Structure of 2,4-Dinitrobenzenesulphenylimino(triphenyl)phosphorane, $Ph_3PNSC_6H_3(NO_2)_2$-2,4[†]

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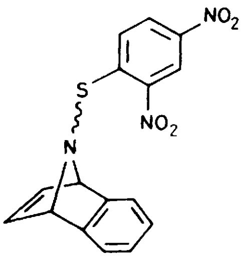
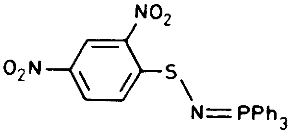
The compound $Ph_3PNSC_6H_3(NO_2)_2$-2,4 was isolated from the reaction of the 2,4-dinitrobenzenesulphenamide of 1,4-dihydro-1,4-iminonaphthalene with *trans*-[IrCl(CO)(PPh$_3$)$_2$], and its structure has been determined. Bond angles at N [123.1(5)°] and S [101.4(5)°] and the bond distances P=N [1.566(7) Å], S–N [1.660(8) Å], and C–S [1.728(11) Å] indicate the presence of localised double and single bonds with no significant declocalisation of the lone-pair charge at nitrogen. The 2,4-dinitrophenyl ring is −8.9° out of the N,S,C plane and the PNSC torsion angle is −134.6°.

The report[1] that at 120 °C the 2,4-dinitrobenzenesulphenamide of 1,4-dihydro-1,4-iminonaphthalene (**1**) efficiently generates 2,4-dinitrobenzenesulphenylnitrene, $NSC_6H_3(NO_2)_2$-2,4, prompted us to investigate the use of (**1**) in the synthesis of transition-metal nitrene complexes. A preliminary experiment revealed that compound (**1**) reacted with *trans*-[IrCl(CO)-(PPh$_3$)$_2$] in refluxing toluene to afford a dark red solution from which red crystals of the 2,4-dinitrobenzenesulphenylimino-(triphenyl)phosphorane (**2**) were isolated and characterised by an *X*-ray diffraction study. The iminophosphorane (**2**), which contains a S–N single bond, may be formed by attack of the sulphenylnitrene $NSC_6H_3(NO_2)_2$-2,4 upon either co-ordinated or free triphenylphosphine liberated by the iridium during the course of the reaction. In view of the limited amount of structural data available for singly bonded SN compounds[2,3] we report the structure of $Ph_3PNSC_6H_3(NO_2)_2$-2,4 (**2**).



(**1**)



(**2**)

Experimental

Compound (**1**) (0.08 g, 0.23 mmol) and *trans*-[IrCl(CO)-(PPh$_3$)$_2$] (0.18 g, 0.23 mmol) were refluxed in toluene for 12 h under an atmosphere of nitrogen. The resulting dark red solution was evaporated to dryness and the residue was washed with light petroleum (3 × 50 cm^3, b.p. 40—60 °C), extracted with toluene (2 × 15 cm^3), and filtered. The filtrate was concentrated and cooled to 0 °C to afford a mixture of dark red and white crystals which were dissolved in dichloromethane (2 cm^3) and chromatographed on a short silica column (15 cm). Elution, initially with light petroleum (b.p. 40—60 °C) and then with diethyl ether, gave a red solution. This solution was concentrated to 5 cm^3 and cooled to 0 °C to give red crystals of compound (**2**), m.p. 200—201 °C, yield 0.065 g [60% based on (**1**)].

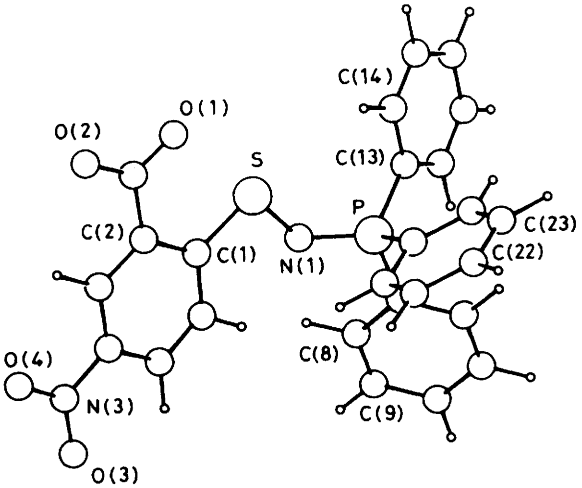


Figure. Molecular structure of compound (**2**) showing the atom numbering scheme

Crystal Structure Determination.—A crystal of compound (**2**) of dimensions *ca.* 0.5 × 0.2 × 0.15 mm was sealed in a Pyrex capillary. The cell dimensions were obtained from an oscillation photograph about the *c* axis of the crystal, and from the least-squares refinement of 22 reflections. Intensity data were collected at 293 K on a Stoe STADI-2 Weissenberg diffractometer using an ω-scan technique in the range $7 < 2\theta < 48°$. 3 517 Independent reflections were measured from Weissenberg layers $hk(l = 0—9)$. The 1 270 unique reflections having $I \geqslant 3\sigma(I)$ were corrected for Lorentz and polarisation effects.

Crystal data. $C_{24}H_{18}N_3O_4PS$, $M = 476.6$, monoclinic, $a = 14.603(6)$, $b = 16.651(6)$, $c = 9.505(12)$ Å, $\beta = 100.8(1)°$, $U = 2\,270.3$ Å^3, $Z = 4$, $D_c = 1.39$ g cm^{-3}, $F(000) = 984$, space group $P2_1/a$, Mo-K_α *X*-radiation, $\lambda = 0.710\,69$ Å, μ(Mo-K_α) = 2.03 cm^{-1}.

The structure was solved by direct methods using the TREF option of SHELXS 84,[4] and subsequent calculations were carried out using the computer program SHELX.[5] The final stages involved full-matrix least-squares refinement of all non-hydrogen atoms with anisotropic thermal parameters. The hydrogen atoms were placed in calculated positions with

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[†] *Supplementary data available* (No. SUP 56382, 4 pp.): thermal parameters, complete bond lengths and angles. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii—xx. Structure factors are available from the editorial office.

Table 1. Atomic positional (fractional co-ordinates) parameters, with estimated standard deviations in parentheses, for $Ph_3PNSC_6H_3(NO_2)_2$-2,4 (**2**)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
C(1)	0.012 2(7)	−0.007 8(6)	−0.241 0(14)	H(61)	0.113 5(7)	−0.072 6(6)	−0.090 5(13)
C(2)	−0.056 5(7)	−0.017 7(6)	−0.361 0(14)	H(81)	0.181 1(5)	−0.046 9(5)	0.156 4(10)
C(3)	−0.075 4(7)	−0.091 3(7)	−0.432 2(12)	H(91)	0.283 7(5)	−0.137 7(5)	0.322 2(10)
C(4)	−0.023 4(8)	−0.155 9(6)	−0.379 2(13)	H(101)	0.448 5(5)	−0.100 8(5)	0.411 3(10)
C(5)	0.043 1(8)	−0.149 8(7)	−0.250 5(13)	H(111)	0.510 8(5)	0.026 8(5)	0.334 6(10)
C(6)	0.060 7(7)	−0.077 1(6)	−0.186 3(13)	H(121)	0.408 3(5)	0.117 6(5)	0.168 8(10)
C(8)	0.253 1(5)	−0.030 8(5)	0.195 3(10)	H(141)	0.112 3(6)	0.245 2(6)	−0.071 3(9)
C(9)	0.310 9(5)	−0.082 0(5)	0.288 7(10)	H(151)	0.089 2(6)	0.377 0(6)	0.037 4(9)
C(10)	0.403 8(5)	−0.061 2(5)	0.339 0(10)	H(161)	0.160 8(6)	0.404 0(6)	0.290 2(9)
C(11)	0.438 9(5)	0.010 8(5)	0.295 7(10)	H(171)	0.255 5(6)	0.299 2(6)	0.434 3(9)
C(12)	0.381 1(5)	0.061 9(5)	0.202 3(10)	H(181)	0.278 6(6)	0.167 4(6)	0.325 9(9)
C(7)	0.288 2(5)	0.041 1(5)	0.152 0(10)	H(201)	0.231 2(5)	0.022 7(4)	−0.220 4(10)
C(14)	0.143 5(6)	0.257 0(6)	0.039 0(9)	H(411)	0.318 2(5)	0.050 6(4)	−0.414 8(10)
C(15)	0.130 5(6)	0.331 3(6)	0.100 3(9)	H(241)	0.410 1(5)	0.175 7(4)	−0.411 0(10)
C(16)	0.170 9(6)	0.346 5(6)	0.242 8(9)	H(231)	0.415 0(5)	0.273 0(4)	−0.212 8(10)
C(17)	0.224 3(6)	0.287 4(6)	0.324 0(9)	H(241)	0.327 9(5)	0.245 0(4)	−0.018 4(10)
C(18)	0.237 3(6)	0.213 1(6)	0.262 7(9)	O(1)	−0.091 8(5)	0.116 0(5)	−0.368 3(9)
C(13)	0.196 9(6)	0.197 9(6)	0.120 3(9)	O(2)	−0.171 2(5)	0.040 9(4)	−0.530 9(10)
C(20)	0.271 3(5)	0.077 3(4)	−0.218 8(10)	O(3)	0.008 2(6)	−0.290 5(5)	−0.402 9(11)
C(21)	0.320 3(5)	0.093 0(4)	−0.328 3(10)	O(4)	−0.096 6(7)	−0.235 9(5)	−0.564 8(13)
C(22)	0.372 1(5)	0.163 5(4)	−0.326 2(10)	N(1)	0.119 2(5)	0.056 4(5)	−0.016 6(10)
C(23)	0.374 9(5)	0.218 3(4)	−0.214 5(10)	N(2)	−0.110 8(6)	0.050 4(6)	−0.424 8(11)
C(24)	0.325 8(5)	0.202 6(4)	−0.104 9(10)	N(3)	−0.038 9(8)	−0.232 0(6)	−0.453 1(14)
C(19)	0.274 0(5)	0.132 1(4)	−0.107 0(10)	S	0.037 50(19)	0.083 09(17)	−0.154 7(4)
H(31)	−0.129 7(7)	−0.096 5(7)	−0.526 1(12)	P	0.211 8(2)	0.104 72(18)	0.031 5(4)
H(51)	0.079 6(8)	−0.202 6(7)	−0.203 6(13)				

Table 2. Selected intramolecular bond lengths (Å) and angles (°)

C(7)–P	1.789(10)	C(2)–N(2)	1.450(12)
C(13)–P	1.799(11)	C(4)–N(3)	1.445(12)
C(19)–P	1.793(10)	N(2)–O(1)	1.226(10)
P–N(1)	1.566(7)	N(2)–O(2)	1.219(10)
N(1)–S	1.660(8)	N(3)–O(3)	1.237(11)
S–C(1)	1.728(11)	N(3)–O(4)	1.227(12)
C(13)–P–C(7)	109.0(4)	S–C(1)–C(2)	123.7(9)
C(19)–P–C(7)	106.3(4)	S–C(1)–C(6)	119.8(9)
C(19)–P–C(13)	104.3(4)	O(1)–N(2)–C(2)	116.9(9)
N(1)–P–C(7)	106.4(4)	O(2)–N(2)–C(2)	120(1)
N(1)–P–C(13)	114.0(4)	O(2)–N(2)–O(1)	123(1)
N(1)–P–C(19)	116.4(4)	O(3)–N(3)–C(4)	118(1)
P–N(1)–S	123.1(5)	O(4)–N(3)–C(4)	119(1)
N(1)–S–C(1)	101.4(5)	O(4)–N(3)–O(3)	122(1)

d(C–H) = 1.08 Å and U_{iso} fixed at 0.05 Å^2 and allowed to ride with associated carbon atoms. Final refinement cycles employed a weighting factor $w\,[= 3.103/(\sigma^2 F + 0.000\,087 F^2)]$. The final Fourier difference map revealed no maxima >0.3 e Å^{-3} and an analysis of the weighting scheme over $|F_o|$ and $(\sin\theta)/\lambda$ was satisfactory. The final residual indices were R = 0.079 and R' = 0.057.

Fractional atomic co-ordinates are given in Table 1.

Results and Discussion

Bond lengths and angles are in Table 2, and a diagram of the molecule is shown in the Figure. The geometry at phosphorus is approximately tetrahedral, the P=N(1)–S angle of 123.1(5)° is close to the trigonal value and the short P–N(1) bond length [1.566(7) Å] is typical of P=N bonds found in iminophosphoranes.[6] The long SN bond distance [1.660(8) Å], typical for an SN single bond,[2,3] and the low C(1)SN(1) angle [101.4(5)°] are consistent with predominantly localised lone pairs at sulphur. The lack of any conjugation in the C(1)SN(1)P chain is also demonstrated by the C(1)SN(1)P torsion angle of −134.6°. The C(1)–S single bond [1.728(11) Å] is close to the sum of the covalent radii [C(sp^2) 0.76, S 1.02 Å]. The C(2)C(1)SN torsion angle of −8.92° indicates that the 2,4-dinitrophenyl group is approximately coplanar with the SN(1) bond.

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