Parallel chains also link through different hydrogen bonds. All the possible hydrogen bonds are in Table 4.

A last paragraph must be added about the geometry of the oxime group obtained from the results in the small Pbcn cell (which entails a binary axis along the molecule). The two C–C–NO bond angles are different, and there are two short intramolecular distances N(7)···N(5) = 2·459 (4) Å and N(7')···O(6) = 2·765 (4) Å. These results were interpreted in two ways yielding the following models:

(1) Atoms N(7) and N(7') in the real molecule are chemically different: one is NH_2 and the other NH. The first forms a very strong hydrogen bond to N(5), the second directs its lone electron pair towards N(5) [see Fig. 2(a)]. Both cause the difference in C–C–NO bond angles. In this model O(1a) would be protonated.

(2) atoms N(7) and N(7') are chemically identical (NH_2) and there is a two fold symmetry within the thiadiazine ring. The oxime group would be completely twofold disordered around this binary axis, both positions being energetically fixed by the cooperation of the two intramolecular hydrogen bonds N(7)H··· N(5) and N(7')H···O(6) [see Fig. 2(b)]. This model would preclude protonation of O(1a).

Fig. 2 shows the probable electron-distribution molecular models for both molecules. Linnett's (1966) ideas about electron-repulsion theory have been followed.

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9-Trimethylsilylphenanthrene*

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Abstract. $C_{17}H_{18}Si$, $M_r = 250·42$, orthorhombic, space group Pbca, $a = 17·385$ (25), $b = 12·728$ (9), $c = 13·091$ (7) Å (from P$\bar{1}$ Syntex diffractometer), $Z = 8$, $D_c = 1·15$, $D_x = 1·14$ (2) g cm^{-3} (by flotation), m.p. 61–63 °C. The compound was recrystallized from n-hexane. The structure was solved primarily by the symbolic addition method. The final R value is 0·061. The effect of the trimethylsilyl group on the phenanthrene appears to be a partial reduction in π-electron delocalization.

Introduction. Preliminary crystal structure data of the compound have previously been reported (Lu, 1975). For further refinement, a single, transparent, roughly spherical crystal of diameter 0·3 mm was cut to re-col-

lect a total of 1251 ($I > 3\sigma$, $\sin \theta/\lambda < 0·56$) independent reflexions on a Syntex P$\bar{1}$ auto-diffractometer with Cu Kα (Ni) radiation. Systematic absences (0kl, k odd; h0l, l odd; hk0, h odd) uniquely determine the space group Pbca (D_{2h}^{15}). The linear absorption coefficient for Cu Kα radiation is 12·98 cm^{-1}. Azimuthal rotations (North, Phillips & Mathews, 1968) about the three strong reflexions 333, 060 and 440 fluctuate within 5%. Intensities of three reflexions were remeasured periodically as a check on crystal and instrument stability. No time-decay correction was made since only random fluctuations (within 2·7%) in these check reflexions were observed. The Si atom, located by the conventional heavy-atom method, was found to be on a glide plane perpendicular to the a axis. Half the calculated structure factors have zero contribution from Si. An attempt to locate the C positions from a difference Fourier map (DFM) was unsuccessful. The non-

hydrogen atoms were finally located by direct methods (Karle & Karle, 1966) using the computer program *LSAM* (Main, Woolfson & Germain, 1972). Full-matrix least-squares refinement of the non-H coordinates and anisotropic vibrational parameters with the weighting scheme given by Stout & Jensen (1968) resulted in an R of 0·08. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$, where F_c and F_o are the calculated and observed structure factors, respectively, and w is the weight. After an extinction correction (Zachariasen, 1968), a DFM showed that the number of peaks was greater than the expected number of H atoms. The three highest peaks, corresponding to H atom positions around the three C atoms in the CH_3 groups, were chosen for the calculation of the other six H positions on a tetrahedral basis. The C—H bond distances and Si—C—H bond angles were adjusted to be 0·95 Å and 109°28' respectively. The H positions on the aromatic rings were assigned in the radial direction from the ring centre and situated with C—H bond lengths also equal to 0·95 Å. The calculated H atom positions agreed with 18 peaks of the DFM. The isotropic temperature factors of the H atoms were fixed according to the relative peak heights in the DFM. Two cycles of full-matrix least-squares refinement of scale, and positional and anisotropic thermal parameters of all non-H atoms reduced R to 0·061.* The coefficient

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32307 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

C^1 [equation (5) in Zachariasen (1968)] was 1·21 × 10^{-3}. The standard deviation of an observation of unit weight, $|\Sigma w(|F_o| - |F_c|)^2/(m - n)|^{1/2}$, is 1·3, where m (1251) is the number of observations ($|F_o|$) and n (163) the number of variables in the least-squares refinement. The final coordinates and temperature factors are shown in Table 1.

The final average and maximum parameter shifts were about 0·2σ and 0·4σ. C—H bond lengths ranged from 0·93 to 0·98 Å. The scattering curves for Si, C, H were taken from *International Tables for X-ray Crystallography* (1962). The curve for Si was not corrected for anomalous dispersion.

Discussion. 9-Trimethylsilylphenanthrene (TMSP) was the only oily silylated derivative obtained by trimethylsilylation of 9-bromophenanthrene (Hwang, 1971). In contrast to various oily silylated hydroaromatic derivatives from direct trimethylsilylation of phenanthrene (Yang & Liu, 1975), TMSP is a solid (m.p. 61–63°C). The chemical shifts of the methyl protons of TMSP and corresponding hydroaromatic compounds also showed significant differences (Yang & Liu, 1975). Si differs from C mainly in its ability to utilize its 3d orbitals (Cotton & Wilkinson, 1966) and in having a lower electronegativity (Pauling, 1960). The crystal form of TMSP allows us to study the extent of the effect of Si substitution on the aromatic ring system by means of an X-ray structure determination.

Figs. 1 and 2, prepared with *ORTEP* (Johnson, 1965), show the molecular structure and numbering scheme without the hydrogens. The displacements from

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Table 1. *Fractional coordinates* ($\times 10^4$) *and temperature factors*

$T = \exp[-(B11h^2 + B22k^2 + B33l^2 + B12hk + B13hl + B23kl) \times 10^{-4}]$.

	X/A	Y/B	Z/C	B11	B22	B33	B12	B13	B23
SI	-2393(1)	7025(1)	3972(1)	39(1)	55(1)	62(1)	-3(2)	-2(2)	-1(3)
C(1)	-569(4)	4798(4)	1616(5)	50(5)	84(9)	90(9)	11(14)	-8(14)	-12(18)
C(2)	-40(4)	3998(6)	1421(5)	42(5)	123(11)	146(12)	35(14)	-22(15)	-83(23)
C(3)	197(4)	3354(5)	2180(6)	35(4)	90(9)	154(13)	21(12)	-18(16)	-26(22)
C(4)	-58(4)	3453(4)	3179(5)	39(4)	80(8)	138(11)	11(12)	-24(15)	-31(19)
C(5)	-652(3)	3823(4)	5311(5)	37(4)	53(7)	119(10)	9(10)	-5(14)	7(18)
C(6)	-947(4)	3992(5)	6251(5)	64(6)	80(8)	79(8)	-22(14)	-9(15)	23(17)
C(7)	-1477(4)	4762(4)	6419(4)	59(6)	83(8)	68(7)	11(14)	-5(13)	-21(15)
C(8)	-1725(4)	5382(4)	5627(4)	53(5)	72(7)	67(6)	0(12)	4(12)	-30(14)
C(9)	-1687(3)	5918(3)	3794(4)	37(4)	59(6)	77(6)	8(9)	-2(10)	-55(13)
C(10)	-1380(3)	5739(4)	2838(4)	48(5)	51(5)	78(7)	7(10)	-32(12)	-10(13)
C(11)	-839(3)	4926(4)	2636(4)	31(4)	72(7)	89(8)	8(10)	0(12)	-44(15)
C(12)	-585(3)	4271(4)	3424(5)	22(4)	54(6)	112(9)	8(9)	1(12)	-9(16)
C(13)	-892(3)	4439(4)	4443(4)	29(4)	55(7)	70(7)	-5(10)	17(12)	10(14)
C(14)	-1429(3)	5245(4)	4631(4)	32(4)	46(6)	56(6)	10(10)	7(10)	16(13)
C(15)	-2536(4)	7725(4)	2737(4)	48(4)	88(8)	70(6)	-4(12)	40(12)	-29(14)
C(16)	-1995(3)	8008(4)	4890(4)	64(5)	55(6)	75(7)	24(12)	-11(12)	16(14)
C(17)	-3336(3)	6478(5)	4416(5)	52(5)	99(8)	138(10)	-5(13)	-43(14)	-13(18)

	X/A	Y/B	Z/C	B		X/A	Y/B	Z/C	B
H(1)	-741	5262	1086	3.50	H(2)	145	3911	723	6.00
H(3)	558	2812	2019	4.00	H(4)	125	2987	3725	3.50
H(5)	-275	3285	5220	3.50	H(6)	-782	3560	6813	8.00
H(7)	-1691	4865	7083	3.00	H(8)	-2106	5921	5747	3.50
H(10)	-1550	6182	2290	3.50	H(11)	-2859	7318	2292	3.00
H(12)	-2054	7832	2402	5.00	H(13)	-2775	8389	2845	3.50
H(21)	-1756	8561	4549	8.50	H(22)	-2420	8294	5298	5.00
H(23)	-1651	7677	5354	5.00	H(31)	-3393	6579	5140	8.00
H(32)	-3378	5758	4264	5.00	H(33)	-3754	6848	4088	4.00

the least-squares plane are also given on Fig. 1. The differences among the Si—C bond distances are not very significant $(1 \sim 2\sigma)$. The average Si—C bond length is 1·872 (8) Å. The corresponding values in $Si(CH_3)_4$ (Sheehan & Schomaker, 1952) and $Si_2(CH_3)_6$ (Brockway & Davison, 1941) are 1·888 (20) and 1·90 (2) Å respectively. The C—Si—C angles not shown on Fig. 2, C(15)—Si—C(16) and C(10)—Si—C(17), are 106·7 (3) and 109·3 (2)° respectively. Therefore, —Si(CH_3)_3 has the usual tetrahedral geometry.

The unweighted least-squares plane (referred to the crystal coordinate system) for the C atoms in ring II is $12·99x + 8·083y + 2·572z = 3·573$ and that for the C atoms in the three rings, excluding C(3), C(4), C(5) and C(6), is $13·02x + 8·066y + 2·541z = 3·544$. The displacements of the C atoms in phenanthrene from the former plane range from 0·0005 to 0·0451 Å (Fig. 1) with an average value of the absolute displacement equal to 0·017 Å [the root-mean-square (r.m.s.) of the displacement from the plane is 0·023 Å] and those from the latter range from 0·0026 to 0·0394 Å, with an average value 0·015 Å (r.m.s. = 0·018 Å). The Si atom is displaced from these planes at a distance comparable to the above average values. However, the displacements of C(16) and C(17) of —Si(CH_3) from the least-squares plane are 1·57 and 1·53 Å respectively. The phenanthrene plane thus almost bisects the angle C(16)—Si—C(17).

While the distance between two H atoms on C(4) and C(5) is 2·11 Å and the angles between the planes of rings I and II, II and III, I and III (1·0, 1·0, 2·0° respectively) are essentially the same as those in phenanthrene (Kay, Okaya & Cox, 1971), some of

the C—C bond distances differ quite significantly $(>2\sigma$, Fig. 1). The principal differences are in C(9)—C(10), C(5)—C(13), C(5)—C(6), C(6)—C(7) and C(9)—C(14), which are 0·022–0·044 Å longer or shorter than their corresponding values in phenanthrene. Inasmuch as the averaged C—C bond distance in TMSP (1·402 Å) is the same as that in phenanthrene [1·40 Å, X-ray data without correction for rigid-body motion (Kay et al., 1971)], it seems that trimethylsilyl substitution on phenanthrene may affect the π-electron delocalization which extends over the molecule. However, the precision of the present determination does not permit any definite conclusion regarding this effect.

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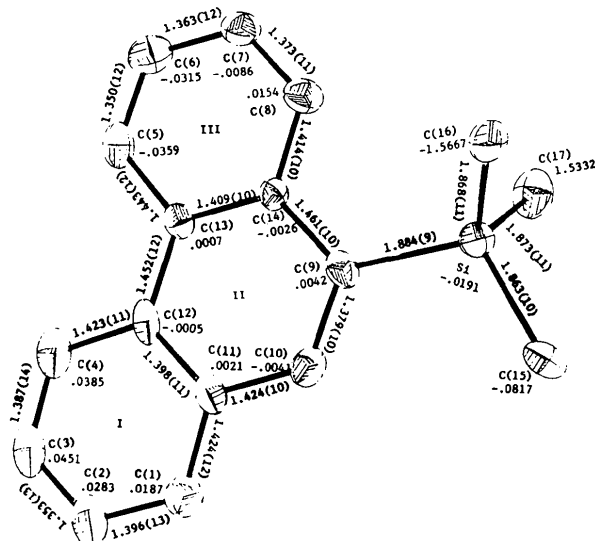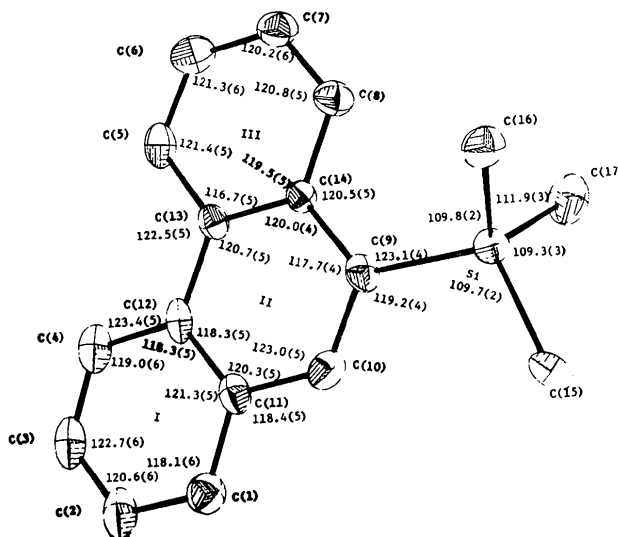LU, T. H. (1975). *Chin. J. Phys.* **13**, 247–251.

Fig. 1. Molecular structure of 9-trimethylsilylphenanthrene (excluding H atoms), showing bond distances, estimated errors (in parentheses) and displacements from the least-squares plane of the C atoms in ring II (all in Å).

Fig. 2. Molecular structure of 9-trimethylsilylphenanthrene (excluding H atoms), showing bond angles and estimated errors (in parentheses) (°).

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Tetramethyl 3-Bromo-7a,8,9,9a-tetrahydrocyclobuta[4,5]pyrrolo[1,2-*a*]quinoline-7,*r*-7a,*t*-9,*c*-9a-tetracarboxylate

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Abstract. $C_{22}H_{20}NO_8Br$, monoclinic, $P2_1/c$, $a = 10.088$ (5), $b = 12.307$ (5), $c = 17.482$ (8) Å, $\beta = 83.27(2)°$, $Z = 4$, $D_m = 1.56$, $D_c = 1.556$ g cm^{-3}, $\mu = 20.46$ cm^{-1} (Mo $K\alpha$ radiation). The X-ray crystal structure of one adduct from 6-bromo-2-methylquinoline and dimethyl acetylenedicarboxylate shows that it possesses a fused 5:4 ring system in place of the seven-membered ring postulated previously, and consequently the published structures of many similar adducts must be revised.

Introduction. The title compound was prepared by R. F. Flowerday by the published method (Acheson, Gagan & Harrison, 1968), and crystallized from methanol.

Weissenberg photographs gave the systematic absences $h0l$ for l odd, $0k0$ for k odd, which uniquely determined the space group. A crystal ($1.5 \times 0.2 \times 0.4$ mm) was mounted on a Hilger & Watts Y290 four-circle diffractometer fitted with a monochromator. Accurate cell dimensions and orientation matrix were obtained by a least-squares fit to the setting angles of 16 reflexions (Dobler & Duerr, 1969) and a complete data set was collected with Mo $K\alpha$ radiation to $2\theta \le 60°$ by an $\omega/2\theta$ scan, ordinate analysis method (Watson, Shotton, Cox & Muirhead, 1970) with 50 steps of $0.02°$. 3561 independent reflexions were measured of which 2154 were considered observed [$I > 3\sigma(I)$]. Lorentz and polarization corrections were applied, as was an empirical absorption correction (North, Phillips & Mathews, 1968).

The structure was solved by the heavy-atom method, and refined by full-matrix least squares to $R = 0.134$ with isotropic temperature factors. Further refinement with anisotropic thermal motion led to the location of all the H atoms except H(163) (placed by calculation), from a difference synthesis. Further blocked-matrix refinement with H atoms included with isotropic temperature factors fixed at 0.05 Å^2, and weights $w = \{[(F_o -0.30)/0.35]^2\}^{-1}$, gave a final $R = 0.051$. The H atoms were constrained so that all C—H lengths were 1.00 ± 0.02 Å, and all individual X_n—C—H angles ($X = O,C,H$) were equal ($\pm 2°$) to the mean of each group (Carruthers, 1975). Anomalous scattering factors were included for Br during the final refinements.

Final atomic coordinates are listed in Table 1. Fig. 1 shows the molecular geometry, omitting the H atoms.* Tables 2, 3 and 4 give bond distances, bond angles and deviations from the best plane.

Discussion. The reaction of 2-methylquinoline with dimethyl acetylenedicarboxylate was investigated by Diels & Alder (1934) who tentatively proposed a structure with which they were not satisfied. Acheson *et al.* (1968) suggested azepine structures such as (1) for this and related compounds, on the basis of UV, NMR and mass spectra. A scheme for the formation of most of

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32309 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.