

Supramolecular architectures based on As(lone pair)... π interactions†

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SUPPLEMENTARY MATERIAL

Summary of As(lone pair)... π (aryl) Interactions

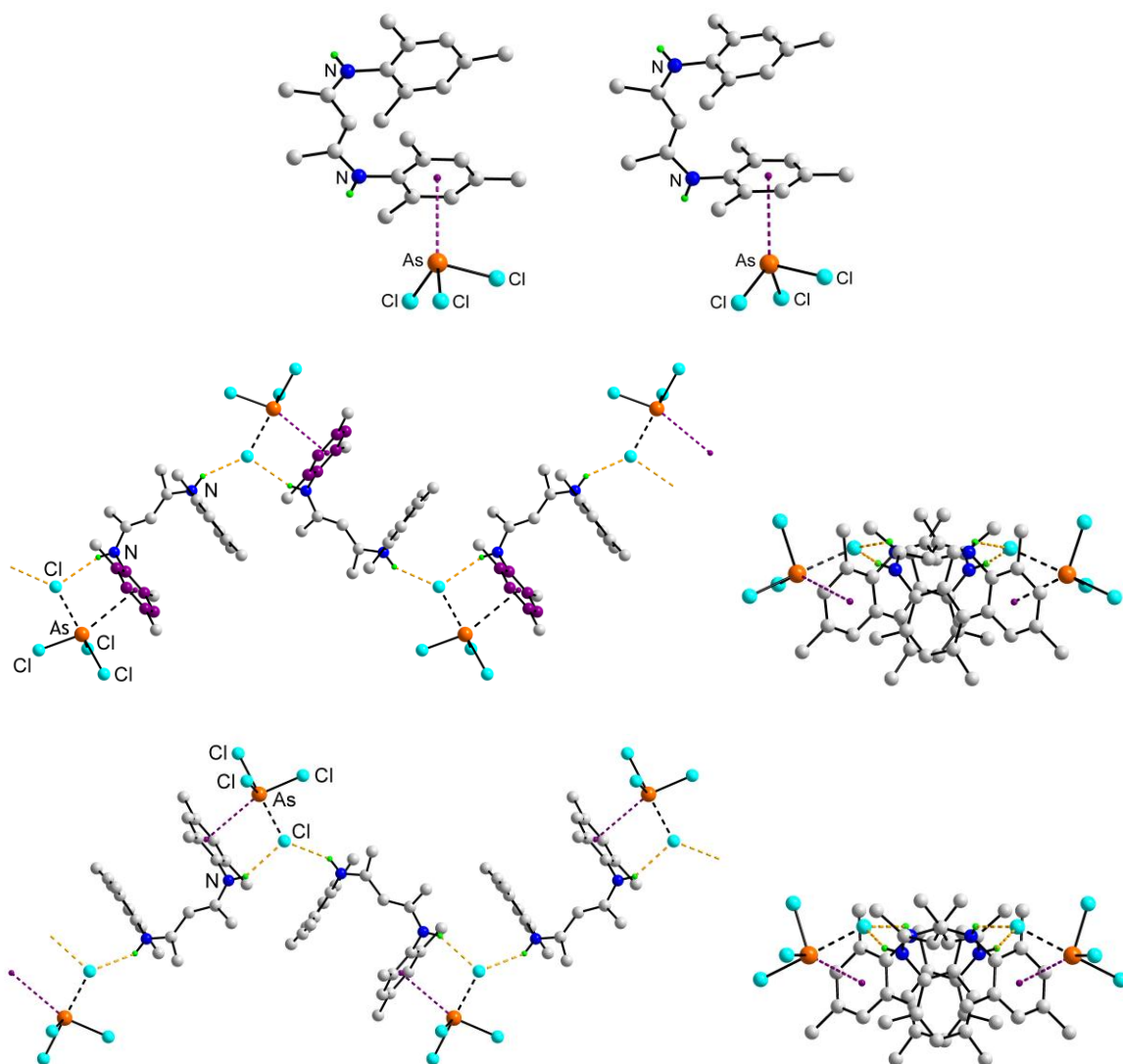
Zero-dimensional Aggregation via As(lone pair)... π (aryl) Interactions

Monomers with a single As(lone pair)... π (aryl) Interaction

3.38 Å, 7.8°; 3.41 Å, 7.9°

Two independent molecules: RMS Bond Fit = 0.0283 Å, RMS Angle Fit = 2.020° [L. A. Lesikar and A. F. Richards, *J. Organomet. Chem.* 2006, **691**, 4250] **NEVZEU**

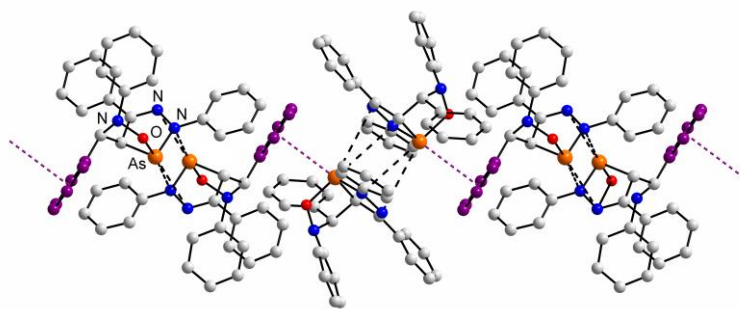
For each molecule an As... π aryl interaction leads to a 0-D aggregate. Each symmetry independent aggregate self-associates to form a supramolecular chain with the non-bound chloride atom playing a pivotal role by forming a bridge between neighbouring molecules via N-H...Cl...H-N hydrogen bonding while simultaneously forming an interaction with the arsenic atom {As...Cl = 2.679(3) & 2.733(3) Å}. The resulting supramolecular chains are essentially equivalent and have a zig-zag topology.



3.47 Å; 3.6°

[A. I. Yanovsky, Yu. T. Struchkov, E. N. Dianova, N. A. Chadaeva and B. A. Arbuzov, *Dokl. Akad. Nauk SSSR (Russ.) (Proc. Nat. Acad. Sci. USSR)*, 1979, **249**, 120] **ASAZOC**

There are two independent molecules in the asymmetric unit. The As1-containing molecules self-associate into supramolecular dimers via As...N interactions as do the As2-containing molecules. The As1 atoms form As... π (aryl) interactions with aryl rings derived from the As2-dimers with the result that a supramolecular chain is formed.



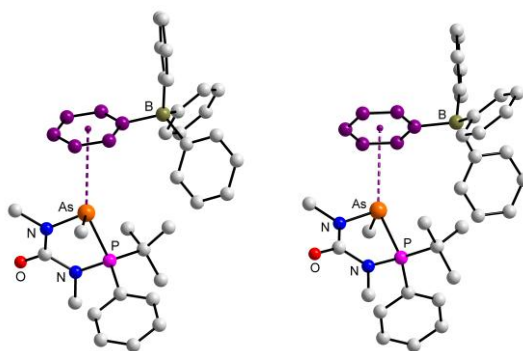
3.56 Å, 13.3° & 3.59 Å, 8.3°

Two independent molecules: RMS Bond Fit = 0.0134 Å, RMS Angle Fit = 0.719° [R. Vogt,

P. G. Jones and R. Schmutzler, *Chem. Ber.* 1993, **126**, 1271] **PELDUF**

Each independent molecules forms an As...π aryl interactions to generate a 0-D aggregate.

The closest As...O interaction is > 4.0 Å.

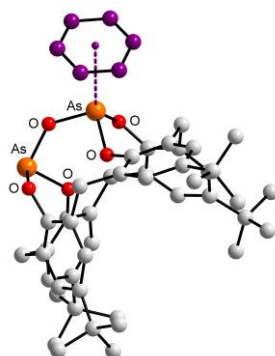


3.57 Å, 3.6°

[S. Shang, D. V. Khasnis, H. Zhang, A. C. Small, M. Fan and M. Lattman, *Inorg. Chem.*

1995, **34**, 3610] **ZALHAV**

The molecule forms an As...π aryl interaction leading to a 0-D aggregate. The closest As...O interaction is > 4.0 Å.



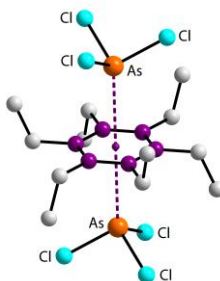
Dimers with Two As(lone pair)... π (aryl) Interactions

3.14 Å, 0.0° (x two)

[H. Schmidbaur, R. Nowak, O. Steigelmann and G. Muller, *Chem. Ber.* 1990, **123**, 1221]

TADFAF

The three-molecule aggregate is located about a crystallographic site of symmetry, $\bar{3}$. Two As... π aryl interactions sustain the 0-D aggregate.

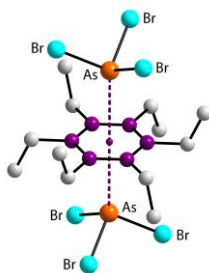


3.16 Å, 0.0° (x two)

[H. Schmidbaur, W. Bublak, B. Huber and G. Muller, *Angew. Chem., Int. Ed.* 1987, **26**, 234]

SALCIR

The three-molecule aggregate is located about a crystallographic site of symmetry, $\bar{3}$. Two As... π aryl interactions sustain the 0-D aggregate.



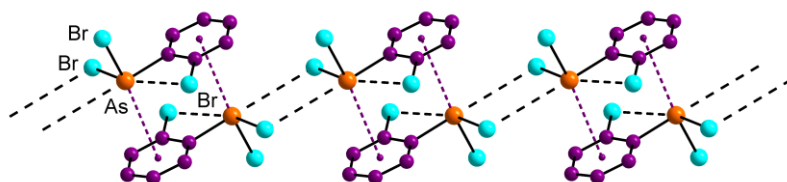
Dimers with Two As(lone pair)... π (aryl) Interactions

3.50 Å, 7.7°

[I. A. Litvinov, V. A. Naumov and N. A. Chadaeva, *J. Struct. Chem.*, 1986, **27**, 174.]

FAFWAK

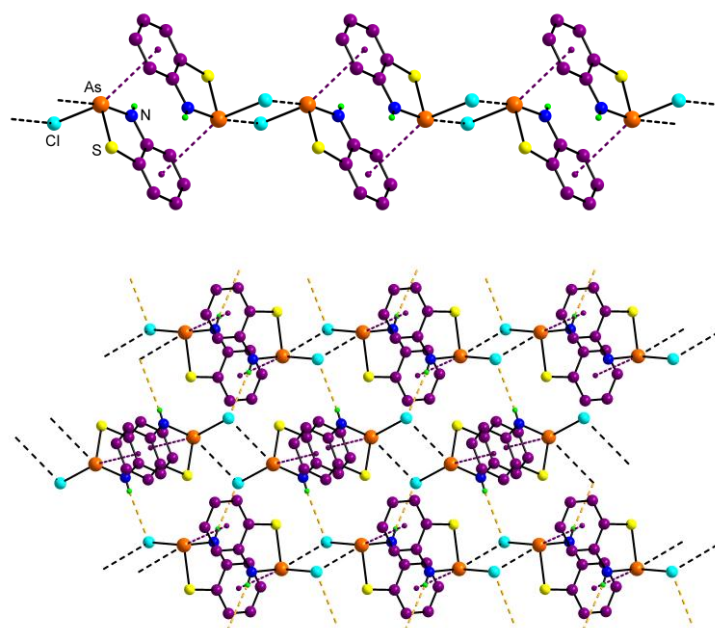
Centrosymmetric molecules associate into a dimer via As... π aryl interactions. The coordination number of the As atom is increased by an intramolecular As...Br (3.22 Å) as well as intermolecular As...Br contacts (3.81 Å). The latter connect dimeric units into a supramolecular chain.



3.58 Å, 15.6°

[N. Burford, T. M. Parks, B. W. Royan, J. F. Richardson and P. S. White, *Can. J. Chem.* 1992, **70**, 703] **KUNSIV**

Centrosymmetric pairs are sustained by As... π aryl interactions and these are connected into rows by As...Cl (3.38 Å) contacts. Rows are linked into a 2-D array by N-H...Cl hydrogen bonding interactions. Rows are connected into the 3-D structure by As...S interactions (3.43 Å).

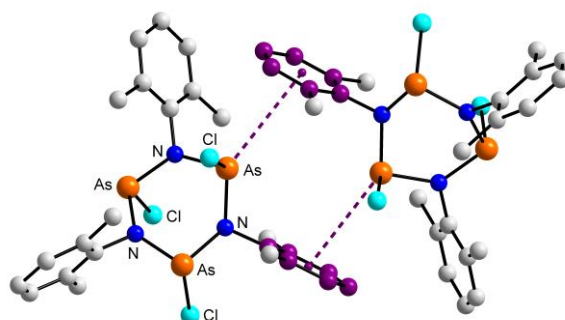


3.78 Å, 14.2°

[N. Burford, J. C. Landry, M. J. Ferguson and R. McDonald, *Inorg. Chem.* 2005, **44**, 5897]

LARYUZ

Centrosymmetric pairs are sustained by As... π aryl interactions. No additional interactions involving As < 4.0 Å are observed.

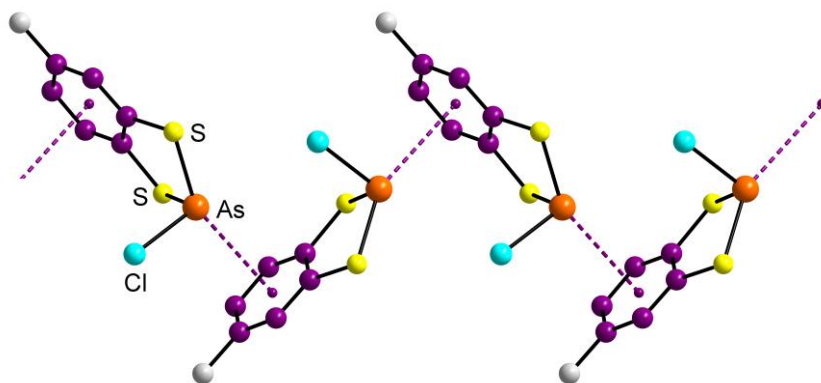


One-dimensional Aggregation Via As(lone pair)... π (aryl) Interactions

3.30 Å, 3.6°

[J. M. Kisenyi, G. R. Willey, M. G. B. Drew and S. O. Wandiga, *J. Chem. Soc., Dalton Trans.* 1985, 69.] **DAXLOD**

As... π aryl interactions lead to a zig-zag chain (glide symmetry). Weak As...Cl interactions of 3.82 Å are formed in the chain but the contacts are longer than the sum of their van der Waals radii of 3.60 Å.

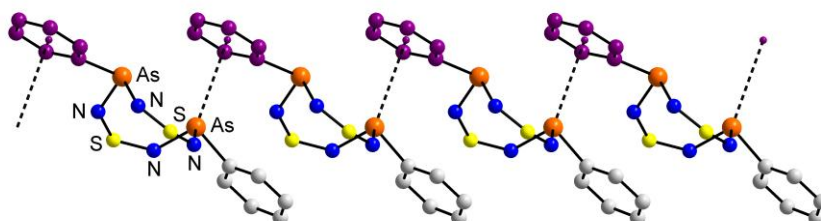


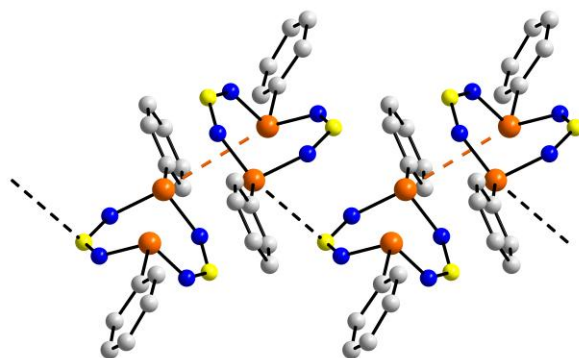
3.47 Å, 4.7°

Two independent molecules with different conformations, RMS Bond Fit = 0.794 Å. [N. W. Alcock, E. M. Holt, J. Kuyper, J. J. Mayerle and G. B. Street, *Inorg. Chem.* 1979, **18**, 2235]

PHTZAS

One independent molecule has mirror symmetry as forms As... π aryl interactions to form a linear chain. The second independent molecule also forms a chain but mediated by alternating As...As (3.7909(4) Å) and As...S (3.7582(4) Å) interactions.



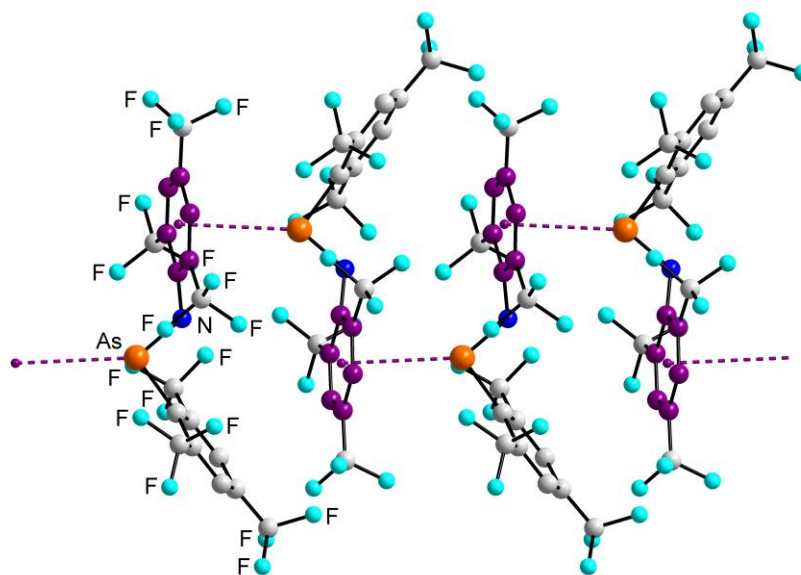


3.48 Å, 6.9 °

[J.-T. Ahlemann, A. Kunzel, H. W. Roesky, M. Noltemeyer, L. Markovskii, H.-G. Schmidt,

Inorg. Chem. 1996, **35**, 6644] **TUNYOQ**

A zig-zag chain (glide symmetry) is sustained by As... π aryl interactions. The closest As...F contact is 3.83 Å.



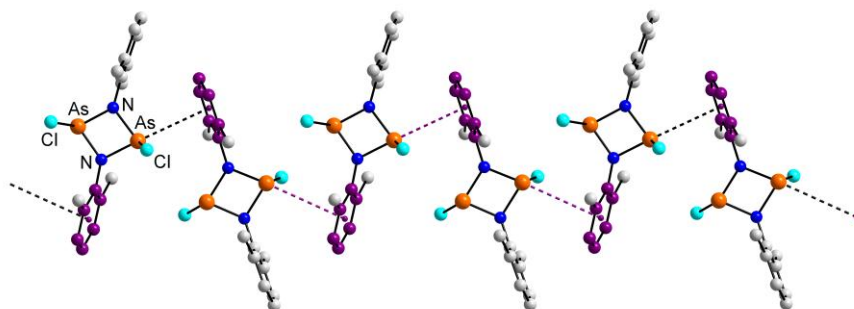
3.51 Å, 5.8°

Two independent molecules: RMS Bond Fit = 0.0048 Å, RMS Angle Fit = 1.485°. the other

As forms a similar interaction just outside the specified criterion with 3.86, 20.5 [N. Burford,

J. C. Landry, M. J. Ferguson and R. McDonald, *Inorg. Chem.* 2005, **44**, 5897] **LARYIN**

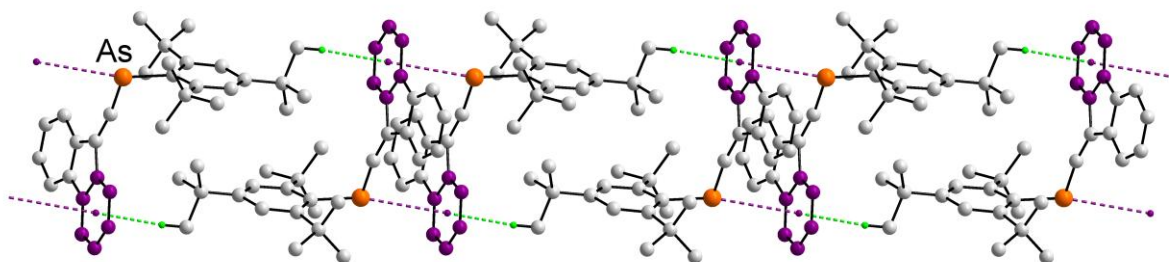
The two independent molecules are connected through a single As... π aryl interaction into a dimeric aggregate. If a second, marginally weaker, As... π aryl interaction is considered, the dimeric units are connected into a zig-zag supramolecular chain. The closest As...Cl contacts less than 4.0 Å are 3.82 Å and 3.94 Å.



3.51 Å, 12.7°

[M. Bouslikhane, H. Gornitzka, H. Ranaivonjatovo and J. Escudie, *Organometallics*, 2002, **21**, 1531] **XIQBEE**

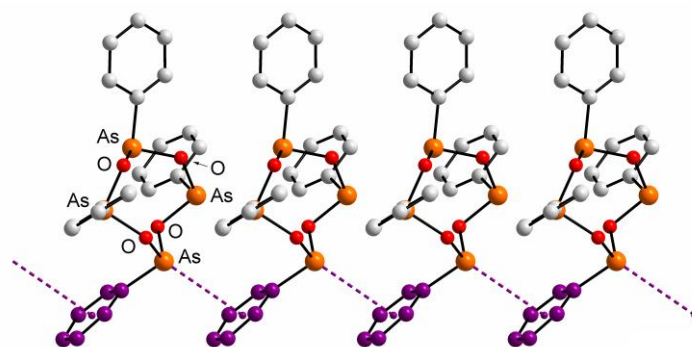
As... π aryl interactions lead to a zig-zag chain (generated by glide symmetry) with additional stabilisation due to the formation of C-H... π aryl interactions.



3.52 Å, 11.8°

[I. M. Muller and J. Muhle, *Z. Anorg. Allg. Chem.* 1999, **625**, 336.] **HAVMEW**

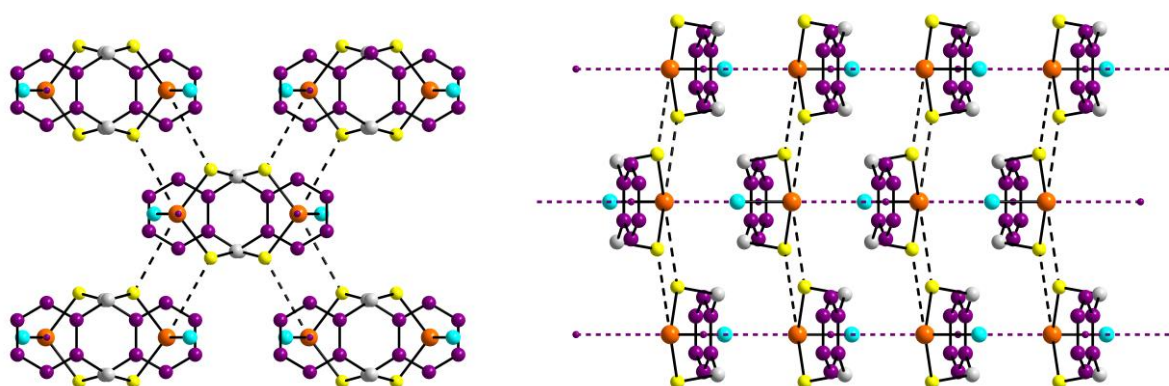
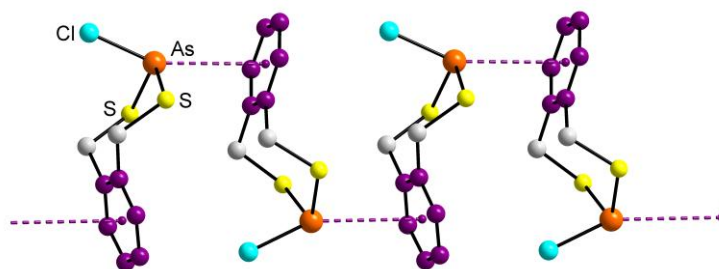
An As... π aryl interaction leads to linear chain, involving one of the As atoms only. The closest intermolecular As...O is 3.68 Å.



3.53 Å, 12.7 °

[T. A. Shaikh, R. C. Bakus II, S. Parkin and D. A. Atwood, *J. Organomet. Chem.* 2006, **691**, 1825] **NEJQID**

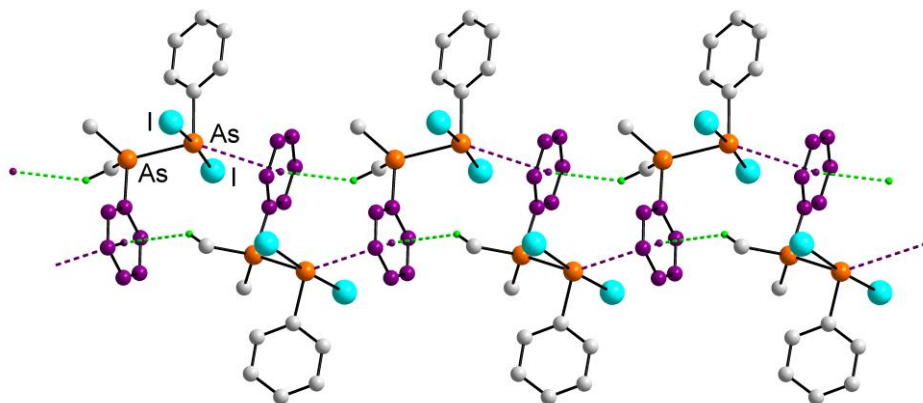
As... π aryl interactions (involving one of the As atoms only) lead to a stepped chain with As...S interactions (3.65 Å) leading to a 3-D network.



3.54 Å, 6.5°

[S. Petrie, R. Stranger, A. D. Rae, A. C. Willis, X. Zhou and S. B. Wild, *Organometallics*, 2006, **25**, 164.] **KODREB**

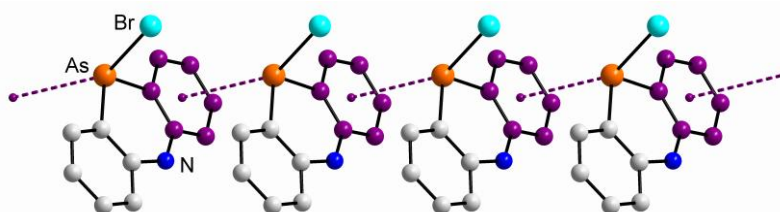
As... π aryl interactions (involving one of the As atoms only) lead to a helical chain (2_1 screw) with additional stabilisation due to the formation of C-H... π aryl interactions. No As...I interactions < 4.0 Å are noted.



3.58 Å, 16.2°

[M. Fukuyo, K. Nakatsu and A. Shimada, *Bull. Chem. Soc. Jpn.* 1966, **39**, 1614.] **BRPHAS**

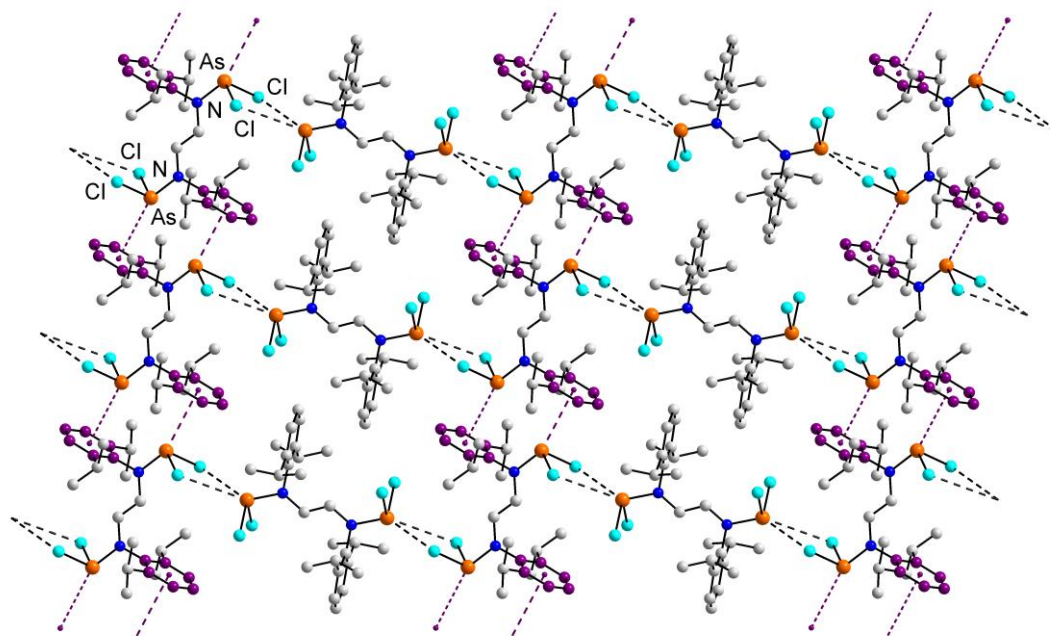
As... π aryl interactions leads to a linear chain; no additional interactions involving As < 4.0 Å are observed.



3.60 Å, 3.2°

Two independent molecules, each located about an inversion centre: RMS Bond Fit = 0.0071 Å, RMS Angle Fit = 1.348°. [R. J. Baker, C. Jones, D. P. Mills, G. A. Pierce and M. Waugh, *Inorg. Chim. Acta*, 2008, **361**, 427] **SIXQUM**

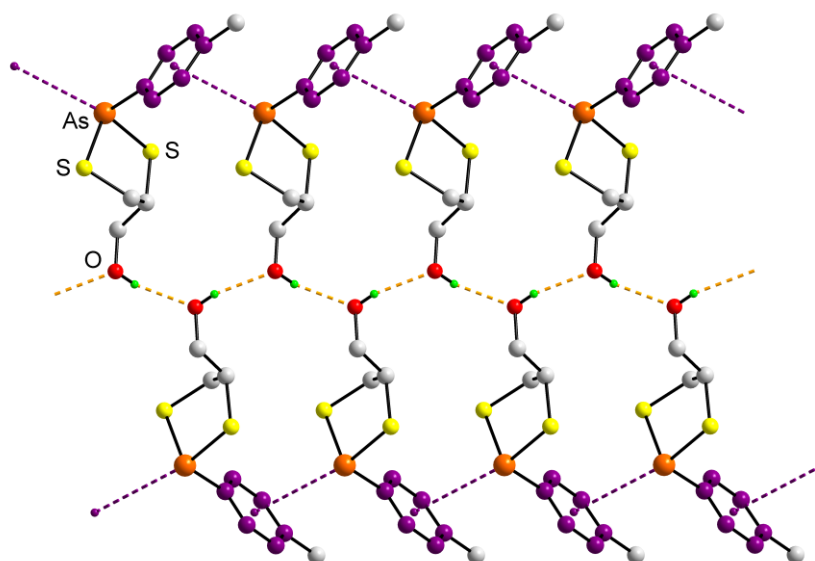
Two aromatic rings of one independent molecule form As... π aryl interactions with the As atoms derived from the second molecule to form strands. These are connected into a 2-D array via As...Cl secondary interactions (3.5635(15) and 3.6914(18) Å).



3.84 Å, 17.8°

[E. Adams, D. Jeter, A. W. Cordes and J. W. Kolis, *Inorg. Chem.* 1990, **29**, 1500] **VETDAZ**

A linear supramolecular chain is sustained by As... π aryl interactions. Chains are linked via a row of ...O-H...O... hydrogen bonds into a double chain.



Summary of Intermolecular Interactions Involving Arsenic in the 20 Structures
Featuring As(lone pair)... π (aryl) Interactions

Refcode	Intermolecular contacts involving the As atom that forms a π(aryl) interaction	Other potential Lewis bases in the molecule that do not form interactions to As
NEVZEU	1 x Cl	2 x Cl {per As atom} ^a
AZAZOC	1 x N	1 x N; 1 x O {per As atom}
PELDUF	n/a	1 x O {per As atom}
ZALHAV	n/a	5 x O
TADFAF	n/a	3 x Cl
SALCIR	n/a	3 x Br
FAFWAK	1 x Br	2 x Br
KUNSIV	1 x Cl; 1 x S	n/a
LARYUZ	n/a	3 x Cl
DAXLOD	n/a	1 x Cl; 2 x S
PHTZAS	n/a	2 x N; 1 x S {per As atom}
TUNYOQ	n/a	18 x F; 1 x N
LARYIN	n/a	1 x Cl {per As atom}
XIQBEE	n/a	n/a
HAVMEW	n/a	1 x Cl {per As atom}
NEJQID	1 x S	1 x Cl
KODREB	n/a	1 x I {per As atom}
BRPHAS	n/a	1 x Br; 1 x N

SIXQUM	1 x Cl	1 x Cl {per As atom}
VETDAZ	n/a	2 x S

a Two molecules in the crystallographic asymmetric unit OR two or more As atoms in the molecule

Plot of d (Å) versus α (°) for all As(lone pair)... π (aryl) Interactions

{*n.b.* there are more than 20 data points as several structures have more than one

As(lone pair)... π (aryl) interaction}

