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Unravelling Lawesson's Reagent – The Structure of Monomeric (4-Methoxyphenyl)phosphine Disulfide

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We describe the isolation, IR and UV/Vis spectroscopic characterization of (4-methoxyphenyl)phosphine disulfide in argon matrices at 10 K. The title compound proved to be highly photolabile; irradiation with UV light (λ =334 nm) led to rearrangement to the equally unreported 3-(4-methoxyphenyl)-1,2,3-dithiaphosphirane. Photoreversion can be achieved upon irradiation at λ =465 nm.

Lawesson's reagent (2,4-bis(4-methoxyphenyl)-1,3,2,4dithiadiphosphetane-2,4-dithione; 2), first synthesized by Lecher and co-workers,¹ is the most widely used reagent for the synthesis of large number of S-heterocyclic compounds.¹⁻⁶ The active form of the reagent is assumed to be its monomer 4methoxy-phenylphosphine disulfide (1, Scheme 1) but this species has never been observed spectroscopically.^{3,7,8} The difficulty in isolating compounds of type RPE_2 (R = aryl, alkyl; E=O, S, Se) is mainly due to the strong electrophilicity of the phosphorus center; RPE2 species instantly undergo selfaggregation to form cyclic or linear polymeric compounds.9-13 Numerous attempts have been undertaken to synthesize the monomeric RPE₂ species. Their detection generally is only possible in gas-phase^{14, 15} or through low-temperature matrix isolation spectroscopy.¹⁶⁻¹⁸ The kinetic lability of these species can be compensated by using bulky substituents that inhibit dimerization as successfully demonstrated with the preparation of isolable dithioxophosphoranes.¹⁹ N-Heterocyclic carbene (NHC) are strong σ -donors and can be utilized as ligands for the stabilization ArPE₂ compounds.²⁰

Recently, we reported the synthesis of the previously elusive phenyldioxophosphorane (the phosphorus analogue of nitrobenzene, PhPO₂) under matrix isolation conditions by the reaction of triplet phenylphosphinidene with triplet molecular oxygen (³P-O₂).^{18,20} To the best of our knowledge, there are no

band at 1467 cm⁻¹ shows a strong red shift of 357 cm⁻¹ and can thus be assigned to the CH3 asymmetric deformation (computed at 1176 cm⁻¹) of 1, in good agreement with the computed shift of 372 cm⁻¹. Other weak bands at 1462, 1186, and 1035 cm⁻¹ show large and moderate isotope shifts of 399, 228 and 41 cm⁻¹, also in good agreement with computed shifts of 415, 237, and 43 cm⁻¹, respectively. The good agreement

To confirm these assignments, we also prepared d_3 -1 from d_3 -2,



reports on the identification and characterization of 1, which we

Scheme 1. 4-Methoxy-phenylphosphine disulfide (1) generated from Lawesson's reagent 2 via pyrolysis and trapping in an argon matrix. Subsequent photochemistry to 3-(4methoxyphenyl)-1,2,3-dithiaphosphirane (3). Previously prepared lighter congeners of 1 and 3, 4 and 5, respectively.

Compound 1 was prepared from 2 via evaporation into the gas phase (at 150 °C), where it effectively dissociates to give two equivalents of 1; these are subsequently trapped with an excess of argon at 10 K. Dissociation of 2 to 1 is indeed the generally accepted mechanism for the preparation of 1 in solution as well (even though it has never been identified in solution). The excellent agreement between the experimental and unscaled B3LYP/6-311++G(3df,3pd) computed IR spectrum is taken as evidence for the successful preparation of 1 (Figures 1, S1, and Table S1). The most prominent IR bands attributed to 1 at 1591, 1267, and 1096 cm⁻¹ can be assigned to the C=C stretch, C–O, and C-P stretching vibrations. With the aid of the computations, the additional other intense IR bands of medium intensity can also be assigned to 1 (Figure 1, Figure S1, and Table S1).

which leads to characteristic isotopic shifts. For example, the IR

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1.0

0.8

0.4

0.2

0.0

200

0.6

Absorbance I

0.

300

263

329

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between the computed (B3LYP/6-311++G(3df,3pd)) and experimental frequencies of the **1** and d_3 -**1** isotopologues underscores the successful preparation of **1** (Figure 1, Figure S2, and Table S1).

Figure 1. IR spectra showing the product of pyrolysis of 2 in argon matrix with subsequent trapping in an argon matrix at 10 K. (a) IR spectrum of 1 computed at B3LYP/6-311++G(3df,3pd) (b) IR difference spectra showing the (unscaled). photochemistry of **1** after irradiation with λ = 334 nm in argon at 10 K. Downward bands assigned to 1 disappear while upward bands assigned to 3 appear after 5 min irradiation time. (c) IR spectrum of 3 computed at B3LYP/6-311++G(3df, 3pd) (unscaled). (d) IR spectrum of d_3 -1 computed at B3LYP/6-311++G(3df,3pd) (unscaled). (e) IR difference spectra showing the photochemistry of d_3 -1 after irradiation with λ = 334 nm in argon at 10 K. Bands pointing downwards assigned to d_3 -1 disappear and bands pointing upwards assigned d_3 -3 appear after 5 min irradiation time. (e) IR spectrum of d_3 -3 computed at B3LYP/6-311++G(3df,3pd) (unscaled).

The UV/Vis spectrum of matrix isolated **1** reveals a strong absorption band at $\lambda_{max} = 329$ nm (Figure 2), which is in good agreement with its computed UV/Vis spectrum using time-dependent density functional theory (TD-DFT); TD-B3LYP/6-311++G(3df,3pd) computations exhibit two strong transitions at 333 nm (f = 0.342) and 323 nm (f = 0.087) as well as four weak transitions at 290 nm (f = 0.017), 249 nm (f = 0.046), 237 nm (f = 0.048), and 234 nm (f = 0.027), respectively (Figure 2 solid line).

Irradiation (λ = 334 nm) of **1** in an argon matrix at 10 K resulted in the almost complete bleaching of the IR bands of **1** and formation of a new compound with strong IR absorptions at 1596, 1260, 1092, and 826 cm⁻¹ (Figure 1b). The major constituent of the photolysis products of **1** was identified as 3-(4-methoxyphenyl)-1,2,3-dithiaphosphirane **3**. The formation of **3** from **1** is also strongly supported by isotopic labeling experiments using *d*₃-**1**. The large shifts are found to the CH₃ asymmetric deformation and CH₃ rocking modes of **3** of 350 and 225 cm⁻¹, in good agreement with computed shifts of 379, and 233 cm⁻¹ (Figure 1, Table S2). The shift of the C–O stretching mode is only 36 cm⁻¹ (44 cm⁻¹ at the B3LYP/6-311++G(3df,3pd)

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level of theory). The IR frequencies, intensities, vand isotopic shifts of two isotopologs (**3** and d_3 -**3**) descharge with the computed data.

Figure 2. Solid line: UV/Vis spectrum of **1** isolated at 10 K in Ar. Dashed line: UV/Vis spectrum of **3** at 10 K; the photochemistry of **1** after irradiation at $\lambda = 334$ nm in argon at 10 K. Inset: computed [TD-B3LYP/6-311++G(3df,3pd)] electronic transitions for **1** and **3**.

400

Wavelength, nm

The UV/Vis spectrum of matrix-isolated **3** shows transitions at 263 nm (strong), 297 nm (weak), and 493 (weak, broad) (Figure 2, dashed line). All bands of **3** correlate well with the values of the electronic excitations at 263 nm (f = 0.325), 297 nm (f = 0.063), and 442 nm (f = 0.007) computed at TD-B3LYP/6-311++G(3df,3pd). According to the orbitals involved in the electronic excitations, the weak absorption band in the visible at 442 nm is an $n \rightarrow \pi^*$ transition, while the strong band at 263 nm corresponds to a $\pi \rightarrow \pi^*$ transition (Figure S3).

Irradiation of the sample at λ = 465 nm led to the simultaneous disappearance of both IR as well as UV/Vis bands of **3**, with concomitant appearance of the IR and UV/Vis bands of **1**. The reversible photochemistry (Scheme 1) demonstrates that **1** and **3** exist in a stationary equilibrium.

Next we examine the nature of the phosphorus-sulfur bonds in 1 and how this relates to its reactivity, which often invokes some ylide-type resonance form (1a) (Figure 3).^{3,4} Phosphorus compounds featuring P=S double bonds are rare and only a few examples have been isolated and characterized by single-crystal X-rav diffraction analysis, dithioxo(tri-terte.g., butylphenyl)phosphorene (6).^{19,20} The P=S bond distances in 1 are 1.920 and 1.919 Å at B3LYP/6-311++G(3df,3pd) (1.919 and 1.918 Å at MP2/cc-pVTZ) and hence in the same range as in 6 (1.90 Å).¹⁸ They are only slightly shorter than the P=S bond distances (1.978 and 1.968 Å) in the N-Heterocyclic carbene (NHC) adduct of (phenyl)phosphine disulfide (7).²⁰ The slight differences in the two P=S bond lengths arises from the nonsymmetric orientation of the para-methoxy group in 1. The P–S bond distances in **3** are computed to be 2.134 Å (B3LYP/6-311++G(3df,3pd)) and 2.124 Å (MP2/cc-pVTZ), respectively (Figure 3). The NBO charges at the phosphorus and at the sulfur atoms in 1 are 0.99, -0.38 (anti), and -0.40 (syn). That is, there

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is no indication of an ylide-type structure on the basis of the rather symmetric charge distribution. As expected, compound **1** has large singlet—triplet energy separation of $\Delta E_{ST} = -37.3$ kcal mol⁻¹ at B3LYP/6-311++G(3df,3pd), underlining its singlet ground-state nature.

The nature of the P=S bond in **1** can also be judged by comparison with the P=S stretching modes in related compounds. Several unstable thiophosphines (X–P=S; X = Cl, Br, F) have been characterized spectroscopically either in the gas phase²¹ or have been isolated in argon matrix.^{22,23} F–P=S shows a strong P=S stretching frequency at 720 cm⁻¹, while Br–P=S absorbs at 712 cm⁻¹. The IR absorption corresponding to the SPS asymmetric vibration for **1** is found at 805 cm⁻¹ (computed at 798 cm⁻¹) (Figure 1, Figure S2 and Table S1). Figure S4 presents the spanned vector displacements of the SPS asymmetric vibration; the displacement vector of the P–S_{anti} bond from the initial position to the final position marginally larger than that of the P–S_{syn} bond. That is, on spectroscopic grounds, **1** displays two rather similar, typical P=S double bonds.



Figure 3. Resonance structure for **1** (top). Bottom: Bond lengths (Å) of **1** and **3** at the B3LYP/6-311++G(3df,3pd) level. Values in parentheses at MP2/cc-pVTZ. The P–S bond lengths in **6** and **7** are from ref 18 and 19.

The question then remains why 1 reversibly rearranges to 3 upon irradiation while the closely related phenyldioxophosphorane (4, Scheme 1) does not rearrange upon photoexcitation.¹⁷ To gain more information on the photochemical reactivity of both 1 and 3, we looked at the energy differences and transition states for ring-opening connecting these pairs of species. The relative energy ordering of the two isomers (1 and 3) shows that 3 lies 16.8 kcal mol⁻¹ (including zero-point vibrational energy correction, ZPVE, denoted as ΔH_0) above the **1**. The transition structure for the **1** \rightarrow 3 conversion is associated with a barrier of +20.2 kcal mol⁻¹ This is in marked contrast to the (ΔH_0^{\ddagger}) (Figure 4). corresponding structures of the oxygen analogues (4 and 5), where the dioxophosphorane structure 4 is much more stable (90.7 kcal mol⁻¹ at the B3LYP/6-311++G(3df,3pd)) than the dioxophosphirane form 5.18 This is due to the much higher polarizability of sulfur and its comparable electronegativity relative to phosphorus,²⁴ which is supported by the large reaction enthalpy of the homodesmotic reaction showing eq. (ΔH_r) of -73.9 kcal mol⁻¹ at the B3LYP/6-3914-0(300,300,0034D) 10



ζ (reacton coordinate)

Figure 4. Isomerization pathways $1 \rightarrow 3$, and $4 \rightarrow 5$, respectively. Stationary points and transitions structures were computed at B3LYP/6-311++G(3df,3pd).



In summary, we present the synthesis, IR and UV/Vis spectroscopic characterization of elusive 4-methoxyphenylphosphine disulfide (1), isolated in an argon matrix at 10 K for the first time. This hitherto unreported molecule has been postulated to as the key intermediate derived from Lawesson's reagent (which is its dimer) that is extremely useful in sulfur transfer reactions. Structure **1** proved to be highly photolabile and irradiation with light of λ = 334 nm led to rearrangement to the hitherto unknown cyclic isomer 3-(4-methoxyphenyl)-1,2,3dithiaphosphirane (3), which represents the first threemembered organophosphorus-chalcogen ring incorporating a phosphorus atom in the oxidation state +3.11,25 Structure 3 rearranges back to **1** upon irradiation at λ = 465 nm. Since the activation barrier for the $\mathbf{1} \rightarrow \mathbf{3}$ conversion is only +20.2 kcal mol⁻¹ (ΔH_0^{\dagger}), this conversion is also thermally accessible at elevated temperatures. The structures and IR spectra of 1 and **3**, and their deuterated isotopologues $(d_3-1 \text{ and } d_3-3)$ were unambiguously assigned through matching of experimental and DFT computations at B3LYP/6-311++G(3df, 3pd) level of theory. According to B3LYP and MP2 computations and spectral comparisons, the sulfur atoms in the two isomers each are essentially indistinguishable. An NBO analysis reveals negative charges at the sulfur atoms of-0.38 (anti), and -0.40 (syn) and a positive charge at the phosphorus of +0.99 for 1, and -0.18(sulfur) and +0.64 (phosphorus) for 3 (B3LYP/6-311++G(3df, 3pd)). The charge separation is also apparent from the computed high dipole moment of 6.26 D for 1, compared to 4.37 D for 3. Our bonding analysis finds no indications for ylide-

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or biradical-type species and the structure of **1** is best depicted with two nearly equal P=S double bonds.

- 24 M. T. Molina, M. Yanez, O. Mo, R. Notario and J. L. M. Abboud, Wiley, 1977-1997, 1997, pp. 1355-1496DOI: 10.1039/C8CC00034D
- 25 D. Gudat, Coord. Chem. Rev., 1997, 163, 71-106.

Conflicts of interest

No competing financial interests have been declared.

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Notes and references

- H. Z. Lecher, R. A. Greenwood, K. C. Whitehouse and T. H. Chao, 1 J. Am. Chem. Soc., 1956, 78, 5018-5022.
- S. Scheibye, B. S. Pedersen and S. O. Lawesson, Bull. Soc. Chim. 2 Belg., 1978, 87, 229-238.
- 3 T. Ozturk, E. Ertas and O. Mert, Chem. Rev., 2007, 107, 5210-5278.
- 4 M. Jesberger, T. P. Davis and L. Barner, Synthesis, 2003, 1929-1958.
- 5 G. Mloston, R. Hamera-Faldyga, M. Celeda, A. Linden and H. Heimgartner, J. Sulfur Chem., 2017, 38, 475-487.
- 6 G. Mloston, R. Hamera-Faldyga and H. Heimgartner, Phosphorus, Sulfur Silicon Relat. Elem., 2017, 192, 732-736.
- L. Legnani, L. Toma, P. Caramella, M. A. Chiacchio, S. Giofre, I. 7 Delso, T. Tejero and P. Merino, J. Org. Chem., 2016, 81, 7733-7740.
- M. A. Chiacchio, L. Legnani, P. Caramella, T. Tejero and P. Merino, 8 Eur. J. Org. Chem., 2017, 2017, 1952-1960.
- 9 L. D. Quin, Coord. Chem. Rev., 1994, 137, 525-559.
- 10 M. S. J. Foreman and J. D. Woollins, Dalton, 2000, 1533-1543.
- 11 W. E. van Zyl and J. D. Woollins, Coord. Chem. Rev., 2013, 257, 718-731.
- 12 F. D. Henne, F. A. Watt, K. Schwedtmann, F. Hennersdorf, M. Kokoschka and J. J. Weigand, Chem. Commun., 2016, 52, 2023-2026.
- 13 B. Cetinkaya, P. B. Hitchcock, M. F. Lappert, A. J. Thorne and H. Goldwhite, J. Chem. Soc., Chem. Commun., 1982, 691-693.
- 14 L. N. Heydorn, P. C. Burgers, P. J. A. Ruttink and J. K. Terlouw, Chem. Phys. Lett., 2003, 368, 584-588.
- 15 H. Keck, W. Kuchen, H. Renneberg, J. K. Terlouw and H. C. Visser, Angew. Chem. Int. Ed., 1991, 30, 318-320.
- 16 R. Ahlrichs, C. Ehrhardt, M. Lakenbrink, S. Schunck and H. Schnoeckel, J. Am. Chem. Soc., 1986, 108, 3596-3602.
- 17 S. N. Jenny and J. S. Ogden, J. Chem. Soc., Dalton Trans., 1979, 1465-1467.
- 18 A. Mardyukov, D. Niedek and P. R. Schreiner, J. Am. Chem. Soc., 2017, 139, 5019-5022.
- 19 R. Appel, F. Knoch and H. Kunze, Angew. Chem., 1983, 95, 1008-1009.
- 20 D. Bockfeld, T. Bannenberg, P. G. Jones and M. Tamm, Eur. J. Inorg. Chem., 2017, 2017, 3452-3458.
- 21 M. Binnewies, B. Solouki, H. Bock, R. Becherer and R. Ahlrichs, Angew. Chem., 1984, 96, 704-705.
- 22 H. Schnoeckel and S. Schunck, Z. Anorg. Allg. Chem., 1987, 552, 163-170.
- 23 H. Schnoeckel and S. Schunck, Z. Anorg. Allg. Chem., 1987, 552, 155-162.