# Configurational Isomerism in Trithiatetrazocines; Preparation and Crystal Structures of *exo*- and *endo*-3-Triphenylarsinimino-7-phenyl-1,3,5,2,4,6,8-trithiatetrazocine, $PhCN_4S_3NAsPh_3$

**René T. Boeré,[a] A. Wallace Cordes,[b] Scott L. Craig,[b] James B. Graham,[b] Richard T. Oakley,*[a] and J. Ann James Privett[b]**

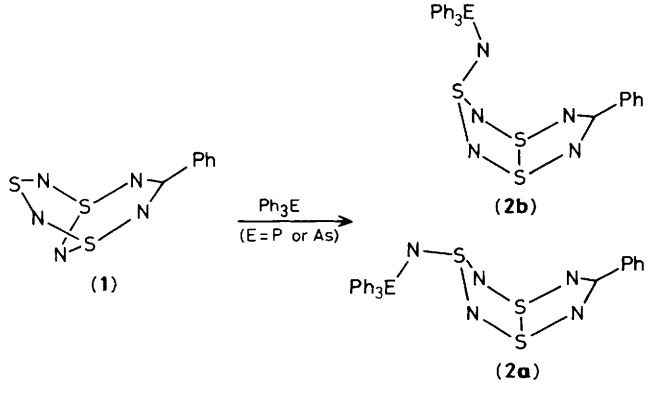
[a] *Guelph Waterloo Centre for Graduate Work in Chemistry, Guelph Campus, Department of Chemistry and Biochemistry, University of Guelph, Guelph, Ontario N1G 2W1, Canada*
[b] *Department of Chemistry, University of Arkansas, Fayetteville, Arkansas 72701, U.S.A.*

The reactions of triphenylphosphine and triphenylarsine with the bicyclic thiazyl heterocycle $PhCN_5S_3$ produce the corresponding 3-imino-7-phenyl-1,3,5,2,4,6,8-trithiatetrazocines $PhCN_4S_3NEPh_3$ (E = P or As); the *exo*- and *endo*-isomers of $PhCN_4S_3NAsPh_3$ have been characterized by *X*-ray crystallography.



The synthesis and structural properties of heterocyclic thiazene derivatives are subjects of current interest. As a continuation of our recent work on the preparation and interconversion of dithiatriazine derivatives[1,2] we are examining the interaction of these compounds with nucleophiles. We have found that the bicyclic derivative (**1**) reacts with triphenylphosphine and triphenylarsine to produce the trithiatetrazocine derivatives (**2**) (Scheme 1). These reactions not only represent an extremely efficient synthetic route to the 1,3,5,2,4,6,8-trithiatetrazocine ring system,[3—5] but also provide the first characterized example of configurational isomerism in sulphur–nitrogen ring systems.

The reaction of triphenylphosphine (7.82 mmol) with (**1**) (7.82 mmol) in toluene (80 ml) affords an orange solution which slowly fades during 24 h to pale yellow and produces a yellow crystalline precipitate of $PhCN_4S_3NPPh_3$† [m.p.194—196 °C, $\delta(^{31}P)$ 21.4 p.p.m.] in an overall yield of 91% (7.15 mmol); virtually no triphenylphosphine sulphide can be detected by t.l.c. or $^{31}P$ n.m.r. spectroscopy. A similar reaction occurs when triphenylarsine (0.98 mmol) is warmed with (**1**) (0.98 mmol) in acetonitrile (10 ml); a yellow crystalline precipitate of $PhCN_4S_3NAsPh_3$ (0.85 mmol, 87%, decomp. 163—165 °C) is immediately formed. The same material is produced when the reaction is performed at room temperature in toluene. However, a second product, an orange–red crystalline material (decomp. 158—159 °C), $\lambda_{max.}$ ($CH_2Cl_2$) 422 nm, ε 1 × $10^3$ $dm^3$ $mol^{-1}$ $cm^{-1}$, with the same elemental composition (save for a mole of toluene solvate) as the first, is also obtained, albeit in low (<5%) yield. The two products (yellow and orange) can be separated manually.




**Scheme 1**

† The elemental composition of each of the compounds reported was confirmed by chemical analysis.

In order to establish the structural identity of the compounds generated in the latter reaction we have carried out a single-crystal *X*-ray analysis of both products.‡ The results establish that the red and yellow solids are, respectively, the *exo*- and *endo*-isomers of 3-triphenylarsinimino-7-phenyl-1,3,5,2,4,6,8-trithiatetrazocine (**2a**) and (**2b**) (E = As). The yellow phosphorus compound has also been characterized as the *endo*-isomer (**2b**) (E = P).[6]

ORTEP drawings of both (**2a**) and (**2b**) (E = As) are shown in Figure 1. The small differences observed between the equivalent bonds in the two isomers (see Table 1) mirror almost exactly the differences between the two halves of *exo–endo*-$Ph_3PNS(NSN)_2SNPPh_3$.[7] The intramolecular dimensions are generally similar to those reported for the related trithiatetrazocines $Me_2NCN_4S_3Cl$[3] and $Bu^tCN_4S_3Cl$,[4] both of which exhibit *endo*-geometries with short transannular

**Table 1.** Selected structural parameters for *exo*- and *endo*-3-triphenylarsinimino-7-phenyl-1,3,5,2,4,6,8-trithiatetrazocine.

| Distance (Å) | *endo* | *exo* | Angle (°) | *endo* | *exo* |
|---|---|---|---|---|---|
| S(1)–N(1) | 1.612(3) | 1.576(6) | N(1)–S(1)–N(2) | 108.1(2) | 104.9(3) |
| S(1)–N(2) | 1.651(4) | 1.703(6) | N(1)–S(1)–N(5) | 106.7(2) | 105.7(3) |
| S(1)–N(5) | 1.647(4) | 1.683(6) | N(2)–S(1)–N(5) | 100.8(2) | 99.2(3) |
| S(2)–N(2) | 1.591(4) | 1.574(6) | N(2)–S(2)–N(3) | 115.6(2) | 114.0(3) |
| S(2)–N(3) | 1.631(4) | 1.649(6) | N(4)–S(3)–N(5) | 114.6(2) | 114.0(3) |
| S(3)–N(4) | 1.630(4) | 1.655(6) | As–N(1)–S(1) | 115.9(1) | 120.7(3) |
| S(3)–N(5) | 1.589(4) | 1.574(6) | S(1)–N(2)–S(2) | 118.6(2) | 115.4(3) |
| C(1)–N(3) | 1.342(5) | 1.340(9) | S(2)–N(3)–C(1) | 117.4(3) | 117.0(5) |
| C(1)–N(4) | 1.321(5) | 1.319(8) | S(3)–N(4)–C(1) | 118.5(3) | 118.1(5) |
| As–N(1) | 1.755(3) | 1.769(5) | S(1)–N(5)–S(3) | 118.4(2) | 116.9(3) |
| As–C(av.) | 1.911(9) | 1.91(1) | N(3)–C(1)–N(4) | 125.6(4) | 126.5(7) |
| S(2)–S(3) | 2.419(2) | 2.420(3) | N–As–C(av.) | 110(5) | 111(8) |
| | | | C–As–C(av.) | 109(2) | 108(1) |

‡ *Crystal data* (both isomers). Data were collected on an Enraf–Nonius CAD-4 automated diffractometer with graphite-monochromated Mo-$K_\alpha$ radiation (λ = 0.71073 Å) using ω–2θ scans ($\theta_{max.}$ 25°), and were corrected for absorption. The structures were solved by Patterson and Fourier methods and refined by full-matrix least-squares with weights based on counting statistics. *endo*-$C_{25}H_{20}AsN_5S_3$, $M$ = 561.7, monoclinic, space group $P2_1/c$, $a$ = 13.841(2), $b$ = 9.499(2), $c$ = 19.655(2) Å, β = 104.54(2)°, $Z$ = 4, $U$ = 2501 Å$^3$, $D_c$ = 1.49 g $cm^{-3}$, μ = 16.2 $cm^{-1}$. 367 Parameters were refined using 2646 independent reflections ($I > 3\sigma_I$) to give $R$ = 0.033 and $R_w$ = 0.040. *exo*-$C_{25}H_{20}AsN_5S_3 \cdot C_7H_8$, $M$ = 653.7, triclinic, space group $P\bar{1}$, $a$ = 9.133(1), $b$ = 11.700(3), $c$ = 14.439(3) Å, α = 89.87(2), β = 84.93(1), γ = 82.49(2)°, $Z$ = 2, $U$ = 1524 Å$^3$, $D_c$ = 1.42 g $cm^{-3}$, μ = 13.4 $cm^{-1}$. 307 Parameters were refined using 3088 unique reflections ($I > 3\sigma_I$) to give $R$ = 0.073 and $R_w$ = 0.096. Atomic co-ordinates, bond lengths and angles, and thermal parameters, have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1, 1986.

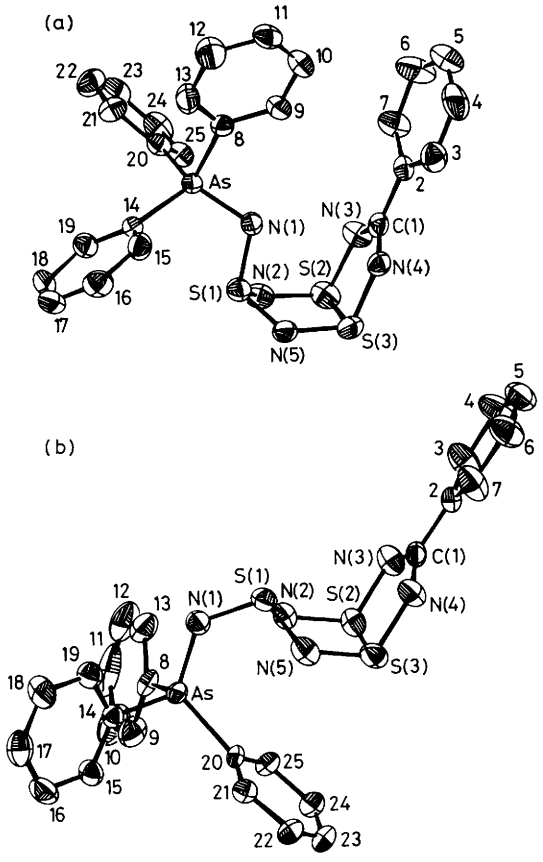
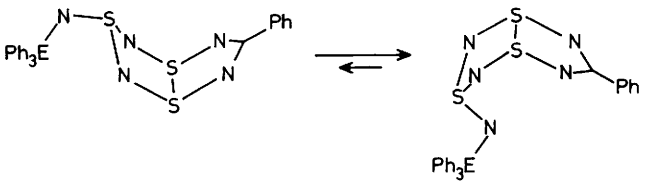



**Figure 1.** ORTEP drawings (30% probability ellipsoids) of (a) *endo*- and (b) *exo*-3-triphenylarsinimino-7-phenyl-1,3,5,2,4,6,8-trithiatetrazocine, showing atom numbering schemes. The (slightly disordered) molecule of toluence in the *exo*-structure is not shown.

S–S contacts. The exocyclic S–N and N–As distances can be compared to those found in $Ph_3AsNS_3N_3$.[8]

When solutions of (**2a**) (E = As) are dissolved in acetonitrile at room temperature the red colour of the solution slowly fades, and a yellow precipitate of (**2b**) (identified by i.r. analysis) is formed. This irreversible conversion of the *exo*- into the *endo*-isomer establishes that the latter is the more thermodynamically stable. Moreover, that the isomerization occurs rapidly at room temperature suggests a low activation energy. However, the nature of the transition state is by no means obvious. The inversion barriers in thiadiazole oxides are notably high,[9] and would be increased in (**2**) if the five-membered SNSNS ring were inflexible.[10] If the transannular S–S interaction is weak, ring opening followed by ring inversion (Scheme 2) rather than sulphur inversion may provide a low energy pathway for the conversion *exo* → *endo*. Further synthetic, kinetic, and theoretical studies are required to elucidate these points.



**Scheme 2**

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