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The Reactions of 2*H*-1,2,3-Diazaarsoles with Phenyl Azide

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ABSTRACT

2-Phenyl-5-methyl- and 2,5-diphenyl-2H-1,2,3-diazaarsoles **1a,b** *react with phenyl azide to give several crystalline products: tricyclic derivatives* **2a,b** *and 4,4'-bis(2H-1,2,3-diazaarsoles)* **5a,b** *formed at room temperature, and a cycloadduct* **6a** *obtained at +4°C. Compound* **6a** *undergoes a fast rearrangement in solutions of Et_3N or pyridine to give a stable dicoordinate arsenic compound, the 2H-1,2,3-diazaarsole* **7a**. *Heating solutions of* **2a** *under reflux in an inert atmosphere leads to* **5a** *and of* **2b**, *in the presence of water, to* **4b**.

The structures of **2a**, **4b**, *and* **7a** *were characterized by X-ray crystal structure determinations. © 1996 John Wiley & Sons, Inc.*

RESULTS AND DISCUSSION

Dicoordinate phosphorus compounds are known to react with azides [1–5]. The analogous reactions of dicoordinate arsenic compounds have, to our knowledge, not been investigated. Here we report on the reactions of 2*H*-1,2,3-diazaarsoles **1a,b** [6] with phenyl azide.

The products formed from these reactions (Scheme 1) depend on the reaction conditions. For reactions carried out at ambient temperatures, the colorless crystalline compounds **2a,b** (mp 237–238°C and 251–252°C, respectively) were isolated in 30–40% yields. The products were characterized by ^1H NMR, mass, and IR spectroscopy, and elemental analysis, and they exhibit analogous structures for the a and b series. Mass spectrometry revealed that the products were composed of two molecules of the starting diazaarsole and phenyl nitrene. ^1H NMR spectra of both products revealed proton signals of an As–CH fragment as the only one singlet at δ 3.86 and 4.62, respectively.

The structure of **2a** (Figure 1) was determined by X-ray crystal structure analysis. The molecule consists of three condensed heterocyclic rings substituted by three phenyl and two methyl groups. The molecule has the noncrystallographic symmetry C_2: a C_2 axis goes through the N^2 atom and the center of the C^7–C^8 bond. The central azadiarsole ring has a twist conformation, while the lateral diazaarsole het-

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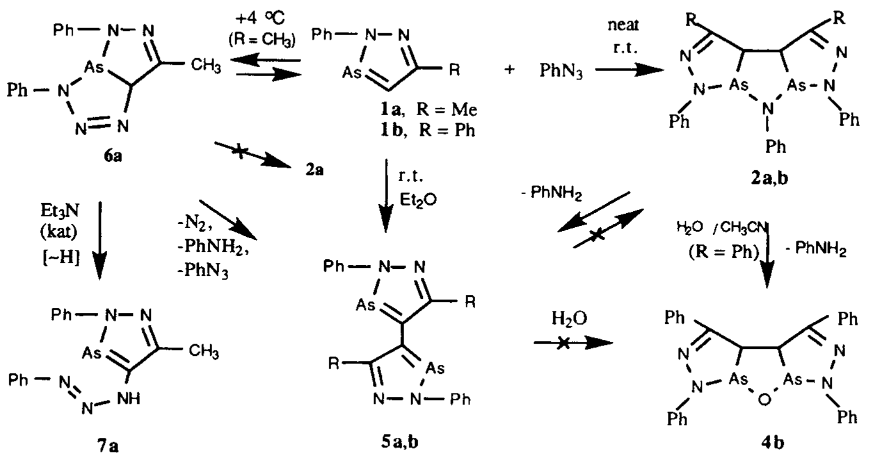


SCHEME 1

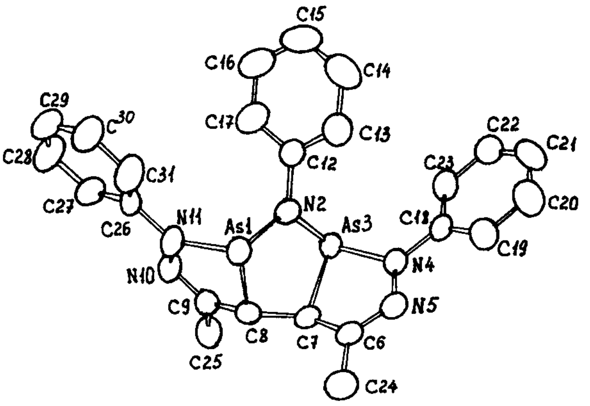


FIGURE 1 Crystal structure of the molecule **2a**.

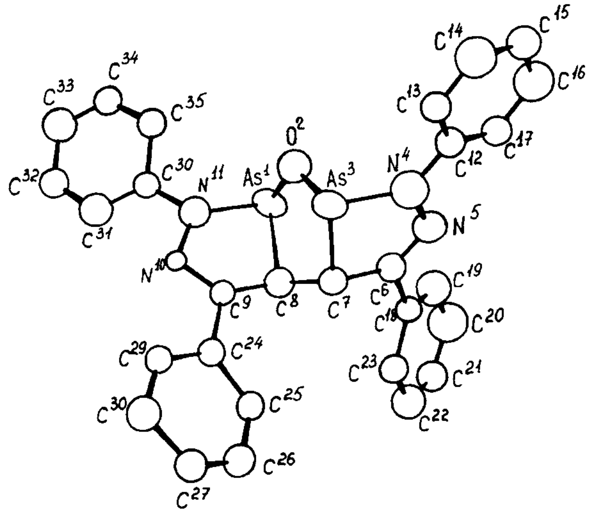
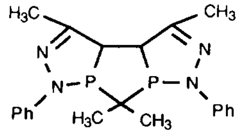


FIGURE 2 Crystal structure of the molecule **4b**.

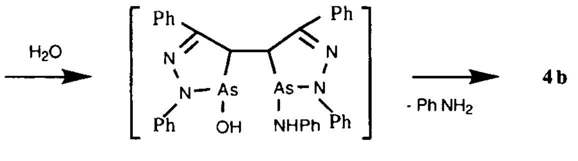
erocyclic rings are envelopes with the As atoms deviating from a plane of the other four atoms. The heterocyclic rings in **2a** are connected in a *cis*-anti-*cis* fashion. The phenyl rings at the atoms N^4 and N^{11} are almost coplanar with the corresponding heterocyclic rings; the dihedral angles are 4.9° and 4.0°, respectively.

A similar conformation of the tricyclic skeleton had been found earlier [7] for one of the isomers of **3** obtained from the reaction of 5-methyl-2-phenyl-1,2,3-diazaphosphole with 2-diazopropane, the tricyclic system **2a** being more folded than **3**, however.



3

The structure of **2b** was determined indirectly by identification of its hydrolysis product. While **2b** is stable to hydrolysis in the crystalline state, it was hydrolyzed gradually and completely in solutions during repeated recrystallizations with moisture inadvertently present, or with water being intentionally added. The hydrolysis yielded colorless crystals, mp 264–265°C, which were insoluble in a wide range of solvents. Therefore, NMR spectra could not be obtained. Mass spectroscopy of the new compound showed its molecular mass (M$^+$ 580) to be 75 mass units less than that of **2b** (M$^+$ 655). That the molecular structure of the hydrolysis product is **4b** (Scheme 1) was revealed by a single-crystal X-ray structure determination (Figure 2). The tricyclic structure of **4b** contains an oxygen atom instead of the NPh fragment of **2b** in a central ring. The three



SCHEME 2

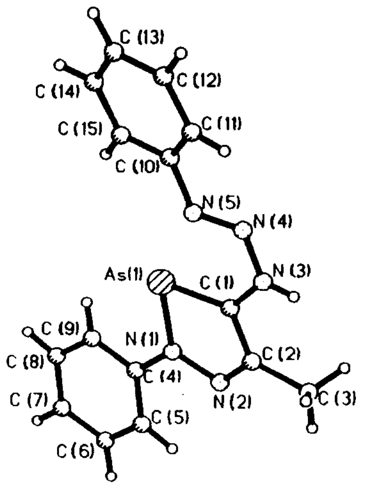
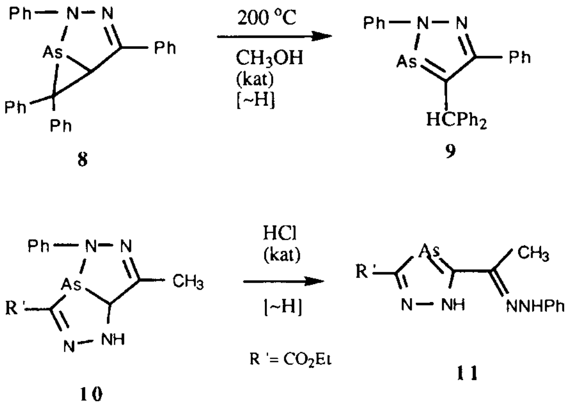


FIGURE 3 Crystal structure of the molecule **7a**.



SCHEME 3

condensed heterocyclic components of **4b** are substituted by a total of four phenyl rings. The geometry of **4b** is analogous to that of **2a** and **3**. The central heterocyclic ring is in a twist conformation, the deviation of atoms As^1 and As^2 from the plane $N^2C^7C^8$ being −0.756 and 0.708 Å, respectively.

The formation of **4b** from **2b** may be explained by a hydrolytic cleavage of the As–N bond of the central heterocyclic component of the tricyclic structure and subsequent elimination of a molecule of aniline (Scheme 2).

Next, we tried to identify intermediates in the formation of **2a,b**. For this purpose, the reactions were performed (1) at room temperature in solution or (2) at 0–5°C without a solvent. Unlike the reactions at room temperature without a solvent that are described in the foregoing, the reactions of **1a,b** with PhN_3 in Et_2O or benzene solution at ambient temperatures furnished a mixture of **2** and **5** (**a** or **b**, respectively.). 4,4′-Bis(2*H*-1,2,3-diazaarsoles) **5** had already been obtained earlier in the reactions of **1a,b** with methylphenyldiazomethane; the structure of **5b** had been determined by X-ray crystal structure analysis [8].

According to the following experiments, **5a,b** are not the precursors of **2a,b**, but the final products of interaction of diazaarsoles **1a,b** with PhN_3. Formally, addition of $PhNH_2$ to **5a,b** would give **2a,b**, respectively. But the attempted reaction of **5a** with $PhNH_2$ in CH_3CN did not proceed even with heating under reflux. On the contrary, **2a,b** were slowly and completely converted to **5a,b**, respectively, and $PhNH_2$ on heating under reflux in CH_3CN/petroleum ether of bp 40–60°C. It is worth mentioning that conversion of **2b** to the tricycle **4b** on heating does not proceed *via* **5b**; **5** is stable to hydrolysis even on heating under reflux in CH_3CN/H_2O.

A new product was obtained in the reaction of **1a** with phenyl azide at 4°C without a solvent: low-melting colorless crystalline **6a** (mp 64–65°C) was isolated (Scheme 1). Its elemental analysis corresponded to a 1:1 adduct that was unstable at room temperature. In crystalline form, it decomposed completely within 3 hours under elimination of N_2 to yield a dark, oily product mixture. One of the products was bis(diazaarsole) **5a**, isolated by precipitation with CH_3CN. At 4°C, **6a** can be kept for up to 2 months without decomposition. Mass spectroscopy of **6a** did not reveal its molecular peak; during evaporation in a mass spectrometer, **6a** underwent a chemical transformation to give **5a** (M^+ 438), **1a** (M^+ 220), and aniline (M^+ 93). Attempts to record ^1H NMR and IR spectra of **6a** in solutions ($CDCl_3$, CH_2Cl_2) failed; instead, **1a**, **5**, and PhN_3 (ν 2200 cm^{-1} of N_3 group in CH_2Cl_2 in its IR spectrum) were observed as the products of decomposition of **6a** (Scheme 1).

The decomposition of **6a** depends on the solvent. In triethylamine or pyridine, **6a** dissolved gradually and completely, giving as the only product a yellow crystalline compound (mp 156–158°C) insoluble in Et_3N and pyridine. The mass spectrum of the new product showed a molecular peak M^+ 339 corresponding to an adduct of PhN_3 with diazaarsole **1a**. Unlike **6a**, it was much more stable in solutions. Its ^1H NMR and IR spectra revealed the presence of an NH group. A number of structures are conceivable for the NH-containing adduct. A single-crystal X-ray investigation solved the problem in favor of a dicoordinate arsenic compound, a new 1,2,3-diazaarsole **7a** (Figure 3). It seems reasonable that compound **7a** can only originate from **6a** and not from the other theoretically possible regioisomer (Scheme 1). Therefore, the structure of **7a** simultaneously allows the assignment of structure **6a** to the adduct obtained at 0–5°C. The product **7a** was also obtained from **1a** and PhN_3 in Et_3N solution at room temperature (61% yield) (see Experimental).

Earlier [9,10], we had observed isomerization of bicyclic compounds of $\lambda^3\sigma^3$As compounds to monocyclic compounds of $\lambda^3\sigma^2$As as in the examples shown in Scheme 3.

The X-ray structure determination of **7a** revealed the diazaarsole heterocyclic moiety to be planar within 0.02 Å. Deviations of the N^3, N^4, and N^5 atoms from the plane of the five-membered ring are 0.04, 0.10, and 0.10 Å, respectively. A peculiarity of the molecule is a short intramolecular contact As···N^5 (2.50 A°); N^5 that lies nearly on a prolongation of the As–N^1 bond (the bond angle N^1 AsN^5 is 149.9(6)°). The geometrical parameters of the substituents in **7a** are not unusual.

EXPERIMENTAL

Infrared spectra were recorded on a Specord 75 IR instrument. ^{1}H NMR spectra were measured on a Varian HA-100 D NMR spectrometer; hexamethyl disiloxane (δ = 0.06 relative to tetramethylsilane) was used as an internal standard. The 13C NMR spectrum was recorded on a Bruker AC 200 spectrometer (δ in ppm from the internal tetramethylsilane). Mass spectra (EI and CI) were obtained on a Hitachi M-80 B spectrometer (70 eV).

Summaries of the X-ray structure* determinations are given in Table 1. Atomic coordinates and geometrical parameters are listed in Tables 2 through 8. A very small crystal of **4** gives a poor diffraction and decomposes during collection of the reflections.

6,9-Dimethyl-2,4,11-triphenyl-2,4,5,10,11-pentaza-1,3-diarsatricyclo[6,3,0,0^{3,7}]undeca-5,9-diene **2a**

A 1.05 g (8.81 mmol) quantity of phenyl azide was dropped slowly (under an inert atmosphere) into 1.93 g (8.77 mmol) of **1a**. The reaction was exothermic with elimination of N_2. The temperature of the reaction mixture was kept at 20°C by cooling. Colorless crystals of **2a** were isolated the next day from the oily, dark reaction mass by precipitation with Et_2O and were filtered off and washed with Et_2O.

0.75 g (32% yield). Mp 237–238°C. IR (ν, cm^{-1}): 493, 642, 650, 688, 738, 800, 873, 898, 922, 981, 1050, 1082, 1220, 1300, 1431, 1481, 1580. ^{1}H NMR (CD_2Cl_2): 2.22 s (6H, CH_3), 3.86 s (2H, CH), 6.50–7.78 m (15H, 3Ph). Mass spectrum (*m/z*; relative intensity): 531 (M^+, 32%), 311 (M^+–PhNN=C(CH_3)-CH=As, 15%), 220 (PhNN=C(CH_3)CH=As, 19%), 166 (PhNAs, 21%), 105 (PhN_2, 13%), 77 (Ph, 100%); anal. calcd (%) for C, 54.25; H, 4.36; N, 13.18; $C_{24}H_{23}As_2N_5$. Found (%); C, 53.98; H, 4.21; N, 13.25.

4,4′-Bis(5-methyl-2-phenyl-1,2,3-diazaarsole) **5a**

A 0.27 g (2.27 mmol) amount of phenyl azide in 2 mL of Et_2O was added dropwise to 0.49 g (1.74 mmol) of **1a**. The reaction mixture became dark at once. The elimination of N_2 and formation of tiny crystals were observed. After 3 days, two kinds of crystalline compounds **5a** (yellow colored) and **2a** (colorless) were filtered off together (0.15 g) and washed with cold Et_2O, and **5a** was separated from the mixture of crystals manually for identification.

Mass spectrum (*m/z*; relative intensity): 438 (M^+, 9%), 333 (10%), 219 (6%), 166 (23%), 142 (7%), 91 (PhN, 16%), 78 (C_6H_6, 19%), 77 (Ph, 100%); ^{1}H NMR (CCl_4): 2.6 s (6H, CH_3), 7.0–7.6 m (10H, Ph); IR (ν, cm^{-1}): 510, 635, 678, 740, 892, 898, 970, 1005, 1015, 1063, 1262, 1318, 1480, 1578.

2,4,6,9,11-Pentaphenyl-2,4,5,10,11-pentaza-1,3-diarsatricyclo[6,3,0,0^{3,7}]undeca-5,9-diene **2b**

A solution of 0.85 g (7.16 mmol) of phenyl azide in 3 mL of Et_2O was added dropwise to a solution of 2.02 g (7.16 mmol) of **1b** in 5 mL of Et_2O at ambient temperature. The reaction mixture gradually became dark. The next day, colorless crystals of **2b** were filtered off and washed with Et_2O to remove oily, dark reaction products.

1.01 g (43% yield). Mp 254–256°C (recrystallized from CCl_4); IR (ν, cm^{-1}): 500, 692, 700, 748, 772, 795, 810, 888, 920, 940, 1010, 1070, 1100, 1115, 1175, 1262, 1335, 1495, 1540, 1597. ^{1}H NMR (CD_2Cl_2): 4.62 s (2H, CH), 6.95–7.75 m (25H, 5Ph). Mass spectrum (*m/z*; relative intensity): 655 (M^+, 27%), 373 (M^+–PhNN=C(Ph)CH=As, 16%), 207 (PhNNC, 9%), 166 (PhNAs, 100%), 104 (PhCHN, 25%), 77(Ph, 80%); anal. calcd (%) for C, 62.30; H, 4.15; N, 10.68; $C_{34}H_{27}As_2N_5$. Found (%): C, 62.03; H, 4.04; N, 11.24.

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*Expanded tables of bond distances, bond angles, refined anisotropic thermal parameters, positional parameters, and structure amplitudes (10*F_{obs} plus 10F_{calc}) are available and may be obtained from the Fachinformationszentrum Energie Physik Mathematik, D-7514 Eggenstein-Leopoldshafen 2, Germany.

TABLE 1 Structure Determination Summary for **2a**, **4b**, and **7a** at Room Temperature

	2a	**4b**	**7a**
Empirical formula	$C_{24}H_{23}As_2N_5$	$C_{28}H_{22}As_2N_4O$	$C_{15}H_{14}AsN_5$
Color, habit	colorless, prismatic	colorless, prismatic	yellow, needlelike
Crystal size (mm)	0.2·0.2·0.3	0.05·0.05·0.1	0.05·0.05·0.5
Crystal system	Triclinic	Monoclinic	Orthorombic
Space group	P1	$P2_1/c$	Fdd2
Unit cell dimensions	a = 8.258(1) b = 0.870(1) c = 14.158(2) Å α = 70.00(1) β = 71.95(1) γ = 84.82(1)	a = 13.506(9) b = 18.654(9) c = 10.051(6) Å β = 105.42(50)	a = 24.816(9) b = 44.63(1) c = 5524(10) Å
Volume, V (Å)	1135.3(8)	2441.(3)	5820.(7)
Z	2	4	16
Formula weight	531.33	580.36	340.24
Density (calcd)	1.55 g/cm^3	1.58 g/cm^3	1.55 g/cm^3
Absorption coefficient	29.6 cm^{-1}	27.58 cm^{-1}	23.3 cm^{-1}
F(000)	536	1168	2768
Diffractometer		Enraf-Nonius CAD-4	
Radiation		Mok$_\alpha$, λ = 0.71073 Å	
2Θ range	$4° < 2\theta < 50°$	$4° < 2\theta < 50°$	$3° < 2\theta < 50°$
Scan mode	$\omega/2\theta$	$\omega/(5/3\theta)$	ω
Scan speed, variable:	2–20°/min in θ		2–20°/min in ω
Scan weight	$\omega = 1.35 + 0.35\mathrm{tg}\theta$		$\omega = 1.30 + 0.35\mathrm{tg}\theta$
Standard reflections	Two orientations and two intensities control reflections every 200 measured reflections		
Index range	$-9 < h < 9$ $-11 < k < 12$ $0 < l < 15$	$-15 < h < 6$ $0 < k < 23$ $0 < l < 13$	$0 < h < 26$ $0 < k < 46$ $0 < l < 7$
Reflections collected	4116	2304	2136
Observed reflections	2147 ($I > 3\sigma(I)$)	867 ($I > 2\sigma(I)$)	1161 ($I > 2\sigma(I)$)
Absorption correction	Empirical correction (12 reflections with $\chi > 80°$ were measured by azimuthal scan mode)	Not applied (crystal decomposed)	Not applied
Decay correction	Not applied	Linear decay correction	Not applied
System	SDP-PLUS, PDP 11/23		SHELX, IBM PC/AT
Solution	Patterson function analysis		
Refinement method	Full-matrix least-squares		
Quantity minimized		$w(\lvert F_o\rvert - \lvert F_c\rvert)^2$	
Extinction correction	Not applied		
Hydrogen atoms	Refined isotropically from difference Fourier maps	Not refined, were placed in calculated positions	Not refined, from difference Fourier
Weighting scheme	$w^{-1} = (\sigma(I))^2 = 0.07\ (\lvert F_o\rvert)^2$ (non-Poisson contribution)		$w^{-1} = (\sigma^2(F) + 0.05923(F^2))^2$
Final R-indexes	R = 0.038 R_w = 0.048	R = 0.114 R_w = 0.087	R = 0.0352 R_w = 0.036
Goodness of fit	1.183	1.64	0.553
Largest Δ/σ	0.3	0.18	0.14
Data to parameters ratio	5.77:1	4.66:1	6.14:1
Largest difference peak	0.3e/Å^3	0.5e/Å^3	0.4e/Å^3

4,4'-Bis(2,5-diphenyl-1,2,3-diazaarsole) 5b

A solution of 0.12 g (1.01 mmol) of phenyl azide in 7 mL of Et_2O was added dropwise to a solution of 0.27 g (0.96 mmol) of **1b** in 10 mL of Et_2O at ambient temperature. After 3 days, Et_2O was evaporated *in vacuo*. Yellow-colored crystals of **5b** were precipitated with CH_3CN and filtered off.

0.11 g (41% yield). Mp 248–249°C (recrystallized from CH_3CN); IR (ν, cm^{-1}): 445, 510, 520, 545, 655, 660, 670, 681, 730, 739, 865, 962, 1010, 1050, 1071, 1158, 1268, 1332, 1435, 1480, 1581; ^{1}H NMR ($CDCl_3$ or CD_2Cl_2): 7.21–7.84 m (Ph).

4,6,9,11-Tetraphenyl-4,5,10,11-tetraza-2-oxa-1,3-diarsatricyclo[6,3,0,0^{3,7}]undeca-5,9-diene 4b

An aqueous solution of **2b** in CCl_4/CH_3CN was heated under reflux for 3 hours, during which period of time the colorless solution became yellow. Colorless crys-

TABLE 2 Coordinates of Nonhydrogen Atoms and their Equivalent Isotropic Thermal Parameters $B^{eqv} = 4/3 \sum_{i=1}^{3} \sum_{j=1}^{3} (a_i \cdot a_j)B(i,j)$ (Å^2) in **2a**

Atom	*x*	*y*	*z*	*B*
As(l)	0.28399(7)	0.77554(6)	0.69683(4)	3.22(1)
As(3)	0.01503(7)	0.93594(6)	0.82945(4)	2.95(1)
N(2)	0.0651(6)	0.7983(4)	0.7768(3)	3.3(1)
N(4)	0.0503(6)	0.8636(5)	0.9631(3)	3.5(1)
N(5)	0.2195(6)	0.8487(5)	0.9620(4)	3.8(1)
N(10)	0.2577(6)	0.9861(5)	0.5232(3)	3.6(1)
N(11)	0.2713(7)	0.8508(5)	0.5584(3)	3.7(1)
C(6)	0.3245(7)	0.9079(6)	0.8709(4)	3.6(1)
C(7)	0.2582(7)	0.9851(5)	0.7795(4)	3.2(1)
C(8)	0.3431(7)	0.9558(6)	0.6776(4)	3.3(1)
C(9)	0.2921(7)	1.0388(5)	0.5832(4)	3.3(1)
C(12)	−0.0688(7)	0.7066(5)	0.8004(4)	5.5(1)
C(13)	−0.1245(9)	0.6156(7)	0.8986(5)	5.0(2)
C(14)	−0.259(1)	0.5294(7)	0.9234(6)	6.8(2)
C(15)	−0.332(1)	0.5352(7)	0.8456(6)	6.9(2)
C(16)	−0.2741(9)	0.6262(7)	0.7475(6)	6.2(2)
C(17)	−0.1448(9)	0.7091(7)	0.7255(5)	5.1(2)
C(18)	−0.0712(7)	0.7968(5)	1.0566(4)	3.2(1)
C(19)	−0.0273(8)	0.7160(6)	1.1445(5)	4.1(2)
C(20)	−0.152(1)	0.6487(7)	1.2361(5)	5.4(2)
C(21)	−0.3195(9)	0.6595(7)	1.2415(6)	5.3(2)
C(22)	−0.3658(8)	0.7417(7)	1.1551(5)	4.6(2)
C(23)	−0.2426(8)	0.8104(7)	1.0637(4)	4.1(2)
C(24)	0.5112(8)	0.9037(8)	0.8590(5)	5.5(2)
C(25)	0.2866(9)	1.1833(6)	0.5549(5)	4.6(2)
C(26)	0.2419(8)	0.7826(5)	0.4957(4)	3.4(1)
C(27)	0.2037(8)	0.8475(6)	0.4025(5)	3.9(1)
C(28)	0.1818(9)	0.7764(7)	0.3427(5)	4.9(2)
C(29)	0.1968(9)	0.6422(7)	0.3747(5)	4.8(2)
C(30)	0.234(1)	0.5786(6)	0.4668(5)	5.5(2)
C(31)	0.261(1)	0.6479(6)	0.5263(5)	5.4(2)

TABLE 3 Coordinates of Nonhydrogen Atoms and Their Equivalent Isotropic Thermal Parameters $B^{eqv} = 4/3 \sum_{i=1}^{3} \sum_{j=1}^{3} (a_i \cdot a_j)B(i,j)$ (Å^2) in **4b**

Atom	*x*	*y*	*z*	*B*
As(1)	0.4897(3)	0.1516(2)	0.2920(3)	3.69(8)
As(3)	0.3274(2)	0.2419(2)	0.0780(3)	3.50(8)
O(2)	0.426(1)	0.236(1)	0.229(2)	7.4(7)
N(4)	0.219(2)	0.239(1)	0.157(2)	5.2(7)
N(5)	0.195(2)	0.169(1)	0.197(2)	4.1(6)
N(10)	0.587(1)	0.140(1)	0.083(2)	1.5(5)
N(11)	0.595(2)	0.162(1)	0.217(2)	4.2(7)
C(6)	0.245(2)	0.120(2)	0.153(3)	3.3(7)
C(7)	0.318(2)	0.132(1)	0.059(2)	0.6(5)
C(8)	0.424(2)	0.102(1)	0.114(2)	0.8(6)
C(9)	0.495(2)	0.115(1)	0.032(3)	2.3(7)
C(12)	0.164(2)	0.295(1)	0.201(3)	3.3(7)
C(13)	0.176(2)	0.363(1)	0.148(3)	3.2(7)
C(14)	0.127(2)	0.418(2)	0.194(3)	6.0(9)
C(15)	0.073(2)	0.406(2)	0.294(3)	4.3(8)
C(16)	0.064(2)	0.336(2)	0.339(3)	5.9(9)
C(17)	1.110(2)	0.280(1)	0.293(3)	3.3(7)
C(18)	0.222(2)	0.042(1)	0.180(3)	3.0(7)
C(19)	0.208(2)	0.026(2)	0.301(3)	5.5(9)

TABLE 4 Coordinates of Nonhydrogen Atoms and Their Equivalent Isotropic Thermal Parameters $B^{eqv} = 4/3 \sum_{i=1}^{3} \sum_{j=1}^{3} (a_i \cdot a_j)B(i,j)$ (Å^2) in **7a**

Atom	*x*	*y*	*z*	*B*
As(1)	0.1005(1)	0.0245(1)	0[a]	3.76(8)
N(1)	0.0594(6)	0.0610(4)	0.027(4)	3.5(6)
N(2)	0.0737(6)	0.08351(4)	−0.131(4)	3.2(6)
N(3)	0.1773(6)	0.0373(4)	−0.407(4)	5.0(8)
N(4)	0.1966(6)	0.0095(4)	−0.389(4)	4.0(7)
N(5)	0.1723(5)	−0.0055(4)	−0.215(4)	2.7(6)
C(1)	0.1341(7)	0.0467(4)	−0.239(4)	4.2(8)
C(2)	0.1128(7)	0.0766(4)	−0.285(4)	3.6(8)
C(3)	0.1340(8)	0.0994(4)	−0.473(5)	5.1(9)
C(4)	0.0164(7)	0.0653(3)	0.184(3)	2.8(8)
C(5)	−0.0167(8)	0.0908(4)	0.162(4)	3.6(9)
C(6)	−0.0587(9)	0.0943(4)	0.332(4)	5.(1)
C(7)	−0.0723(8)	0.0735(4)	0.512(5)	3.0(8)
C(8)	−0.0388(9)	0.0487(4)	0.530(5)	4.(1)
C(9)	0.0042(9)	0.0451(4)	0.369(4)	5.(1)
C(10)	0.1931(7)	−0.0357(4)	−0.196(3)	2.4(7)
C(11)	0.2269(7)	−0.0480(3)	−0.376(4)	2.8(8)
C(12)	0.2436(8)	−0.0784(4)	−0.342(4)	5.(1)
C(13)	0.2237(8)	−0.0946(4)	−0.142(4)	3.0(9)
C(14)	0.1897(7)	−0.0818(5)	0.023(4)	3.3(8)
C(15)	0.1727(7)	−0.0522(4)	0.001(4)	3.5(8)

[a]Origin fixing parameter.

TABLE 5 Selected Bond Lengths, *d*(Å), of **2a** and **4b**

	2a	**4b**		**2a**	**4b**
As(1)–O(2)	1.858(5)	1.82(2)	N(5)–C(6)	1.292(8)	1.28(3)
As(1)–N(11)	1.881(5)	1.79(2)	N(10)–N(11)	1.388(7)	1.39(2)
As(1)–C(8)	1.968(6)	2.00(2)	N(10)–C(9)	1.282(8)	1.30(3)
As(3)–O(2)	1.851(5)	1.73(2)	N(11)–R(2)	1.418(8)	1.40(3)
As(3)–N(4)	1.888(5)	1.85(2)	C(6)–C(7)	1.514(9)	1.55(3)
As(3)–C(7)	1.969(6)	2.05(2)	C(6)–R(3)	1.496(10)	1.54(3)
N(2)–C(12)	1.439(7)	—	C(7)–C(8)	1.524(9)	1.50(3)
N(4)–N(5)	1.388(7)	1.43(3)	C(8)–C(9)	1.494(9)	1.45(3)
N(4)–R(1)	1.392(7)	1.41(3)	C(9)–R(4)	1.482(10)	1.51(3)

tals of **4b** appeared in the solution, and this compound was filtered off.

Mp 264–265°C. IR spectrum (*ν*, cm^{-1}): 460, 505, 530, 592, 615, 650, 665, 680, 701, 729, 755, 760, 768, 820, 885, 890, 915, 935, 991, 1001, 1010, 1019, 1030, 1042, 1050, 1053, 1070, 1089, 1265, 1331, 1440, 1475, 1480, 1540, 1581, 1591. Mass spectrum (*m*/*z*: relative intensity): 580 (M$^+$, 41%), 563 (M$^+$–17, 8%), 283 ($C_{14}H_{12}AsN_2$, 19%), 257 (13%), 208 ($C_{14}H_{12}N_2$, 7%), 204 (5%), 202 (8%), 166 (PhNAs, 80%), 106 (PhN_2H, 11%), 105 (PhN_2, 8%), 91 (PhN, 20%), 78 (C_6H_6, 100%); anal. calcd (%) for C, 57.95; H, 3.82; N, 9.65; $C_{28}H_{22}As_2N_4O$. Found (%): C, 57.23; H, 3.64; N, 9.75.

The filtrate, dried *in vacuo*, provided a residue of **5b** and $PhNH_2$; **5b** could be isolated from the filtrate

TABLE 6 Bond Angles ω(°) in **2a** and **4b**

	2a	4
N(2)As(1)N(11)	102.4(2)	96.7(9)
N(2)As(1)C(8)	89.3(2)	91.8(9)
N(11)As(1)C(8)	83.4(3)	84.(1)
N(2)As(3)N(4)	102.8(2)	98.(1)
N(2)As(3)C(7)	90.3(3)	91.9(9)
N(4)As(3)C(7)	84.6(2)	88.3(9)
As(1)O(2)As(3)	121.3(3)	123.(1)
As(1)N(2)C(12)	120.0(4)	—
As(3)N(2)C(12)	118.7(4)	—
As(3)N(4)N(5)	115.3(4)	114.(2)
As(3)N(4)R(1)	125.9(4)	131.(2)
N(3)N(4)R(1)	116.9(5)	114.(2)
N(4)N(5)C(6)	113.0(5)	112.(2)
N(11)N(10)C(9)	112.3(5)	108.(2)
As(1)N(11)N(10)	115.6(4)	121.(2)
As(1)N(11)R(2)	126.1(4)	128.(2)
N(10)N(11)R(2)	117.1(5)	109.(2)
N(5)C(6)C(7)	120.2(5)	126.(2)
N(5)C(6)R(3)	118.8(7)	118.(2)
C(7)C(6)R(3)	120.9(6)	116.(2)
As(3)C(7)C(6)	104.2(4)	97.(2)
As(3)C(7)C(8)	109.4(4)	108.(1)
C(6)C(7)C(8)	115.0(6)	115.(2)
As(1)C(8)C(7)	109.4(4)	108.(1)
As(1)C(8)C(9)	104.7(4)	103.(2)
C(7)C(8)C(9)	116.4(6)	116.(2)
N(10)C(9)C(8)	120.2(6)	124.(2)
N(10)C(9)R(4)	118.8(6)	116.(2)
C(8)C(9)R(4)	121.0(6)	120.(2)
As(1)N(11)N(10)	115.6(4)	121.(2)

TABLE 7 Bond Distances *d* (Å) in **7a**

As(1)–N(1)	1.93(1)	N(1)–C(4)	1.36(2)
As(1)–C(1)	1.80(1)	C(1)–N(3)	1.45(2)
As(1)···N(5)	2.50(1)	C(2)–C(3)	1.51(2)
N(1)–N(2)	1.35(2)	N(3)–N(4)	1.34(2)
N(2)–C(2)	1.30(2)	N(4)–N(5)	1.28(2)
C(1)–C(2)	1.45(2)	N(5)–C(10)	1.45(2)

by precipitation with CH_3CN and collection by filtration.

4-Methyl-2,8-diphenyl-2,3,6,7,8-pentaza-1-arsabicyclo[3,3,0]octa-3,6-diene **6a**

A 1.21 g (10.16 mmol) amount of phenyl azide was added dropwise to 2.24 g (10.17 mmol) of diazaarsole **1a** at 4°C in an inert atmosphere. The first crystals of **6a** appeared in the reaction mixture within 0.5 hour. The reaction mixture became crystallized completely in 3 hours and was kept at 4°C until the next day. Colorless crystals of **6a** were precipitated with cold Et_2O and quickly filtered off.

2.57 g (75% yield). Mp 64–65°C; IR (ν, cm^{-1}): 498, 615, 642, 683, 745, 798, 847, 885, 952, 1005, 1017, 1046, 1073, 1120, 1172, 1178, 1224, 1283, 1305, 1441, 1584; anal. calcd (%) for C, 53.11; H, 4.16; N, 20.63; $C_{15}H_{14}AsN_5$. Found (%): C, 53.54; H, 4.32; N, 20.35.

TABLE 8 Bond Angles ω(°) in **7a**

N(1)As(1)C(1)	80.4(7)	N(3)N(4)N(5)	112.(1)
N(1)As(1)···N(5)	149.9(6)	N(4)N(5)C(10)	112.(1)
C(1)As(1)···N(5)	69.6(7)	As(1)C(1)C(2)	117.(1)
As(1)N(1)N(2)	116.(1)	As(1)C(1)N(3)	127.(1)
As(1)N(1)C(4)	126.(1)	C(2)C(1)N(3)	116.(1)
N(2)N(1)C(4)	118.(1)	N(2)C(2)C(1)	113.(1)
N(1)N(2)C(2)	114.(1)	N(2)C(2)C(3)	120.(1)
C(1)N(3)N(4)	119.(1)	C(1)C(2)C(3)	127.(1)

5-Methyl-2-phenyl-4-(1′-phenyl-3′-triazeno)-1,2,3-diazaarsole **7a**

A 0.55 g (4.62 mmol) quantity of phenyl azide was added dropwise at ambient temperature to a solution of 1.01 g (4.59 mmol) of **1a** in 3 mL of Et_3N. A slightly exothermic reaction and darkening of the reaction mixture were observed. After 5 days, Et_3N was evaporated in vacuum. Bright-yellow-colored crystals of **7a** were precipitated with Et_2O and filtered off from a dark, oily reaction mass.

0.95 g (61% yield). Mp 156–158°C (dec.); IR (ν, cm^{-1}): 588, 669, 748, 759, 873, 908, 1019, 1031, 1062, 1139, 1270, 1348, 1375, 1439, 1467, 1578, 3347; ^1H NMR (CD_2Cl_2): 2.47 s (3H, CH_3), 6.60–7.33 m (10H, 2Ph), 10.68 s (1H, NH); ^{13}C NMR ($CDCl_3$): 14.08 (CH_3), 119.02 and 121.00 (C_o of 2Ph), 124.75 and 127.73 (C_p of 2Ph), 129.19 and 129.15 (C_m of 2Ph), 147.50 and 147.44 (C_i of 2Ph), 139.36 (C = As), 157.72 (C = N). Mass spectrum (*m*/*z*; relative intensity): 339 (M^+, 12%), 166 (PhNAs, 43%), 105 (PhN_2, 50%), 78 (C_6H_6, 100%); anal calcd (%) for C, 53.10; H, 4.16; N, 20.64; $C_{15}H_{14}AsN_5$. Found (%): C, 52.73; H, 4.00; N, 21.01.

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