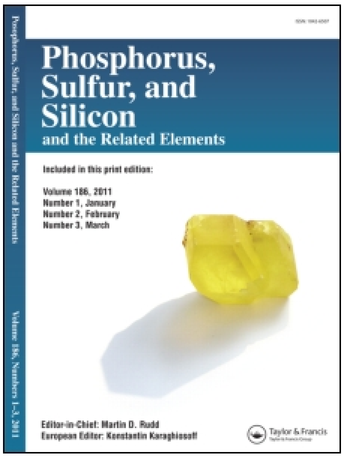

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

THE CRYSTAL STRUCTURE OF 2-PHENYLAZOTRIPHENYLPHOSPHONIUM CYCLOPENTADIENYLIDE

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To cite this Article Hall, C. Dennis , Parkins, Adrian W. and Nyburg, Stanley C.(1991) 'THE CRYSTAL STRUCTURE OF 2-PHENYLAZOTRIPHENYLPHOSPHONIUM CYCLOPENTADIENYLIDE', Phosphorus, Sulfur, and Silicon and the Related Elements, 63: 3, 231 — 235

To link to this Article: DOI: 10.1080/10426509108036824

URL: http://dx.doi.org/10.1080/10426509108036824

Phosphorus, Sulfur, and Silicon, 1991, Vol. 63, pp. 231–235
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THE CRYSTAL STRUCTURE OF 2-PHENYLAZOTRIPHENYLPHOSPHONIUM CYCLOPENTADIENYLIDE

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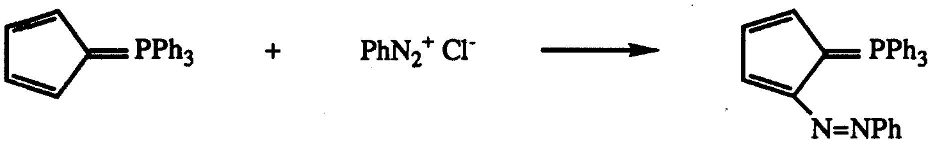
(Received August 14, 1991)

A single crystal X-ray diffraction study confirms that the phenylazo group is substituted in position-2 of the cyclopentadiene ring of the title compound.

Key words: Triphenylphosphonium cyclopentadienylide; phenylazo derivative; X-ray crystallography.

INTRODUCTION

The pioneering work of Ramirez et al.[1] showed that triphenylphosphonium cyclopentadienylide **1** behaves as a non-benzenoid aromatic compound in reacting with electrophiles to form substitution products in the cyclopentadiene ring. Most of these reactions[2–6] were alleged to proceed by substitution at position-2 of the cyclopentadiene ring and indeed, in the case of the azo-derivative **3** a chemical proof of substitution in this position was reported.[2] This proof was used together with multinuclear 2D nmr data to show that in the case of the reaction of tetrahaloquinones with **1** the reaction proceeded by substitution in position-3 of the cyclopentadiene ring.[7] Since this deduction depended upon the structural assignment of **3** it was considered important to confirm the structure of the azo-compound by X-ray analysis and the results of this work are reported below.



(1) (2) (3)

RESULTS AND DISCUSSION

Two perspectives of the crystal structure of (3) are shown in Figs. 1 and 2 and a selection of bond lengths and bond angles are given in Table I. It is immediately obvious from Fig. 1 that the azo-group is bound to position 2 of the cyclopentadiene ring of the ylid **1**. It is also clear that the azo-group adopts the *trans* configuration within the molecule and more surprisingly, that N2 of the azo link is adjacent to the tetrahedral phosphorus atom (Fig. 1). The P—N interatomic distance (2.894

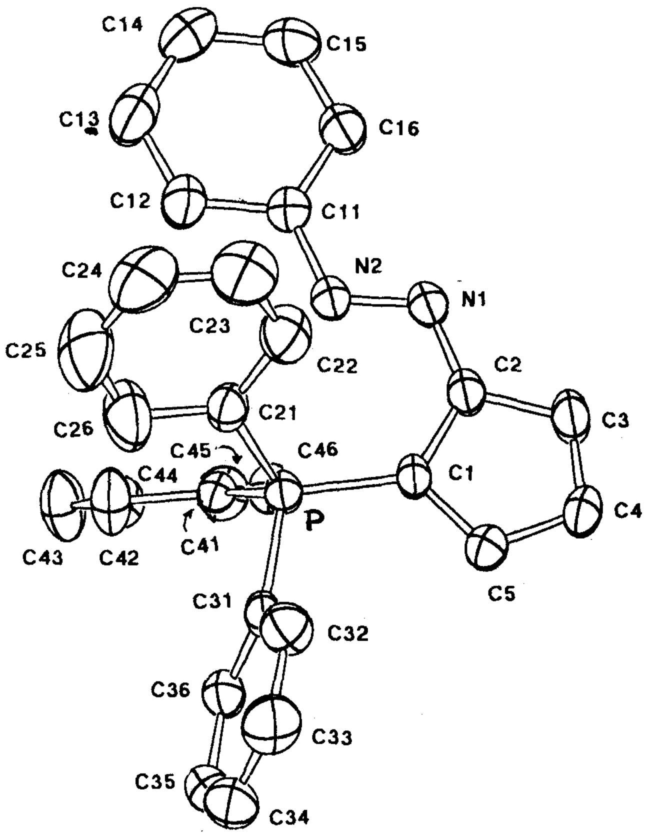


FIGURE 1 X-ray crystal structure of 3 showing the tetrahedral geometry at phosphorus and the substitution of the phenylazo group in position-2 of the cyclopentadiene ring.

Å), is just inside the sum of the van der Waals radii (3.4 Å) which suggests that there may be a slight interaction between the quaternary P-atom and the lone pair on nitrogen. Delocalisation of the charge from the cyclopentadiene ring through the azo link to the phenyl ring is evident in the co-planarity between the cyclopentadiene ring, the azo-link and the phenylazo group (Fig. 2) which, taken together with the other three phenyl groups, gives an almost perfect tetrahedral geometry to the phosphorus atom. The bond lengths throughout the azo link (C2—N1 at 1.369 Å, N1—N2 at 1.290 Å, and N2—Ph at 1.410 Å) are also indicative of a delocalised system since they fall between the values expected for C—C (1.54-1.34 Å) and C—N (1.51-1.29 Å) single and double bonds.

CONCLUSION

The reaction of triphenylphosphoniumcyclopentadienylide with phenyldiazonium chloride results in substitution of the phenylazo group in position 2 of the cyclopentadiene ring.

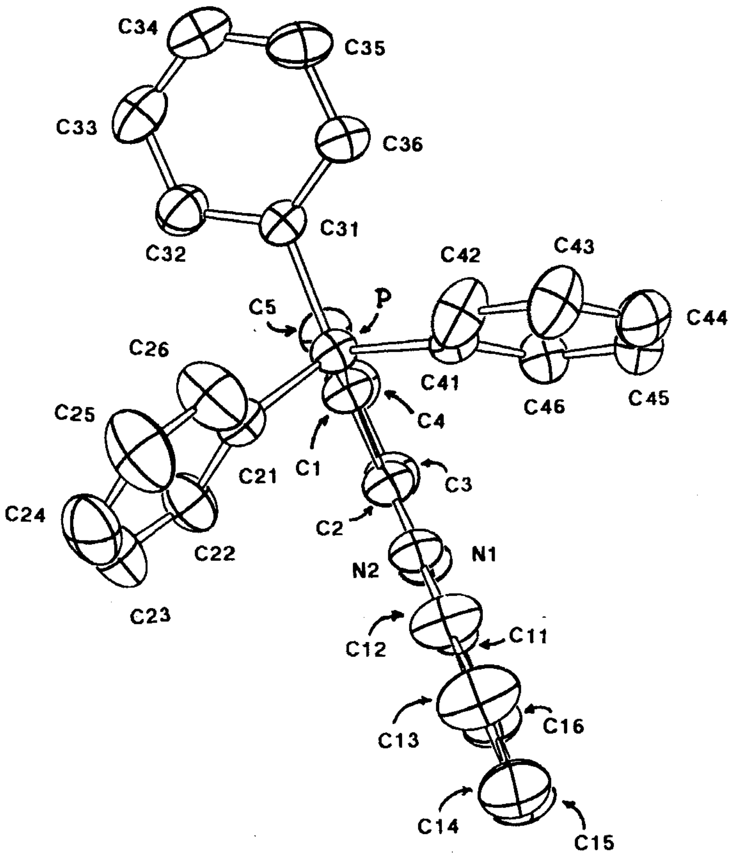


FIGURE 2 X-ray crystal structure of 3 showing the coplanarity of the cyclopentadiene ring with the phenylazo group.

TABLE I

Compilation of bond lengths and bond angles for 2-phenylazotriphenylphosphonium cyclopentadienylide. The numbering is as shown in Figs. 1 and 2

P—C(1)	1.743(3)	C(12)—C(13)	1.384(6)
P—C(21)	1.795(4)	C(12)—H(12)	1.073(4)
P—C(31)	1.814(4)	C(13)—C(14)	1.374(7)
P—C(41)	1.798(4)	C(13)—H(13)	1.082(4)
N(1)—N(2)	1.290(4)	C(14)—C(15)	1.376(6)
N(1)—C(2)	1.369(5)	C(14)—H(14)	1.076(4)
N(2)—C(11)	1.410(5)	C(15)—C(16)	1.391(6)
C(1)—C(2)	1.437(5)	C(15)—H(15)	1.077(4)
C(1)—C(5)	1.401(5)	C(16)—H(16)	1.077(4)
C(2)—C(3)	1.416(5)	C(21)—C(22)	1.388(5)
C(3)—C(4)	1.389(5)	C(21)—C(26)	1.381(5)
C(3)—H(3)	1.081(3)	C(22)—C(23)	1.366(7)
C(4)—C(5)	1.411(5)	C(23)—C(24)	1.368(8)
C(4)—H(4)	1.080(4)	C(23)—H(23)	1.076(5)
C(5)—H(5)	1.082(4)	C(24)—C(25)	1.351(8)
C(11)—C(12)	1.392(5)	C(24)—H(24)	1.070(5)
C(11)—C(16)	1.387(5)	C(25)—C(26)	1.378(7)

TABLE I (*Cont'd*)

C(25)—C(26)	1.378(7)	C(36)—H(36)	1.079(4)
C(25)—H(25)	1.086(5)	C(41)—C(42)	1.397(5)
C(26)—H(26)	1.090(5)	C(41)—C(46)	1.382(5)
C(31)—C(32)	1.380(5)	C(42)—C(43)	1.396(6)
C(31)—C(36)	1.386(5)	C(42)—H(42)	1.080(4)
C(32)—C(33)	1.394(6)	C(43)—C(44)	1.363(6)
C(32)—H(32)	1.080(4)	C(43)—H(43)	1.083(4)
C(33)—C(34)	1.382(7)	C(44)—C(45)	1.378(6)
C(33)—H(33)	1.084(4)	C(44)—H(44)	1.070(4)
C(34)—C(35)	1.366(7)	C(45)—C(46)	1.391(6)
C(34)—H(34)	1.084(4)	C(45)—H(45)	1.081(4)
C(35)—C(36)	1.393(5)	C(46)—H(46)	1.081(4)
C(35)—H(35)	1.080(4)		

C(1)—P—C(21)	113.77(17)	C(22)—C(23)—H(23)	120.2(5)
C(1)—P—C(31)	107.65(17)	C(24)—C(23)—H(23)	118.6(5)
C(1)—P—C(41)	112.59(17)	C(23)—C(24)—C(25)	118.6(4)
C(21)—P—C(31)	103.91(17)	C(23)—C(24)—H(24)	121.3(5)
C(21)—P—C(41)	112.14(17)	C(25)—C(24)—H(24)	120.1(5)
C(31)—P—C(41)	105.98(16)	C(24)—C(25)—C(26)	120.9(5)
N(2)—N(1)—C(2)	112.6(3)	C(24)—C(25)—H(25)	119.6(5)
N(1)—N(2)—C(11)	114.0(3)	C(26)—C(25)—H(25)	119.4(5)
P—C(1)—C(2)	128.1(3)	C(21)—C(26)—C(25)	121.4(4)
P—C(1)—C(5)	124.6(3)	C(21)—C(26)—H(26)	119.3(4)
C(2)—C(1)—C(5)	107.2(3)	C(25)—C(26)—H(26)	119.2(4)
N(1)—C(2)—C(1)	129.3(3)	P—C(31)—C(32)	118.8(3)
N(1)—C(2)—C(3)	123.1(3)	P—C(31)—C(36)	121.3(3)
C(1)—C(2)—C(3)	107.5(3)	C(32)—C(31)—C(36)	119.9(3)
C(2)—C(3)—C(4)	108.1(3)	C(31)—C(32)—C(33)	120.3(4)
C(2)—C(3)—H(3)	126.4(4)	C(31)—C(32)—H(32)	119.9(3)
C(4)—C(3)—H(3)	125.5(3)	C(33)—C(32)—H(32)	119.8(4)
C(3)—C(4)—C(5)	108.8(3)	C(32)—C(33)—C(34)	119.3(4)
C(3)—C(4)—H(4)	125.1(3)	C(32)—C(33)—H(33)	120.7(4)
C(5)—C(4)—H(4)	126.1(4)	C(34)—C(33)—H(33)	120.0(4)
C(1)—C(5)—C(4)	108.4(3)	C(33)—C(34)—C(35)	120.6(4)
C(1)—C(5)—H(5)	125.9(3)	C(33)—C(34)—H(34)	119.5(4)
C(4)—C(5)—H(5)	125.8(3)	C(35)—C(34)—H(34)	119.9(4)
N(2)—C(11)—C(12)	115.4(3)	C(34)—C(35)—C(36)	120.4(4)
N(2)—C(11)—C(16)	125.9(3)	C(34)—C(35)—H(35)	119.5(4)
C(12)—C(11)—C(16)	118.7(3)	C(36)—C(35)—H(35)	120.2(4)
C(11)—C(12)—C(13)	120.3(4)	C(31)—C(36)—C(35)	119.5(4)
C(11)—C(12)—H(12)	120.2(4)	C(31)—C(36)—H(36)	120.2(3)
C(13)—C(12)—H(12)	119.5(4)	C(35)—C(36)—H(36)	120.3(4)
C(12)—C(13)—C(14)	121.0(4)	P—C(41)—C(42)	121.9(3)
C(12)—C(13)—H(13)	119.0(4)	P—C(41)—C(46)	119.6(3)
C(14)—C(13)—H(13)	120.1(4)	C(42)—C(41)—C(46)	118.3(3)
C(13)—C(14)—C(15)	119.1(4)	C(41)—C(42)—C(43)	119.5(4)
C(13)—C(14)—H(14)	119.0(4)	C(41)—C(42)—H(42)	120.6(4)
C(15)—C(14)—H(14)	121.9(4)	C(43)—C(42)—H(42)	119.9(3)
C(14)—C(15)—C(16)	120.7(4)	C(42)—C(43)—C(44)	121.2(4)
C(14)—C(15)—H(15)	119.1(4)	C(42)—C(43)—H(43)	119.5(4)
C(16)—C(15)—H(15)	120.2(4)	C(44)—C(43)—H(43)	119.3(4)
C(11)—C(16)—C(15)	120.3(4)	C(43)—C(44)—C(45)	120.0(4)
C(11)—C(16)—H(16)	120.0(3)	C(43)—C(44)—H(44)	120.2(4)
C(15)—C(16)—H(16)	119.8(4)	C(45)—C(44)—H(44)	119.8(4)
P—C(21)—C(22)	121.1(3)	C(44)—C(45)—C(46)	119.4(4)
P—C(21)—C(26)	122.2(3)	C(44)—C(45)—H(45)	120.4(4)
C(22)—C(21)—C(26)	116.6(4)	C(46)—C(45)—H(45)	120.2(4)
C(21)—C(22)—C(23)	121.2(4)	C(41)—C(46)—C(45)	121.6(3)
C(21)—C(22)—H(22)	119.2(4)	C(41)—C(46)—H(46)	119.5(3)
C(23)—C(22)—H(22)	119.6(4)	C(45)—C(46)—H(46)	119.0(3)
C(22)—C(23)—C(24)	121.2(4)		

SUPPLEMENTARY MATERIAL

A Table of atomic coordinates (Table S1) has been deposited with the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW.

EXPERIMENTAL

The phenylazo derivative of **1** was prepared as described previously[1] and was crystallised from ethyl acetate/ethanol (×2) to give brilliant red crystals, m.p. 242–4°C, (sealed tube) lit., 239–40°C. The 2D-COSY and $^{13}C/^{1}H$ heteronuclear correlation nmr data have been described[7] and are entirely consistent with the proposed structure but do not categorically distinguish between substitution in position 2 or position 3 of the cyclopentadiene ring.

An irregular shaped chip (0.7 × 0.6 × 0.3 mm) from a large crystal was mounted on a glass fibre with epoxy resin and photographed to establish crystal quality. The crystal was then aligned on an automated Picker four circle diffractometer, and the cell dimensions obtained using 20 reflections ($40° < 2\theta < 80°$). Data were collected using Ni filtered CuK α radiation with pulse height analysis. A standard reflection showed no significant change during the data collection.

The structure was solved by direct methods using the NRCVAX program.[8] The hydrogen atoms were placed in calculated positions and refined with isotropic temperature factors; all other atoms were refined anisotropically. The final stages of the refinement were carried out by full matrix least squares with F's weighted according to counting statistics and refined for extinction.

Crystal data. $C_{29}H_{23}N_2P$. $M_r = 430.49$, triclinic, $P\bar{1}$. $a = 9.282(7)$, $b = 10.480(4)$, $c = 13.460(7)$ Å, $\alpha = 97.83(4)°$, $\beta = 99.91(6)°$, $\gamma = 113.26(4)°$. V = 1154.4 Å^3. Z = 2. $D_c = 1.24$ g cm^{-3}, $\lambda(\text{Cu } K_\alpha) = 1.5418$ Å, $\mu = 11.7$ cm^{-1}. F(000) = 452. Temperature = 298 K; R = 0.056, $R_w = 0.064$, GoF = 12.5 for 3071 reflections with $I_{net} > 2.5\,\sigma(I)$ out of a total of 3423. 2θ range 5–120°.

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