

Synthesis and Structure of the First 10-As-3 Species¹

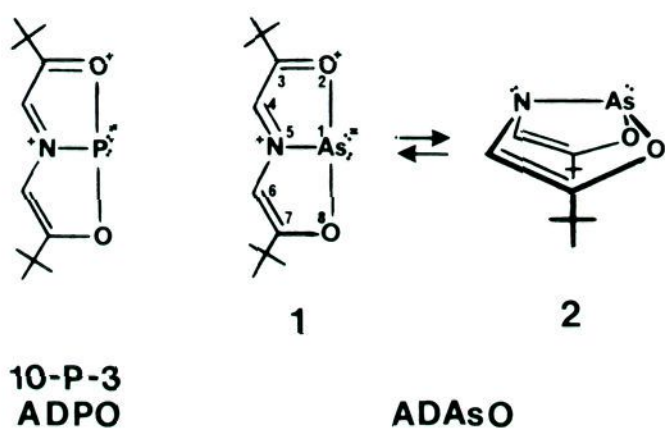
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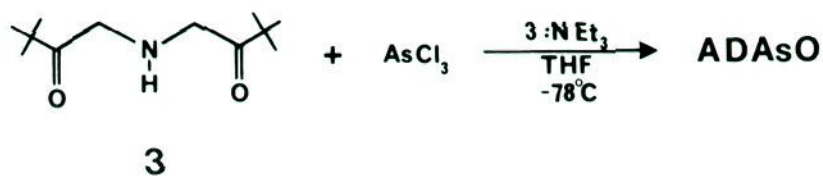
In a recent report² we described the preparation and structure of the first 10-P-3 species (10-P-3 ADPO). This molecule, which contained the previously unknown phosphorane diide function, illustrated the ability of phosphorus to participate in three-center, four-electron bonding while remaining tricoordinate. Questions about the stability trends among hypervalent tricoordinate pnictogens led us to investigate the analogous arsenic system. We now report the remarkable structure of a stable 10-As-3 species (1).

As with the 10-P-3 ADPO system, the 10-As-3 system (1) might exhibit electromorphism² between 10-As-3 and 8-As-3 (2)



states. Examination of the relative stability of 8- and 10-electron arsenic species in the trivalent state would thus be possible.

The 5-aza-2,8-dioxa-3,7-di-*tert*-butyl-1-arsabicyclo[3.3.0]-octa-3,6-diene (ADAsO) ring system is conveniently prepared by reaction of secondary amine 3 with AsCl₃ in THF at -78 °C.



ADAsO exhibits proton NMR resonances at δ 1.31 (s, 9 H) and 7.90 (s, 1 H) in CD₂Cl₂. The proton-decoupled ¹³C NMR (CD₂Cl₂) exhibits resonances at δ 28.3 (CH₃), 36.3 ((C(CH₃)₃)), 113.6 (C-4), and 174.8 (C-3). ADAsO gives a molecular ion in the EI mass spectrum (70 eV) at *m/z* 285. The UV spectrum of ADAsO shows absorbances (pentane) at λ_{\max} (log ϵ) 238 (3.9) and 362 (4.2). Recrystallization from pentane or acetonitrile gave a light green sample of ADAsO with a melting point of 122–124 °C and satisfactory analyses (CHNAs) were obtained.

While ADAsO is thermally stable it undergoes a reversible color change to a deep amber liquid at its melting point. This behavior

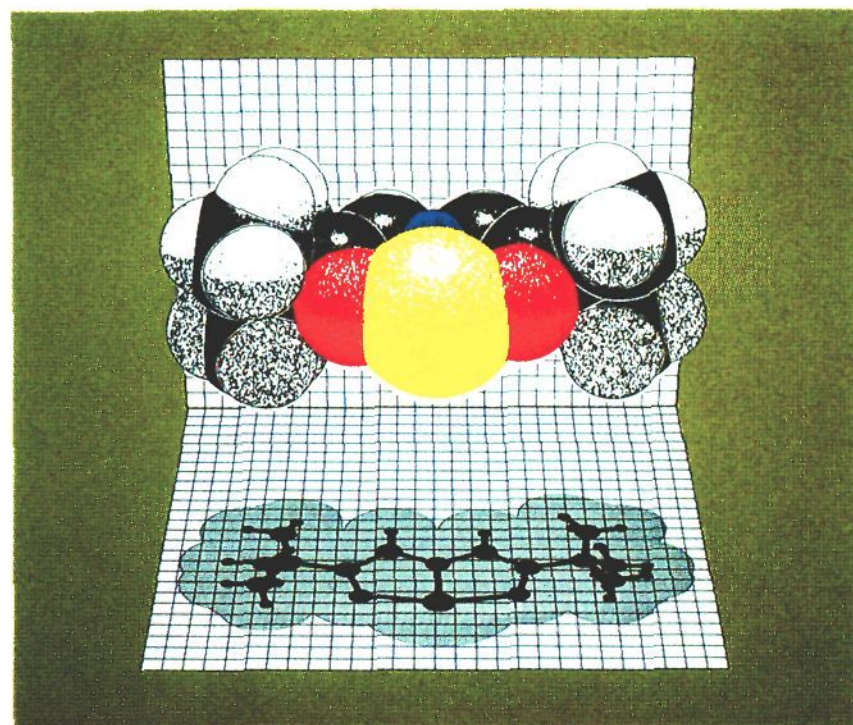


Figure 1. KANVAS³ drawing of 10-As-3 ADAsO.

Table I. Bond Lengths and Angles in 10-As-3 ADAsO

| bond lengths, pm | | bond angles, deg | |
|---------------------|----------------------|------------------|----------------------|
| As-O | 195.5 (3), 199.8 (3) | O-As-O | 160.3 (1) |
| As-N | 183.9 (3) | N-As-O | 80.4 (1), 80.0 (1) |
| C-O | 130.7 (5), 131.0 (4) | C-O-As | 114.7 (2), 113.6 (2) |
| C-C _{ring} | 136.6 (5), 136.0 (5) | C-N-As | 117.6 (2), 117.2 (2) |
| C-N | 137.3 (4), 137.2 (4) | C-C-N | 112.9 (3), 113.5 (3) |
| | | C-C-O | 114.9 (3), 115.3 (3) |

is not exhibited up to 180 °C in a variety of solvents and the liquid-phase ¹H NMR (+130 °C) of the melt of ADAsO exhibits two broad resonances at δ 1.3 (9 H) and 7.9 (1 H); very similar to the room temperature spectrum.

Figure 1 illustrates the solid-state geometry of ADAsO.⁴ Like ADPO this molecule exhibits a T-shaped geometry about the central atom and a planar ring system. The bond angles and distances in ADAsO are presented in Table I. As expected the As-O and As-N bond lengths are longer than the corresponding distances in ADPO. While the larger size of arsenic relative to phosphorus is reflected in the 160° O-As-O angle, the remainder of the ADAsO system is fairly similar in structure to ADPO.

Spectra of ADAsO did not provide any evidence suggestive of the presence of the 8-As-3 electromorph. It is interesting to note the downfield shift of both C-₃₍₇₎ ($\Delta\delta$ = 5.6) and the ring protons at C-₄₍₆₎ ($\Delta\delta$ = 0.55) in the NMR spectra of ADAsO relative to ADPO. These data suggest that the general downfield positions of the ring protons in ADPO and ADAsO is largely due to the influence of the positive charge delocalized over the ligand backbone. The reduced ability of arsenic relative to phosphorus to overlap and participate in π bonding with the neighboring second-row elements (O, N) thus shifts protons at C-4(6) further

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(1) The *N-X-L* system has been previously described (Perkins, C. W.; Martin, J. C.; Arduengo, A. J.; Lau, W.; Alegria, A.; Kochi, J. K. *J. Am. Chem. Soc.* 1980, 102, 7753). *N* valence electrons about a central atom X with *L* ligands.

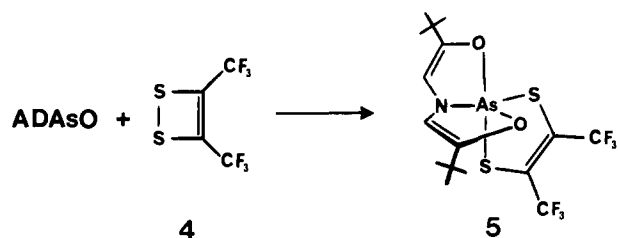
(2) Culley, S. A.; Arduengo, A. J., III *J. Am. Chem. Soc.* 1984, 106, 1164.

(3) This perspective drawing was made with the KANVAS computer graphics program. This program is based on the program SCHAKAL of E. Keller (Kristallographisches Institut der Universität Freiburg, FRG), which was modified by A. J. Arduengo, III (E. I. du Pont de Nemours & Co., Wilmington, DE) to produce the back and shadowed planes.

(4) The crystal data were as follows: C₁₂H₂₀NO₂As, orthorhombic, space group *P*_{bcu}, *a* = 1106.5 (7) pm, *b* = 2303.6 (14) pm, *c* = 1163.07 (7) pm, *Z* = 8, *D*_c = 1.278 g/cm³; crystal size, 0.62 × 0.68 × 0.70 mm. With 1998 reflections of intensity greater than 2.5 σ , the structure was solved by direct methods (MULTAN 80) and standard difference Fourier techniques. The final *R* factors were *R* = 0.040 and *R*_w = 0.048. The final difference Fourier was featureless; the range in residual density was 0.50 < *e* Å⁻³ < -0.27.

downfield (not upfield as would be expected from ring current considerations).

ADAsO undergoes a ready reaction with bis(trifluoromethyl)dithiete (**4**) to give adduct **5**. Compound **5** exhibits a



single *tert*-butyl resonance in the ^1H NMR (CD_2Cl_2) at room temperature at δ 1.17 and a ring proton resonance at δ 7.45. The ^{19}F NMR (CD_2Cl_2) shows a resonance at -54.0 ppm. The low-temperature ^1H and ^{19}F NMR spectra show a split⁵ of the room temperature resonances (^1H NMR (-103 °C, CD_2Cl_2) δ 1.11 (s, 9 H), 1.24 (s, 9 H), 6.94 (s, 1 H), 8.10 (s, 1 H); ^{19}F NMR (-103 °C, CD_2Cl_2) δ -54.42 (q, 3 F, $J_{\text{FF}} = 12$ Hz), -53.02 (q, 3 F, $J_{\text{FF}} = 12$ Hz) suggestive of the frozen structure **5**.

At present it is not known whether the dynamic behavior of **5** at room temperature is a result of equilibration of structures via a pseudorotation or ionization pathway or perhaps proceeds through a 12-As-5 species.⁶ Further work is currently in progress in this and related areas.

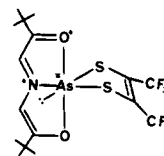
Acknowledgment is made to the National Science Foundation (NSF CHE 81-04980) and E. I. du Pont de Nemours & Co. for their support of this work. This work was also supported in part by the University of Illinois NSF Regional Instrumentation Facility (NSF CHE 79-16100). We are grateful to Dr. Scott R. Wilson for the X-ray structure of 10-As-3 ADAsO and to Mark Mizzen for his work in the synthesis of amine **3**.

Registry No. **1**, 93684-26-5; **3**, 88686-46-8; **4**, 360-91-8; **5**, 93684-27-6; AsCl_3 , 7784-34-1.

Supplementary Material Available: A complete description of the X-ray crystallographic structure determination of 10-As-3 ADAsO and tables of positional and thermal parameters (6 pages). Ordering information is given on any current masthead page.

(5) The coalescence temperature is estimated to be about -55 °C in CD_2Cl_2 on the basis of current data.

(6) A structure like



could be an intermediate if it were to undergo rapid square-pyramidal inversion.