

## Communications

Gas Phase Structure of (Trifluoromethyl)arsinous Diazide,  $\text{CF}_3\text{As}(\text{N}_3)_2$ How Ghee Ang,<sup>1a</sup> Whei Lu Kwik,<sup>1a</sup> Yiew Wang Lee,<sup>1a</sup> and Heinz Oberhammer<sup>\*,1b</sup>

Department of Chemistry, National University of Singapore, Lower Kent Ridge Road, Singapore 0511, Singapore, and Institut für Physikalische und Theoretische Chemie, Universität Tübingen, 72076 Tübingen, Germany

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The first arsenic azide,  $\text{Ph}_2\text{AsN}_3$ , synthesized by Reichle<sup>2</sup> by reacting  $\text{Ph}_2\text{AsCl}$  with  $\text{LiN}_3$  in pyridine, was found to decompose to a tetrameric diphenylarsenonitrile,  $[\text{Ph}_2\text{AsN}]_4$ , at ca. 190 °C. Revitt and Sowerby<sup>3</sup> have also reported the synthesis and thermal decomposition of other arsinous azides,  $(\text{RR}'\text{AsN}_3)$  where R, R' = organic groups). To date, only three fluorinated azides of group 15 elements have been reported, namely bis-(trifluoromethyl)phosphinous azide,<sup>4</sup>  $(\text{CF}_3)_2\text{PN}_3$ , bis(pentafluorophenyl)phosphinous azide,<sup>5</sup>  $(\text{C}_6\text{F}_5)_2\text{PN}_3$ , and phosphorazidous difluoride,<sup>6,7</sup>  $\text{F}_2\text{PN}_3$ . However, very little is known about their reactivities or structures. Thus far, the gas phase structure<sup>8</sup> of  $(\text{CF}_3)_2\text{AsN}_3$  and the crystal structure<sup>9</sup> of  $\text{RP}(\text{N}_3)_2$  (R = 2,4,6-(*t*-Bu)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>) have been studied. We now report the synthesis and a structural investigation of (trifluoromethyl)arsinous diazide,  $\text{CF}_3\text{As}(\text{N}_3)_2$ , using gas electron diffraction.

In a typical preparation, (trifluoromethyl)arsinous dichloride (0.1203 g, 0.560 mmol) was condensed into an evacuated ampule containing excess dry sodium azide cooled to liquid nitrogen temperature. The ampule was then allowed to warm to room temperature. On vacuum trap-to-trap fractionation, a colorless crystalline solid was trapped at -40 °C (passed 0 °C). It was identified as (trifluoromethyl)arsinous diazide (0.1272 g, 0.558 mmol, 99% yield). Its infrared spectrum showed absorptions at 3315 vw ( $\nu_{\text{as}}(\text{N}_3) + \nu_{\text{sym}}(\text{N}_3)$ ), 2444 vw ( $2\nu_{\text{sym}}(\text{N}_3)$ ), 2125 vs ( $\nu_{\text{as}}(\text{N}_3)$ ), 2108 vs ( $\nu_{\text{as}}(\text{N}_3)$ ), 1354 vw ( $2\delta(\text{NNN})$ ), 1234 m ( $\nu_{\text{sym}}(\text{N}_3)$ ), 1218 s ( $\nu_{\text{sym}}(\text{N}_3)$ ), 1192 w, 1164 m, 1142 vs ( $\nu(\text{CF}_3)$ ), 730 vw ( $\delta(\text{CF}_3)$ ), 676 vw ( $\delta(\text{NNN})$ ), 564 vw ( $\pi(\text{NNN})$ ), 486 w ( $\nu(\text{As}-\text{N})$ ), and 466 m ( $\nu(\text{As}-\text{N})$ )  $\text{cm}^{-1}$ . In the <sup>19</sup>F NMR spectrum a singlet at 14.2 ppm with respect to trifluoroacetic acid was observed. The mass spectrum showed

characteristic fragmentation ions at *m/z* (%) 228 (0.2,  $[\text{CF}_3\text{As}(\text{N}_3)_2]^+$ ), 200 (5.6,  $[\text{CF}_3\text{AsN}_4]^+$ ), 186 (17.2,  $[\text{CF}_3\text{AsN}_3]^+$ ), 144 (9.0,  $[\text{CF}_3\text{As}]^+$ ), 113 (59.9,  $[\text{AsF}_2]^+$ ), 94 (18.5,  $[\text{AsF}]^+$ ), 69 (37.8,  $[\text{CF}_3]^+$ ), 50 (3.1,  $[\text{CF}_2]^+$ ), 42 (81.5,  $[\text{N}_3]^+$ ), 28 (100.0,  $[\text{N}_2]^+$ ). Anal. Calcd for  $\text{CAsF}_3\text{N}_6$ : F, 25.0. Found: F, 25.3. *Caution! Explosions have been encountered when the azide came in contact with heat.*

The electron diffraction intensities were recorded with a gas diffractometer<sup>10</sup> at two camera distances (25 and 50 cm) and with an accelerating voltage of about 60 kV. The electron wavelength was calibrated with ZnO diffraction patterns. The sample was kept at room temperature, and the inlet system and nozzle were heated to 30 °C. The camera pressure during the experiment was better than  $1.5 \times 10^{-5}$  Torr. The photographic plates were analyzed by the usual procedures,<sup>11</sup> and averaged molecular intensities in the *s* ranges 2–8 and 8–35 Å<sup>-1</sup> in steps of  $\Delta s = 0.2$  Å<sup>-1</sup> are shown in Figure 1.

The experimental radial distribution function (Figure 2) was derived by Fourier transform of the molecular intensities, using an artificial damping function  $\exp(-bs^2)$  with  $b = 0.002$  Å<sup>2</sup>. Radial distribution functions were calculated for molecular models with different torsional orientations of the two azide groups. This orientation is described by the dihedral angles  $\Phi_1$  ( $\text{CAsN}'_{\alpha}\text{N}'_{\beta}$ ) and  $\Phi_2$  ( $\text{CAsN}'_{\alpha}\text{N}'_{\beta}$ ). Rotations of the two azide groups in opposite directions ( $\Phi_1 = -\Phi_2$ ,  $C_s$  symmetry) or in the same direction ( $C_1$  symmetry) were considered. The best agreement with the experimental curve is obtained with a  $C_s$  model and  $\Phi_1 = -\Phi_2 \sim 125^\circ$ . This angle corresponds to a cis or near-cis orientation of both azide groups relative to the arsenic lone pair.

In the least-squares refinement, the molecular intensities were modified with a diagonal weight matrix and known scattering amplitudes and phases were used.<sup>12</sup> Local  $C_{3v}$  symmetry for the  $\text{CF}_3$  group and overall  $C_s$  symmetry were assumed. Vibrational amplitudes were refined in groups according to their distances. The amplitudes for the two N–N bond distances

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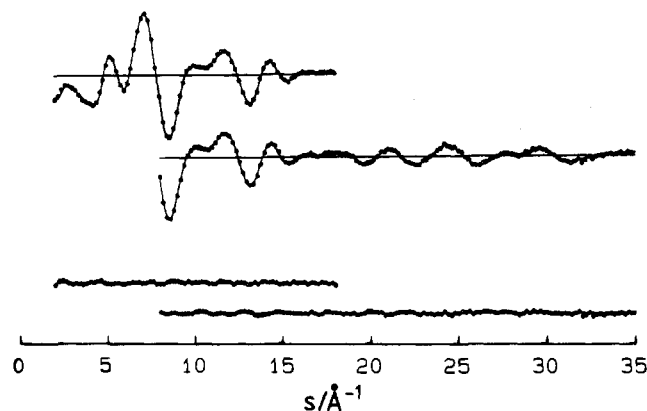


Figure 1. Experimental (dots) and calculated (full line) molecular intensities and differences for 50 and 25 cm camera distances.

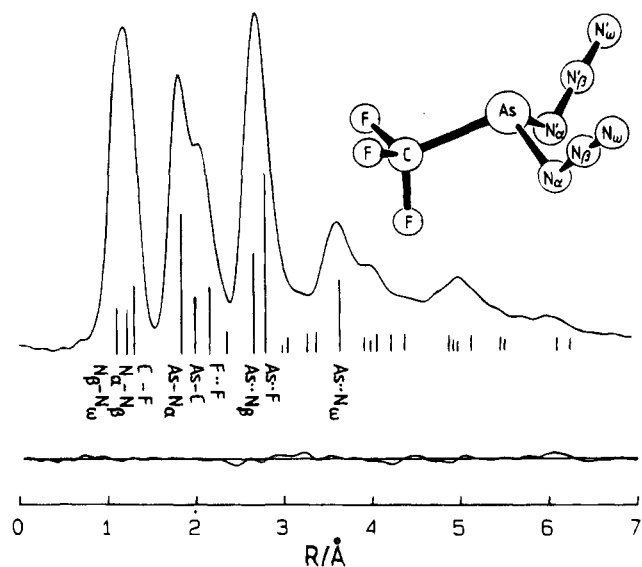


Figure 2. Experimental radial distribution function and difference curve. The positions of interatomic distances are indicated by vertical bars.

were set equal. The value was fixed in the least-squares analyses but varied by  $\pm 0.005$  Å, in order to estimate systematic errors caused by this constraint. With these assumptions, nine geometric parameters  $p_i$  and twelve vibrational amplitudes  $a_k$  were refined simultaneously. The following correlation coefficients had values larger than  $|0.6|$ :  $p_5/p_{10} = -0.81$ ,  $p_9/p_9 = -0.70$ ,  $p_8/a_5 = 0.82$ ,  $p_9/a_5 = -0.67$ ,  $p_6/a_9 = 0.70$ ,  $p_7/a_9 = -0.70$ ,  $a_{11}/a_{12} = 0.62$ . Numbering of the geometric parameters  $p_i$  and vibrational amplitudes  $a_k$  and the final results are given in Table 1.

The most interesting aspect of the molecular structure of this diazide is the orientation of the two azide groups. This orientation is best described by the dihedral angle relative to the As lone pair,  $\Phi(\text{lpAsN}_\alpha\text{N}_\beta)$ . Since the direction of the lp

Table 1. Results of the Electron Diffraction Study of  $\text{CF}_3\text{As}(\text{N}_3)_2^a$

Geometric Parameters			
$\text{N}_\beta=\text{N}_\omega$	1.128(6) ( $p_1$ )	$\text{C}-\text{As}-\text{N}_\alpha$	102.7(14) ( $p_7$ )
$\text{N}_\alpha=\text{N}_\beta$	1.225(7) ( $p_2$ )	$\text{As}-\text{N}_\alpha=\text{N}_\beta$	117.3(11) ( $p_8$ )
$\text{C}-\text{F}$	1.338(2) ( $p_3$ )	$\text{N}_\alpha=\text{N}_\beta=\text{N}_\omega^b$	174.7(21) ( $p_9$ )
$\text{As}-\text{N}_\alpha$	1.862(3) ( $p_4$ )	$\text{F}-\text{C}-\text{F}$	107.5(4) ( $p_{10}$ )
$\text{As}-\text{C}$	2.014(8) ( $p_5$ )	$\Phi_1(\text{CAsN}_\alpha\text{N}_\beta)^c$	127(4) ( $p_{11}$ )
$\text{N}_\alpha-\text{As}-\text{N}'_\alpha$	106.3(21) ( $p_6$ )	$\Phi(\text{lpAsN}_\alpha\text{N}_\beta)^d$	0(4)
Interatomic Distances and Vibrational Amplitudes			
dist	amplitude	dist	amplitude
$\text{N}_\beta=\text{N}_\omega$ 1.13	} 0.037[5] <sup>e</sup>	$\text{N}_\alpha \cdot \text{N}'_\alpha$ 2.98	} 0.09(3) ( $a_6$ )
$\text{N}_\alpha=\text{N}_\beta$ 1.23		$\text{N}_\alpha \cdot \text{C}$ 3.03	
$\text{C}-\text{F}$ 1.34	0.042(4) ( $a_1$ )	$\text{N}_\alpha \cdot \text{F}$ 3.28–3.38	0.20(4) ( $a_7$ )
$\text{As}-\text{N}_\alpha$ 1.86	} 0.060(4) ( $a_2$ )	$\text{As} \cdot \text{N}_\omega$ 3.66	0.10(2) ( $a_8$ )
$\text{As}-\text{C}$ 2.01		$\text{N} \cdot \text{X}^f$ 3.92–4.05	0.15(4) ( $a_9$ )
$\text{F} \cdot \text{F}$ 2.16	0.061(5) ( $a_3$ )	$\text{N} \cdot \text{F}$ 4.22–4.40	0.22(7) ( $a_{10}$ )
$\text{N}_\alpha \cdot \text{N}_\omega$ 2.35	0.052(10) ( $a_4$ )	$\text{N} \cdot \text{X}^f$ 4.64–5.14	0.22(5) ( $a_{11}$ )
$\text{As} \cdot \text{N}_\beta$ 2.66	} 0.091(28) ( $a_5$ )	$\text{N} \cdot \text{Y}^g$ 5.47–6.28	0.31(14) ( $a_{12}$ )
$\text{As} \cdot \text{F}$ 2.80			

<sup>a</sup>  $r_a$  distances in Å and  $\angle_a$  angles in deg. Error limits are  $3\sigma$  values and include possible systematic errors (see text). For atom labels see Figure 2. <sup>b</sup> Bend of azide group in the  $\text{AsN}_\alpha\text{N}_\beta\text{N}_\omega$  plane and away from As. <sup>c</sup>  $\Phi_2(\text{CAsN}'_\alpha\text{N}'_\beta) = -\Phi_1(\text{CAsN}_\alpha\text{N}_\beta)$ . <sup>d</sup> Dihedral angle between As lone pair and azide group. <sup>e</sup> Not refined but varied in the given range for estimation of possible systematic errors. <sup>f</sup> X = N, C, or F. <sup>g</sup> Y = N or F.

is not determined by symmetry, we set this direction opposite to the vector obtained as the sum of unit vectors along the three arsenic bonds. The two azide groups are exactly cis to this direction; i.e., the As and N lone pairs are trans to each other. The same direction has been derived previously for  $(\text{CF}_3)_2\text{AsN}_3$ .<sup>8</sup> Since the intramolecular  $\text{N} \cdot \text{N}$  contacts between the two azide groups ( $\text{N}_\alpha \cdot \text{N}'_\beta = 3.92$  Å,  $\text{N}_\beta \cdot \text{N}'_\beta = 4.64$  Å) are considerably longer than the corresponding van der Waals distance (3.00 Å), no repulsion between these two groups is expected and the conformation is determined primarily by the interaction between the arsenic and nitrogen lone pairs. The conformation of  $\text{CF}_3\text{-As}(\text{N}_3)_2$  is similar to that of the phosphorus(III) bis(azide)  $\text{RP}(\text{N}_3)_2$  ( $\text{R} = 2,4,6\text{-}(t\text{-Bu})_3\text{C}_6\text{H}_2$ ) where again both azide groups point in the direction of the phosphorus lone pair. No values for dihedral angles are given in ref 9.

Within their experimental uncertainties, all bond lengths in  $\text{CF}_3\text{As}(\text{N}_3)_2$  are equal to those in  $(\text{CF}_3)_2\text{AsN}_3$ , except for the  $\text{As}-\text{N}$  distance, which is slightly longer in the diazide (1.862 (3) Å) than in the azide (1.849 (8) Å). All three bond angles around arsenic are larger in the diazide ( $\text{CAsN} = 102.7(14)^\circ$  and  $\text{NAsN} = 106.3(21)^\circ$ ) than in the azide ( $\text{CAsN} = 99.3(10)^\circ$  and  $\text{CAsC} = 97.8(11)^\circ$ ). This increase in the sum of the arsenic bond angles  $\sum \alpha_{\text{As}}$  from  $296^\circ$  in  $(\text{CF}_3)_2\text{AsN}_3$  to  $312^\circ$  in  $\text{CF}_3\text{As}(\text{N}_3)_2$  is most likely due to a change in hybridization of the central arsenic atom and not to steric repulsion between the substituents.

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