white needles of **2** are formed which, after a few days, disappear under the simultaneous formation of **1**. The identity of these crystals was established by comparing their X-ray structure with that of **2**,[5] which has been determined previously.[6] Solutions of **1** decompose in dichloromethane within a few seconds; crystals of **1** are conserved only slightly longer in moist air.

$$2\,Ph_4P^+N_3^- + 20\,Me_3SiN_3 + 22\,H_2S \longrightarrow \underset{\mathbf{1}}{2\,Ph_4P^+S_6^-} + 10\,(Me_3Si)_2S + 11\,NH_4N_3 + 11\,N_2 \quad (1)$$

Compound **1** crystallizes monoclinically in the space group *C*2/*c* with four formula units per unit cell.[7] The P atoms of the cations adopt twofold site symmetry, whereas the S_6^- ions form centrosymmetric rings of C_{2h} symmetry in the chair conformation (Figure 1). The packing is completely equivalent with that in the crystal of $Ph_4P^+NbBr_6^-$.[8] The anions in **1** are separated by the bulky cations, which contributes to their stability in the crystal, similar to the situation for the S_n^- ions in zeolites and sodalites. The S_6^- ions in **1** are disordered in two positions with an occupancy factor 1:1 (Figure 2).[9]

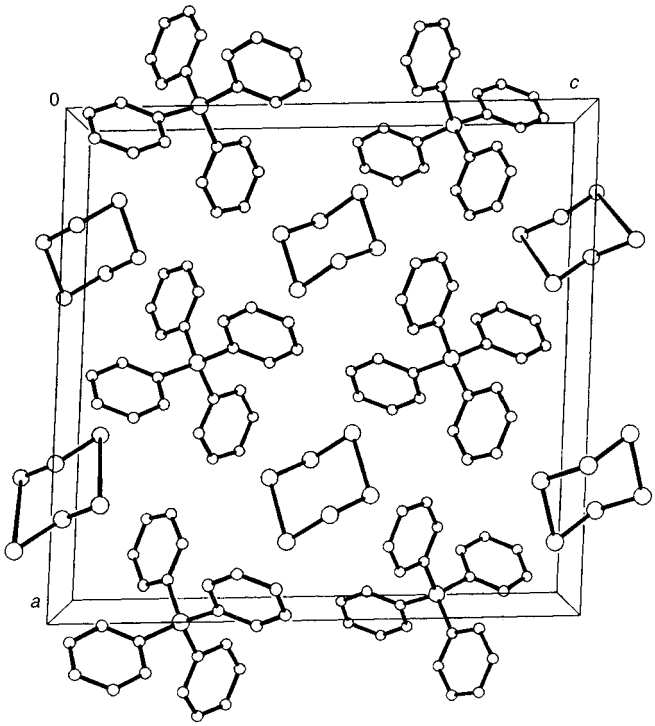

Figure 1. Unit cell of **1** without split positions of the anion.

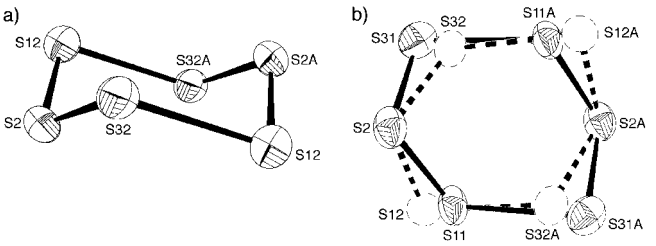

Figure 2. a) Structure of the $S_6^{\bullet-}$ ion and b) the disorder behavior of this ion in the crystal.

The structure of the S_6^- ions is characterized by two long, central S–S bonds with distances of 263.3(4) pm, which connect the S_3 units. The angle between the plane defined by an S_3 unit and the S_4 plane of the S_6^- ions adopts values of 112° and 108° for the two disordered species. The average S–S distance (206.0 pm) in the two S_3 fragments in **1** lies in the range of bond lengths in neutral sulfur rings and is characteristic for a normal S–S single bond.[10] Note that significantly longer S–S distances have been associated with bonds, for example, 239 pm in $Na_2S_2O_4$,[11] 253 pm in $[Re^{VII}Cl_4(N_2S_2)]^-$,[12] as well as 258 pm for the transannular

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bonds in S_4N_4,[13] and 286 pm in the S_8^{2+} ion.[14] The latter is described as an S–S bond with π symmetry.

The radical nature of **1** follows from the EPR spectra[15] of powder samples at $T = 295$ and 115 K. Whereas at room temperature only one broad line at $g_0 = 2.031$ can be observed, an X-band EPR spectrum occurs at $T = 115$ K (Figure 3),

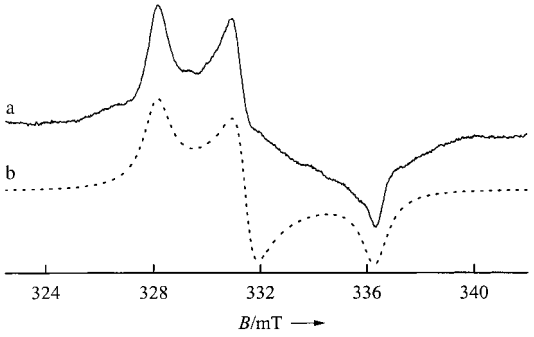

Figure 3. a) Experimental and b) simulated X-band EPR spectrum of a $(PPh_4)S_6$ powder sample at $T = 115$ K.

which is characterized by a rhombic symmetric ***g*** tensor. The eigenvalues of the ***g*** tensor, $g_1 = 2.056$, $g_2 = 2.036$, and $g_3 = 2.003$ (g_i values ± 0.002), are similar to those found in numerous EPR spectra of ultramarine samples that are ascribed to S_2^-, S_4^- and, in particular, S_3^- radical anions.[1, 2, 17] The g_1 value of **1** clearly deviates from the g_1 values of ≈ 2.049 determined for open-chain radicals. This is indicative for differences in s/p hybridization of the S atoms. The weak asymmetry observed for the signals of **1** in the g_1 and g_2 range has its origin in the crystallographic disorder of the S_6^- ions.

To better understand the nature of the $S_6^{\bullet -}$ chair structure in Ph_4PS_6, we have quantum chemically analyzed a series of cyclic $S_6^{\bullet -}$ and S_6 systems using both density functional (BP86/TZ2P)[18] and ab initio (MP2/6-31 + G*)[19] theory. All energies reported are corrected for zero-point vibrational effects ($\Delta E + ZPE$). For explorations of the potential energy surface (PES), see reference [20]. In agreement with the experimentally determined structure of $S_6^{\bullet -}$, we find a stationary point on the BP86/TZ2P PES that corresponds with the C_{2h}-symmetric chair conformation of **1a** (Figure 4). Species **1a** is composed of two loosely bound S_3 fragments ($d_{SS} = 207.5$ pm) connected through somewhat longer sulfur–sulfur bonds of 246.0 pm. Interestingly, **1a** is not a stable minimum on the PES. It turns out, instead, to be a transition state for the automerization of a distorted C_2-symmetric chair **1b**, which is slightly more stable, that is, by 8.4 kJ mol^{-1}. The S_3 fragments in **1b** are connected through a short (212.5 pm) and a long (294.3 pm) sulfur–sulfur bond (Figure 4). The relatively shallow PES explains the differences between the computed and the experimentally determined distances between the S_3 fragments (see below).

A detailed analysis of the electronic structure at the BP86/TZ2P level reveals two distinct bonding mechanisms that keep the S_3 units in the $S_6^{\bullet -}$ six-membered ring systems **1a** and **1b** together (Figure 5): 1) an electron-pair bond between the $2b_1$ SOMOs of both fragments and 2) a three-electron bond between the $1a_2$ SOMO of the diradical $S_3^{\bullet\bullet}$ and the $1a_2$

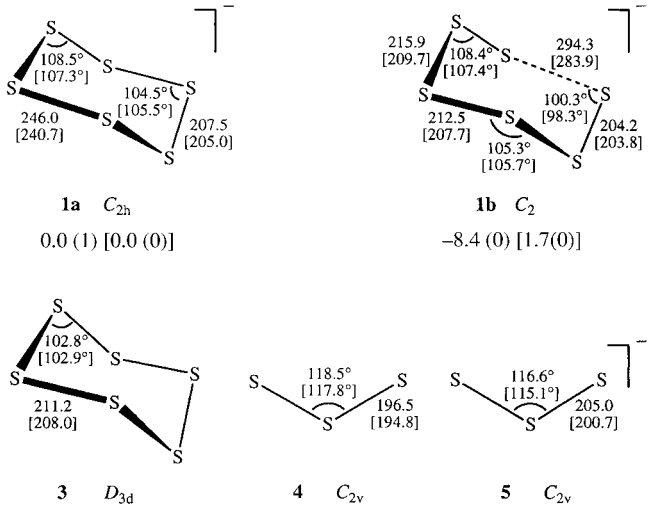

Figure 4. Structures [pm, °] optimized at BP86/TZ2P and MP2/6-31 + G* (in square brackets). For **1a** and **1b**, relative energies [kJ mol^{-1}] and the number of normal modes with negative eigenvalues (in parentheses) are shown.

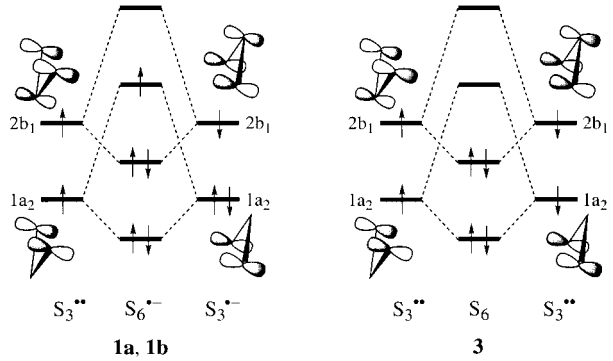

Figure 5. Schematic orbital interaction diagram for $S_6^{\bullet -}$ and S_6 based on the interactions of two S_3 fragments.

HOMO of $S_3^{-\bullet}$. Note that whereas neutral S_3 has a closed-shell ground state, it becomes a diradical after valence excitation of an electron from $1a_2$ to $2b_1$ (Figure 5). The overall bond energies relative to ground state S_3 (**4**) and $S_3^{\bullet -}$ (**5**) amount to -96.7 (**1a**) and -105.0 kJ mol^{-1} (**1b**). An exhaustive discussion of sulfur–sulfur three-electron bonding is given in reference [21]. It is instructive to compare this with the interaction between two $S_3^{\bullet\bullet}$ fragments in the neutral S_6 ring **3** (Figures 4 and 5). The loss of an antibonding electron turns the three-electron bond of $S_6^{\bullet -}$ into a more stabilizing electron-pair bond in S_6 (**3**). Consequently, the sulfur–sulfur bonds between the S_3 fragments in **3** are shorter (211.2 pm) and stronger (overall bond strength: -159.8 kJ mol^{-1}) than the ones in the ions **1a** and **1b**.

The chair conformations **1a** and **1b** are rather close in energy (BP86/TZ2P: 8.4 kJ mol^{-1}). This is confirmed by ab initio MP2/6-31 + G* computations (Figure 4). Note, however, that at the MP2/6-31 + G* level the chair conformation **1a** is a stable minimum which is 1.7 kJ mol^{-1} lower in energy than **1b**. In view of these minimal energy differences, we expect that environment effects (e.g., packing, counterions) play a decisive role in determining which particular geometry

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the $S_6^{\bullet-}$ ring eventually adopts in the crystal. Apparently, in Ph_4PS_6, this is the chair conformation **1a**.

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[6] At the beginning of reaction (1), the surface of the Ph_4PN_3 crystals adopts a green color that disappears again as the reaction proceeds further. This phenomenon is possibly due to the labile S_2^{-}.[1–4, 17] Reaction (1) takes 14 days during which the atmosphere of 1 bar of sulfane is repeatedly refreshed. The side products NH_4N_3 and $S(SiMe_3)_2$ were isolated through vacuum sublimation and distillation, respectively, and characterized by IR spectroscopy.

[7] Crystal structure analysis of **1**: IPDS (Stoe), $Mo_{K\alpha}$ radiation, graphite monochromator, $T = 173(2)$ K, cell determination with 2300 reflections, corrections: Lorentz- and polarization factor, numerical absorption correction, $\mu(Mo_{K\alpha}) = 6.3\ cm^{-1}$, direct methods, refinement with respect to F^2, H atom layers in computed positions. Computer programs: SHELXS-97, SHELXL-97, SHELXTL, PLATON-98. Space group $C2/c$, $Z = 4$, $a = 1800.6(2)$, $b = 744.9(1)$, $c = 1834.8(2)$ pm, $\beta = 93.08(1)^\circ$, $V = 2457.4(5)$ Å^3, $\rho_{calcd} = 1.437\ g\,cm^{-3}$, measurement range $\theta_{max} = 51.91^\circ$. A total of 9648 measured reflections, 2328 of which were independent, 1249 with $F_0 > 4\sigma(F_0)$, 160 parameters, $R_1 = 0.0519$, wR_2 (all data) $= 0.1421$. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-147432. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Conical Intersections in Charge-Transfer Induced Quenching**

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A detailed knowledge of the molecular mechanisms that govern the chemically unproductive and thus undesirable quenching of excited states by external additives is essential for the rational development of efficient photochemical reactions, artificial photosynthetic systems, and functional photonic devices. We are currently employing high-level quantum chemical methods to provide a comprehensive quenching path mapping for n,π*-excited states of compounds such as ketones and azoalkanes. It was shown that quenching by hydrogen donors is induced by a conical intersection (CI) located halfway along the reaction coordinate for hydrogen abstraction (Figure 1a).[1, 2] Herein, we introduce a new quenching mechanism by electron donors that operates in a similar way through a CI, which is located halfway along a

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