N—S distances are 1·849 Å (Hansen & Tomren, 1977) in (V), 1·779 Å (Darmo & Hansen, 1977) in (VI) and 1·863 Å (Hansen, 1977) in (VII), all much longer than the 1·727 Å in (III), while the S—S distances in (V), (VI) and (VII) are 2·435, 2·493, and 2·447 Å respectively, all shorter than the 2·750 Å in (III). The overall N···S distances in (V), (VI) and (VII), 4·273, 4·267, and 4·290 Å respectively, are also rather shorter than the 4·471 Å in (III).

It is interesting that (VIII), the adduct of Hector's base and methyl isothiocyanate, has a skeleton very similar to that of (III) with S—N 1·705 Å, and S—S 2·808 Å (Cuthbertson, Glidewell & Holden, 1980).

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Arsatriptycene and Phosphatriptycene

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Abstract. $C_{19}H_{13}As$, monoclinic, *Cc*, $a = 15·316\,(5)$, $b = 8·310\,(2)$, $c = 13·305\,(3)$ Å, $\beta = 121·02\,(1)°$, $Z = 4$. $C_{19}H_{13}P$, monoclinic, *Cc*, $a = 15·074\,(2)$, $b = 8·210\,(1)$, $c = 13·207\,(2)$ Å, $\beta = 120·53\,(2)°$, $Z = 4$. The two compounds are isostructural and consist of densely packed layers parallel to $(10\bar{1})$ in which the molecular quasi-threefold axes are nearly perpendicular to the layers. Both structures show the same kind of disorder in which a fraction of the molecules have As(P) and the bridgehead C atom interchanged. Phosphatriptycene shows twinning on $(10\bar{1})$.

Introduction. The aim of the investigation was to obtain information about the geometry around As and P.

Arsatriptycene (AT) was prepared by Vermeer, Kevenaar & Bickelhaupt (1972). 1119 reflexions with $I > 2\sigma(I)$ were collected on a Nonius CAD-3 diffractometer with Cu $K\alpha$ radiation. The structure was obtained from a Patterson minimum function based on the positions of the two translation-independent As atoms in the unit cell. During the refinement a ΔF synthesis showed the As atom to be electron deficient, whilst a prominent peak appeared near the bridgehead C(19). (For the atomic numbering see Fig. 1.) This was interpreted as being due to disorder, some of the molecules being in an alternative orientation with As and C(19) interchanged. A peak corresponding to the vector between the two partially occupied As positions was indeed present in the Patterson synthesis. The ring planes in the two orientations more or less coincide but not so the individual atoms. The situation is indicated in Fig. 2. The ring atoms are at most 0·3 Å from their counterparts and could not be refined separately. Anisotropic block-diagonal least-squares refinement of As(I), As(II), C(19)(I), C(19)(II) and average positions for the ring atoms converged to $R = 0·066$. The population parameters for the two positions of As and C(19) refined to 0·65 and 0·35. The H atoms were introduced and kept fixed at calculated positions. Introduction of an absorption correction and an extinction parameter resulted in a final R of 0·041. The final parameters are listed in Table 1.†

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† Lists of structure factors and anisotropic thermal parameters for both compounds have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35041 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Phosphatriptycene (PT) was prepared by Jongsma, de Kleijn & Bickelhaupt (1974). 533 reflexions with $I > 2\sigma(I)$ were collected on a Nonius CAD-4 diffractometer with graphite-monochromatized Cu $K\alpha$ radiation. The intensities of the $hk\bar{h}$ reflexions were halved because 50–50 twinning on (10$\bar{1}$) caused $hk\bar{h}$ of one component to coincide with $\bar{h}kh$ of the other. The effect of the twinning in reciprocal space is indicated in Fig. 3.

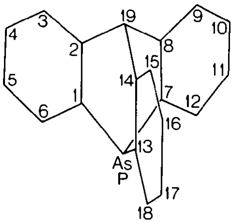

Fig. 1. Atomic numbering in arsa- and phosphatriptycene.

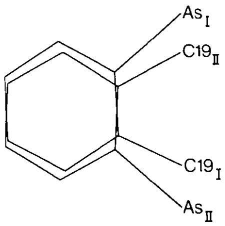

Fig. 2. Disorder in arsatriptycene.

Table 1. *Fractional atomic coordinates* [As(I) × 10^5, As(II) *and* C × 10^4] *of arsatriptycene*

Calculated e.s.d.'s are in parentheses.

	x	y	z	B_{eq} (Å^2)
As(I)*	0	24155 (9)	0	4·3
As(II)†	925 (2)	2431 (3)	−2149 (2)	5·5
C(1)	−681 (5)	1416 (7)	−1519 (6)	5·3
C(2)	−305 (5)	1465 (8)	−2249 (6)	5·0
C(3)	−839 (7)	688 (10)	−3335 (7)	6·7
C(4)	−1715 (8)	−57 (12)	−3655 (8)	8·6
C(5)	−2114 (6)	−130 (12)	−2917 (8)	7·3
C(6)	−1610 (7)	600 (10)	−1845 (8)	6·9
C(7)	1280 (6)	1429 (8)	295 (7)	5·1
C(8)	1561 (5)	1461 (9)	−552 (6)	4·9
C(9)	2424 (7)	733 (12)	−325 (8)	6·1
C(10)	3035 (6)	−96 (11)	779 (10)	7·7
C(11)	2782 (7)	−110 (12)	1588 (8)	7·2
C(12)	1867 (8)	678 (10)	1352 (8)	6·5
C(13)	284 (6)	4287 (6)	−635 (5)	5·0
C(14)	625 (5)	4151 (9)	−1407 (6)	4·9
C(15)	797 (7)	5554 (12)	−1861 (8)	7·5
C(16)	688 (9)	6958 (13)	−1545 (10)	8·9
C(17)	347 (9)	7169 (8)	−790 (12)	9·5
C(18)	120 (6)	5781 (12)	−295 (7)	7·0
C(19)(I)*	709 (9)	2324 (14)	−1638 (8)	5·2
C(19)(II)†	264 (26)	2354 (22)	−439 (23)	7·2

* Population parameter 0·65.
† Population parameter 0·35.

Table 2. *Fractional coordinates* (×10^4) *of phosphatriptycene*

Calculated e.s.d.'s are in parentheses.

	x	y	z	B_{eq} (Å^2)
P(I)*	0	2417 (4)	0	3·2
P(II)†	853 (8)	2374 (13)	−2068 (9)	3·4
C(1)	−716 (9)	1431 (13)	−1463 (11)	3·5
C(2)	−361 (10)	1482 (14)	−2238 (11)	3·7
C(3)	−886 (11)	739 (17)	−3323 (13)	5·1
C(4)	−1813 (12)	−66 (20)	−3615 (12)	5·9
C(5)	−2213 (11)	−98 (19)	−2871 (14)	5·9
C(6)	−1623 (10)	656 (16)	−1742 (12)	4·3
C(7)	1192 (9)	1465 (13)	250 (11)	3·4
C(8)	1515 (10)	1492 (14)	−568 (12)	3·5
C(9)	2418 (11)	678 (19)	−344 (14)	5·4
C(10)	2962 (10)	−135 (18)	685 (13)	5·2
C(11)	2697 (11)	−116 (18)	1514 (13)	5·4
C(12)	1821 (12)	681 (16)	1310 (12)	4·8
C(13)	260 (10)	4260 (14)	−617 (10)	4·0
C(14)	573 (9)	4160 (15)	−1429 (19)	3·5
C(15)	785 (12)	5588 (19)	−1834 (11)	5·6
C(16)	581 (13)	7089 (16)	−1463 (17)	7·2
C(17)	259 (14)	7132 (18)	−689 (16)	7·0
C(18)	123 (11)	5747 (16)	−220 (13)	4·5
C(19)(I)*	681 (9)	2400 (15)	−1737 (10)	2·9
C(19)(II)†	314 (27)	2355 (44)	−273 (32)	2·8

* Population parameter 0·76.
† Population parameter 0·24.

The structure of PT was derived directly from an $E^2 - 1$ Patterson synthesis. As could be expected from the space group and cell constants, PT is isostructural with AT. During the refinement of PT it became apparent that the same kind of disorder is present as in AT. Anisotropic block-diagonal least-squares refinement, similar to that for AT, converged to $R = 0{\cdot}053$ and population parameters of 0·76 and 0·24. The final parameters are listed in Table 2.*

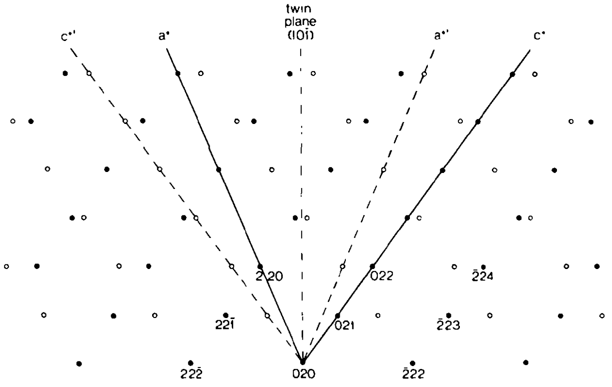

Fig. 3. Reciprocal-lattice plane $h2l$ showing the twinning on (10$\bar{1}$) in phosphatriptycene.

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* See previous footnote.

Discussion. The positions given in Tables 1 and 2 for the ring atoms correspond to the centroids of the composite electron densities of the overlapping atoms of the two orientations, whilst the temperature parameters will largely have absorbed the effects of the non-coincidence of the overlapping atoms. As a result not much value can be attached to the bond distances and angles between these atoms. This is borne out by the results: the calculated aromatic C—C distances range from 1·28 to 1·46 Å for AT and from 1·34 to 1·43 Å for PT; the corresponding angles range from 116 to 122° for AT and from 117 to 123° for PT. The distances and angles involving As(I) and P(I) are probably somewhat more reliable, in the first place because As(I) and P(I) are much less affected by the disorder and, furthermore, because C(1), C(7) and C(13), having relatively small temperature parameters, will probably be near the actual positions for the predominant orientation. The average calculated distances and angles are As(I)—C 1·94, P(I)—C 1·84 Å, C—As(I)—C 90, C—P(I)—C 91°. It is difficult to assess the accuracy of these values; if anything Fig. 2 suggests that the bond distances are too large and the bond angles too small.

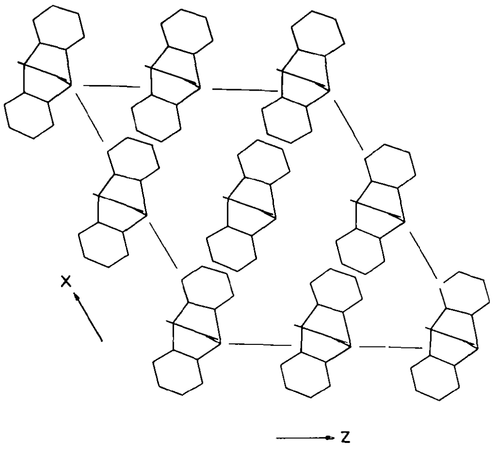

Fig. 4. Projection of the structures of arsa- and phosphatriptycene along [010] showing the layers parallel to (10$\bar{1}$).

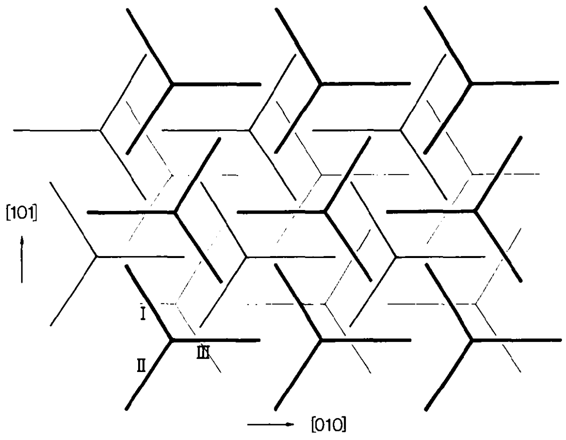

Fig. 5. Schematic projection of the structures of arsa- and phosphatriptycene on to (10$\bar{1}$) showing the packing within a layer and the stacking of the layers.

The crystal structures of AT and PT are closely related to those of diphosphatriptycene (DPT) and diphosphatriptycene dioxide (DPTDO) (Schomburg & Sheldrick, 1975). The latter two compounds are mutually isostructural with space group $C2/c$ and Z = 4. Their cell constants are very similar to those of AT and PT; DPT: a = 15·068 (5), b = 8·276 (3), c = 13·305 (3) Å, β = 120·26°; DPTDO: a = 15·411 (17), b = 8·301 (7), c = 13·827 (9) Å, β = 122·24 (5)°. The molecules in DPT and DPTDO are situated at the space-group dyad axes which pass through one of the benzene rings and are perpendicular to the P–P axes. The dyad axes are missing in AT and PT. The disorder in AT and PT can be seen as an attempt to acquire the dyad axes; if the disorder were 50–50 the average structures of AT and PT would have space group $C2/c$. So all four compounds are in fact isostructural and have a number of features in common such as the packing and the overall shape of the molecules. The molecules are arranged in layers parallel to (10$\bar{1}$), the axes As–C(19), P–C(19), P–P and P–N being approximately perpendicular to (10$\bar{1}$) (86, 84, 82 and 81° respectively). This layer structure is illustrated in Fig. 4 which is a projection of AT along [010]. Within a layer there is dense packing with contacts between the peripheral H atoms of a molecule and the ring C atoms of the surrounding molecules. The packing within the layers and the stacking of the layers is indicated in Fig. 5.

The molecules in the four crystal structures show similar deviations from the threefold symmetry expected for the free molecules. The angles between the corresponding rings (I) [C(1)–C(6)], (II) [C(7)–C(12)] and (III) [C(13)–C(18)] are: (I)–(II): 115, 115, 113, 113°, (I)–(III): 122, 121, 123, 123°, (II)–(III): 122, 124, 123, 123°, for AT, PT, DPT and DPTDO respectively.

It is interesting to note that the twinning plane (10$\bar{1}$) in PT coincides with the plane of the layers.

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