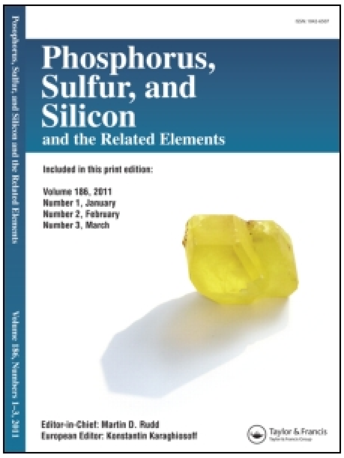

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4' DIPHENYLPHOSPHINO AND BROMO DERIVATIVES OF 10-PHENYL-1,4,7-TRITHIA-10-AZA-CYCLODODECANE 4-R-$C_6H_4N(CH_2CH_2S)_2CH_2CH_2SCH_2CH_2$

Lance R. Hoover[a]; Travis Pryor[a]; Jeremy A. Weitgenant[a]; Peter E. Williams[a]; Bruce N. Storhoff[a]; John C. Huffman[b]
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4′ DIPHENYLPHOSPHINO AND BROMO DERIVATIVES OF 10-PHENYL-1,4,7-TRITHIA-10-AZACYCLODODECANE 4-R-$C_6H_4\overline{N(CH_2CH_2S)_2CH_2CH_2SCH_2CH_2}$

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$4\text{-Br-}C_6H_4\overline{N(CH_2CH_2S)_2CH_2CH_2SCH_2CH_2}$ and $4\text{-}Ph_2P\text{-}C_6H_4\overline{N(CH_2CH_2S)_2CH_2CH_2SCH_2CH_2}$ have been synthesized and characterized. The former cyclododcane has been obtained from the reaction between $4\text{-}BrC_6H_4N(CH_2CH_2Cl)_2$ and $S(CH_2CH_2SH)_2$ in N,N-dimethylformamide containing Cs_2CO_3. The latter has been obtained from the former by way of a low temperature lithium-bromine exchange reaction (butyllithium) that provided the carbanion which was subsequently reacted with chlorodiphenylphosphine. In regard to characterization, X-ray methods have been used to study the former ($P2_1$, a = 8.356(3) Å, b = 12.325(5) Å, c = 16.012 (7), β = 100.81, Z = 4), and two crystallographically independent molecules were found. In both molecules, the nitrogen atoms are nearly planar with short N-C(sp^2) bond lengths, and, second, the sulfur atoms are in exodenate positions. For the phosphine, a ^{31}P signal was observed at −7.1 ppm, and this peak position was considered to be indicative of a structure involving a planar nitrogen atom.

Keywords: Phosphine; thioether; crown; trithiaza; cyclododecane; X-ray

INTRODUCTION

The coordination chemistry of macrocycles with additional appended functional groups continues to be an active area of research. Both Gokel[1], who coined the term "lariat crowns," and Shaw[2] who reported studies of **1** and **2**, respectively, made early contributions to this field of study. In regard to other crown ethers

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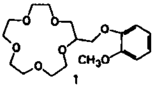
*Corresponding author.

with pendant groups, MacFarland and Landis, for example have recently reported the tartrate-based phosphite-crown systems, **3**, that have neopentyl- or 1,3-propanediol-based phosphorus links[3]. These ligands have been shown to form active hydroformylation catalysts with Rh(I), and they may form the basis for a set of ligands that can be used to explore the role of secondary interactions in catalytic processes[3]. Turning to nitrogen-based systems, Zhang and Busch, for example, have reported the synthesis of the triazacyclododecane, **4**, along with its $M(II)^{2+}$ (M = Fe(II)-Cu(II) and Pd(II)) complexes.[4] Compared to the analogous triazacyclononane ligand, **4**, was found to stabilize the complexes toward oxidation.

Functionalized thioether crowns have also been recognized as having the potential for useful applications, and they have been the target of recent studies[5]. For example, Guy and coworkers have reported a series of C_8H_{17}-substituted thioethers that they investigated for relative abilities to extract Pd(II) from nitric acid media.[6] In contrast to these lipophilic macrocycles, Rorabacher and coworkers have synthesized and studied diol derivatives of 1,4,8,11-tetrathiacyclotetradecane, 14S4, as water soluble ligands.[7] In regard to examples of macrocycles with both N and S donors, Mattes and coworkers have synthesized a series of ligands containing both N and S donors with pendant pyridine groups. Included is **5** which ligates Ni(II) in octahedral fashion with the chemically identical donors coordinated in cis positions[8].



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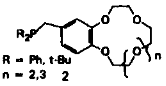
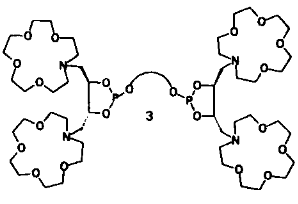


R = Ph, t-Bu
n = 2,3

2



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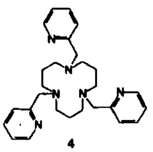

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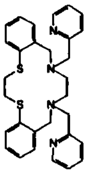

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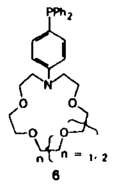

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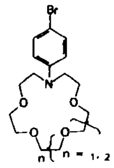

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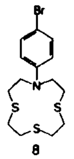

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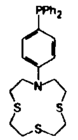


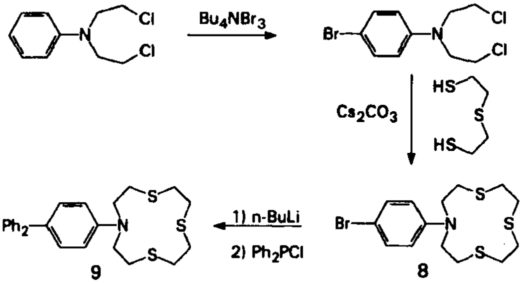
9

Recently, we became interested in the properties of a phosphine system functionalized with crown ether groups as shown in **6**[9]. The synthetic route for these molecules utilized a standard lithium-bromine exchange reaction[10] involving **7** and n-butyllithium at low temperatures. That this exchange reaction was found to readily take place even at very low temperatures was not surprising in view of the fact that 4-bromo-N,N-dimethylaniline forms the basis for Gilman's color test for detecting the presence of alkyl lithium reagents[11]. Since **7** proved to be a useful intermediate for the preparation of phosphine-crown molecules, we elected to prepare a thioether analog, **8**, that we propose could be a precursor for a variety of new types of ligands, molecules and complexes given the presence of a 1,4,7-trithia-10-azacyclododecane ring, an electron-rich *pi* system, and a site for readily generating a carbanion. Herein we report both the synthesis of **8** and its conversion to the diphenylphospino derivative, **9**, by way of the reactions summarized in Scheme 1.

EXPERIMENTAL

Reagents and Materials

N-phenyldiethanolamine, tetrabutylammonium tribromide, cesium carbonate, phosphorus oxychloride, 2-mercaptoethyl sulfide (technical grade), butyllithium and chlorodiphenylphosphine were obtained from Aldrich Chemical Co., Inc. The other reagents and solvents were obtained from our departmental stores.



SCHEME 1 Synthetic Methods for **8** and **9**.

The N,N-dimethylformamide (DMF) and tetrahydrofuran (with sodium benzophenone ketyl) were distilled prior to use. The N,N-bis(2-chloroethyl)aniline was prepared as previously described.[12]

Methods and Instruments

All reactions were carried out under a blanket of argon. NMR spectra were recorded on a Varian Gemini-200 instrument. The elemental analyses were carried out by Midwest Microlab, Ltd., Indianapolis, IN, 46250. The Indiana University Molecular Structure Center (Indiana University, Bloomington, IN, 47405) carried out the X-ray analysis. The SYBYL package (TRIPOS Associates) and PCMODEL (Serena Software) were used to determine structural characteristics from the X-ray data. **9** was purified by using a Biotage® chromatography apparatus.

Synthesis

$4\text{-}BrC_6H_4N(CH_2CH_2Cl)_2$

N,N-bis(2-chloroethyl)aniline (10.00 g, 45.8 mmol) was dissolved in 100 mL of dichloromethane, and the solution was cooled to 10°C. With stirring, solid tetrabutylammonium tribromide (22.13 g 45.9 mmol) was added over a period of 3 min. After stirring for an additional 20 min, the reaction mixture was transferred to a separatory funnel. Aqueous sodium thiosulfate (100 mL, 20%) was added and the mixture was shaken. The organic layer was collected, and the aqueous layer was extracted with an additional 100 mL portion of dichloromethane. The combined organic fractions were dried over magnesium sulfate, and then the solvent was removed by way of a rotary evaporator. The crude product was recrystallized from methyl alcohol providing 8.95 g (65.8%) of product. ^{13}C NMR ($CDCl_3$); δ 40.3 (s), 53.5 (s), 109.8 (s), 113.7 (s), 132.4 (s), 145.5 (s).

$4\text{-}Br\text{-}C_6H_4\overline{N(CH_2CH_2S)_2CH_2CH_2SCH_2CH_2}$ *(8)*

A 3.0 liter flask, fitted with a condenser, mechanical stirrer and constant rate addition funnel, was charged with 1.5 L of freshly distilled DMF and 13.04 g (40.0 mmol) of cesium carbonate[13]. After warming the mixture to 60°C, a mixture of 11.88 g (40.0 mmol) of $4\text{-}BrC_6H_4N(CH_2CH_2Cl)_2$ and 6.17 g (40.0 mmol) of 2-mercaptoethyl sulfide in 500 mL of DMF was prepared, and half of this solution was added over a 24 h period. At this time, the reaction flask was charged with an additional 13.04 g of cesium carbonate, the second half of the solution was added over a period of 24 h, and the mixture was stirred at 60°C for an additional 24 h. The mixture was cooled to room temperature, filtered, and then the DMF was removed under high vacuum. The crude product was dissolved in 100 mL of dichloromethane and shaken with 100 mL of water. The phases were separated, and the aqueous phase was subsequently extracted with an additional 100 mL portion of dichloromethane. Following solvent removal, the crude product was chromatographed on slica gel (flash chromatography) by using triethylamine in dichloromethane (0.10% v/v) providing 7.95 g, (52.5%) of product. Crystals for the X-ray and elemental analyses were obtained by slowly cooling an ethyl acetate solution of **8**. Anal. Calcd for $C_{14}H_{20}BrNS_3$: C, 44.44%, H, 5.33%, Br, 21.12%, N, 3.70%. Found: C, 44.51%, H, 5.43%, Br, 21.06%, N, 3.74%. ^1H NMR ($CDCl_3$); δ 2.9 (m, 12 H), 3.5 (t, 4 H, J_{HH} = 7.5 Hz), 6.6 (m, 2 H), 7.31 (m, 2 H).

$4\text{-}Ph_2P\text{-}C_6H_4\overline{N(CH_2CH_2S)_2CH_2CH_2SCH_2CH_2}$ *(9)*

A dry 100 mL round bottomed flask was fitted with a gas inlet and a septum was charged with previously dried **8** (5.60 g, 14.8 mmol) and 75 mL of THF. With magnetic stirring, this solution was cooled to −80°C, and n-butyllithium in hexane (5.9 mL, 14.8 mmol) was added *via* a syringe over a period of 15 min. The solution was stirred at −80°C for an additional 25 min. At this time freshly distilled chlorodiphenylphosphine (3.27 g, 14.8 mmol) in 10 mL of THF was added over a period of 15 min, and the resulting mixture was warmed to room temperature over a period of 6 h. Triethylamine, 3.5 mL, 20% aqueous ammonium chloride, 15 mL, dichloromethane, 50 mL, and water, 50 mL, were added in sequence, and the nonaqueous layer was collected. The aqueous phase was further extracted with 2 × 50 mL portions of dichloromethane. The nonaqueous fractions were combined, and the solvent was removed to yield 6.91 grams of crude material. A sample of the crude product, 1.2 g in 3 mL of dichloromethane, was chromatographed on a Biotage® 40 column by using a solvent mixture of 85% heptane, 13% ethyl acetate and 2% triethylamine. After the chromatography, the fractions were stored at 10°C overnight, and the colorless crystals that formed were collected and dried under high vacuum, 0.108 g. Anal. Calcd for $C_{26}H_{30}NPS_3$: C, 64.56%, H, 6.25%, N, 2.90%. Found: C, 64.18%, H, 6.30%, N, 2.89%. ^1H NMR ($CDCl_3$); δ 2.9 (m, 12 H), 3.8 (t, 4 H, J_{HH} = 7.6 Hz), 6.8 (m, 2 H), 7.2–7.8 (m, 12 H). ^{31}P NMR ($CDCl_3$) δ −7.1 (s).

RESULTS AND DISCUSSION

$4\text{-}Br\text{-}C_6H_4\overline{N(CH_2CH_2S)_2CH_2CH_2SCH_2CH_2}$ *(8)*

Compound **8** was readily obtained by reacting 2-mercaptoethyl sulfide with $4\text{-}BrC_6H_4N(CH_2CH_2Cl)_2$ in the presence of Cs_2CO_3 as presented in Scheme 1[13]. The analytical and ^1H NMR data presented above are consistent with the proposed formulation. **8** readily forms crystals from warm ethyl acetate that are pure and suitable for X-ray analysis. A crystal with the dimensions of 0.20 × 0.25 × 0.25 mm was selected for the X-ray analysis. Crystallographic data, atomic coordinates, isotropic thermal parameters, bond lengths and bond angles are summarized in Tables I–IV.[4] Two crystallographically independent mol-

TABLE I Crystal and refinement information for **8a** and **8b**

Formula	$C_{14}H_{20}NBrS_3$
Space group	$P2_1$
Cell dimensions (Å) at −171°C	a = 8.356(3), b = 12.325(5), c = 16.012(7), beta = 100.81
Vol. (Å)	1619.66
Calcd density (g/cm^3)	1.552
Z (molecules/cell)	4
max and min 2θ (deg)	6–45
No. of unique reflections collected	2432
No. of unique intensities	2222
No. with F > 2.33 σ F	1894
Final residuals: R, R_W	0.057, 0.0478

TABLE II Fractional coordinates and isotropic thermal parameters[a] for **8a** and **8b**

Atom	*x*	*y*	*z*	*Biso*
Br(1)	4198 (2)	5998*	887 (1)	33
C(2)	3102 (17)	7367 (14)	940 (9)	22
C(3)	1796 (17)	7465 (14)	1305 (8)	20
C(4)	1073 (19)	8460 (13)	1346 (9)	19
C(5)	1656 (16)	9426 (13)	1012 (8)	19
C(6)	3094 (19)	9266 (15)	644 (9)	24
C(7)	3797 (20)	8280 (18)	604 (10)	30
N(8)	904 (14)	10386 (11)	1036 (7)	21
C(9)	−43 (19)	10646 (14)	1704 (9)	24
C(10)	−1797 (19)	10879 (18)	1386 (10)	30
S(11)	−2840 (5)	11442 (4)	2172 (2)	26
C(12)	−1864 (22)	12740 (15)	2422 (9)	26
C(13)	−2228 (18)	13555 (15)	1677 (9)	26
S(14)	−911 (5)	14762 (4)	1870 (3)	30
C(15)	1015 (22)	14194 (15)	1725 (10)	27
C(16)	1102 (19)	13983 (15)	824 (10)	27
S(17)	2928 (5)	13328 (4)	643 (3)	27
C(18)	2713 (19)	11977 (13)	1063 (9)	22
C(19)	1318 (17)	11337 (13)	591 (9)	21
Br(20)	1132 (2)	3842 (2)	4348 (1)	31
C(21)	1837 (19)	2482 (15)	4061 (8)	26
C(22)	1006 (19)	1570 (17)	4205 (9)	25
C(23)	1558 (21)	575 (14)	3989 (10)	26
C(24)	2835 (17)	436 (13)	3613 (9)	21
C(25)	3684 (19)	1378 (15)	3462 (9)	23
C(26)	3164 (18)	2373 (17)	3673 (9)	26
N(27)	3329 (14)	−581 (11)	3378 (7)	22
C(28)	2540 (19)	−1579 (14)	3598 (10)	26
C(29)	3151 (22)	−1946 (17)	4513 (9)	33
S(30)	2640 (5)	−3356 (4)	4687 (3)	29
C(31)	4436 (20)	−4032 (18)	4478 (10)	31
C(32)	4488 (19)	−4283 (15)	3550 (10)	25
S(33)	6449 (5)	−4780 (4)	3399 (3)	31
C(34)	7576 (22)	−3541 (17)	3510 (10)	32
C(35)	7163 (20)	−2798 (16)	2702 (10)	28
S(36)	7794 (5)	−1398 (4)	2855 (2)	24
C(37)	6293 (17)	−874 (14)	3451 (9)	20
C(38)	4597 (18)	−728 (14)	2907 (9)	23

[a] Estimated standard deviations are presented in parenthesis. Equivalent isotropic thermal parameters were estimated by using the formula presented by: W. C. Hamilton, *Acta Crystallog.* **12**, 609 (1959).

TABLE III Bond lengths for **8a** and **8b**

A	*B*	*Distance*
Br (1)	C (2)	1.929 (16)
Br (20)	C (21)	1.862 (18)
S (11)	C (10)	1.799 (16)
S (11)	C (12)	1.806 (20)
S (14)	C (13)	1.842 (19)
S (14)	C (15)	1.809 (18)
S (17)	C (16)	1.797 (16)
S (17)	C (18)	1.817 (17)
S (30)	C (29)	1.823 (20)
S (30)	C (31)	1.802 (18)
S (33)	C (32)	1.807 (17)
S (33)	C (34)	1.785 (20)
S (36)	C (35)	1.807 (20)
S (36)	C (37)	1.829 (16)
N (8)	C (5)	1.343 (19)
N (8)	C (9)	1.479 (19)
N (8)	C (19)	1.447 (18)
N (27)	C (24)	1.393 (19)
N (27)	C (28)	1.470 (20)
N (27)	C (38)	1.422 (18)
C (2)	C (3)	1.336 (21)
C (2)	C (7)	1.418 (26)
C (3)	C (4)	1.373 (23)
C (4)	C (5)	1.427 (21)
C (5)	C (6)	1.447 (21)
C (6)	C (7)	1.357 (25)
C (9)	C (10)	1.486 (22)
C (12)	C (13)	1.545 (21)
C (15)	C (16)	1.481 (22)
C (18)	C (19)	1.490 (21)
C (21)	C (22)	1.364 (24)
C (21)	C (26)	1.375 (22)
C (22)	C (23)	1.377 (24)
C (23)	C (24)	1.331 (22)
C (24)	C (25)	1.405 (22)
C (25)	C (26)	1.365 (24)
C (28)	C (29)	1.526 (22)
C (31)	C (32)	1.527 (21)
C (34)	C (35)	1.570 (24)
C (37)	C (38)	1.528 (20)

TABLE IV Bond angles for **8a** and **8b**

A	*B*	*C*	*Angle*
C (10)	S (11)	C (12)	103.8 (10)
C (13)	S (14)	C (15)	100.6 (8)
C (16)	S (17)	C (18)	101.9 (8)
C (29)	S (30)	C (31)	100.7 (10)
C (32)	S (33)	C (34)	99.9 (9)
C (35)	S (36)	C (37)	101.4 (8)
C (5)	N (8)	C (9)	121.9 (13)
C (5)	N (8)	C (19)	122.9 (12)
C (9)	N (8)	C (19)	113.0 (12)
C (24)	N (27)	C (28)	121.3 (11)
C (24)	N (27)	C (38)	123.1 (13)
C (28)	N (27)	C (38)	115.6 (13)
Br (1)	C (2)	C (3)	122.1 (14)
Br (1)	C (2)	C (7)	116.5 (11)
C (3)	C (2)	C (7)	121.3 (16)
C (2)	C (3)	C (4)	120.3 (16)
C (3)	C (4)	C (5)	122.9 (14)
N (8)	C (5)	C (4)	122.0 (13)
N (8)	C (5)	C (6)	124.1 (14)
C (4)	C (5)	C (6)	113.9 (15)
C (5)	C (6)	C (7)	122.8 (16)
C (2)	C (7)	C (6)	118.8 (15)
N (8)	C (9)	C (10)	114.9 (12)
S (11)	C (10)	C (9)	114.3 (11)
S (11)	C (12)	C (13)	112.9 (11)
S (14)	C (13)	C (12)	111.7 (11)
S (14)	C (15)	C (16)	113.6 (12)
S (17)	C (16)	C (15)	115.7 (11)
S (17)	C (18)	C (19)	114.8 (11)
N (8)	C (19)	C (18)	114.5 (12)
Br (20)	C (21)	C (22)	120.4 (13)
Br (20)	C (21)	C (26)	121.2 (14)
C (22)	C (21)	C (26)	118.3 (18)
C (21)	C (22)	C (23)	119.1 (15)
C (22)	C (23)	C (24)	124.3 (17)
N (27)	C (24)	C (23)	122.7 (15)
N (27)	C (24)	C (25)	120.9 (12)
C (23)	C (24)	C (25)	116.4 (15)
C (24)	C (25)	C (26)	120.4 (15)
C (21)	C (26)	C (25)	121.4 (17)
N (27)	C (28)	C (29)	113.2 (13)
S (30)	C (29)	C (28)	112.5 (12)
S (30)	C (31)	C (32)	116.8 (12)
S (33)	C (32)	C (31)	112.9 (11)
S (33)	C (34)	C (35)	112.8 (12)
S (36)	C (35)	C (34)	115.6 (12)
S (36)	C (37)	C (38)	113.5 (10)
N (27)	C (38)	C (37)	114.6 (12)

ecules were found (labeled **8a** and **8b**), and ORTEP diagrams for both are presented in Figure 1.

In general, all bond lengths (see Table III) are in the ranges expected.[9,14] For example, the C-S distances which range from 1.785(20) Å to 1.842(19) Å are similar to those reported for 1,4,7,10-tetrathiacyclododecane, 12S4, the previously mentioned 14S4, and 1,4,7,10,13,16-hexathiacyclooctadecane, 18S6.[14] In homoleptic thioether crown structures the C-C bond lengths usually range from *ca.* 1.45 to 1.53 Å, distances that are somewhat shorter than expected between sp^3 hybridized carbons.[14] In **8**, these C-C bond lengths which range from 1.481 (22) Å to 1.570(24) Å appear to be longer than expected.

As indicated in Figure 1, in both of the independent molecules all four donor atoms are essentially located in exodentate locations resulting in ring shapes that are somewhat similar to that of 12-S-4[15]. When viewed from above the plane of the macrocyclic rings, the donor atoms can be described as being located at the corners of a parallelogram. More specifically, for both **8a** and **8b** the four N-S-S angles range from 84.91^0 to 86.04^0. Another conspicuous feature is that in both molecules the nitrogen atoms are essentially planar, an outcome that is expected based on previously reported X-ray studies of aniline derivatives including **6**[9] and 4-dimethylaminophenyl sulfide.[16] In **8a** and **8b**, N8 and N27, are both *ca.* 0.05 Å from the planes defined by the neighboring phenyl rings (see Table V). Considering the carbons alpha to the nitrogen atoms, **8b** is more planar because C28 and C38 are above and below this phenyl ring plane by 0.07 Å and −0.17 Å, respectively. In contrast, the comparable atoms in **8a** (C9 and C19) are above and below this plane by 0.51 Å and −0.27 Å, respectively. The N-C(sp2) bond

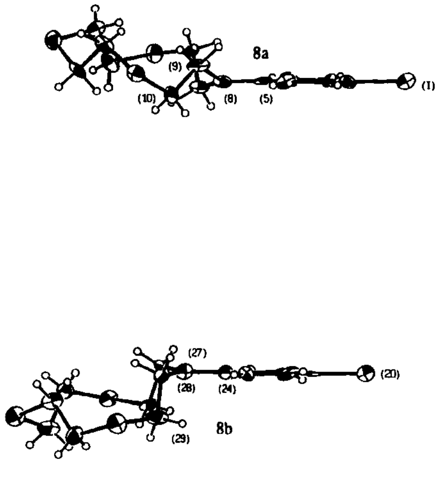


FIGURE 1 ORTEP Diagrams and Atom Numbering Schemes for **8a** and **8b**

TABLE V Distance (Å) of ring atoms from the plane defined by the phenyl carbons

*molecule **8a** atoms 9–19*	*distance from plane*	*molecule **8b** atoms 28–38*	*distance from plane*
N8	−0.050	N27	−0.0.32
C9	0.51	C28	0.071
C10	−0.47	C29	1.50

lengths obtained for **8a** (1.343(19)) and **8b** (1.393(19)) are both in the range expected, and both are indicative of a significant amount of C-to-N multiple bond character.[9,16] As indicated above, the data in Table V and the ORTEP diagrams indicate that the N27 is more planar than N8. In the absence of other effects, the N8-C5 distance would be expected to be longer than the N27-C24 distance as a result of the loss of conjugation associated with loss of planarity. As presented in Table III, the N-C distances are similar, and, if there is a trend, the N8-C5 distance is shorter rather than longer as might be argued. To assist in the description of these differences, the distance of each ring atom from the planes defined by the phenyl rings has been summarized in Table V. Focusing on C10-C13 and C-29-C32, the former and latter are an average of 0.32 Å and 1.57 Å, respectively, from the planes.

$4\text{-}Ph_2P\text{-}C_6H_4\overline{N(CH_2CH_2S)_2CH_2CH_2S}$ (9)

The diphenylphosphino derivative, **9**, was obtained from **8** by carrying out a lithium-bromine exchange reaction and then reacting the resulting carbanion with chlorodiphenylphosphine. As indicated in the EXPERIMENTAL section, the purified product was obtained in *ca.* 10% yield, whereas the yields from similar reactions are usually much higher.[9,10,17] We, however have not attempted to optimize the yield or determine the composition of the remaining materials. Further, we have carried out the reaction twice, and for both experiments **9** was isolated in low yields.

As reported in the EXPERIMENTAL section, the ^{31}P NMR shift is −7.1 PPM, a value that is similar to the previously reported oxocrown analogs **6** for which the 15-crown-5 species is known from X-ray data to have a planar nitrogen.[9] Given this latter information and the similar ^{31}P shifts, it is also likely that the nitrogen in **9** is planar. If the planarity had been lost, the nitrogen in **9** would no longer be conjugated with the phenyl ring which likely would result in a chemical shift similar to that of triphenylphsosphine, *ca.* δ −5.

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