

Fig. 2. Bond lengths (Å) and valency angles (°) in 15-phenyl-14-dehydrosparteine.

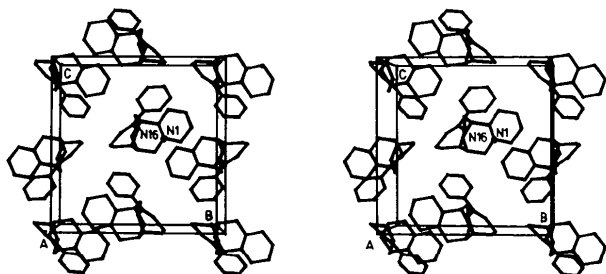


Fig. 3. A stereodiagram of the unit-cell contents along a (*PLUTO*; Motherwell, 1976). H atoms are omitted for clarity.

valency angles of the phenyl ring of (I) are similar to those observed in (II). The only significant difference between the corresponding bonds in (I) and (II) is the length of C(15)—C(18) which is markedly shorter in (I) than the analogous length C(2)—C(18) of 1.502 (4) Å in (II). This shortening of C(15)—C(18) can be correlated with the smaller inclination angle between the phenyl ring and C(14)=C(15), allowing a stronger conjugation between the adjacent bonds. The arrangement of the molecules in the crystal of (I) is presented in Fig. 3. There are no intermolecular contacts shorter than the sums of the van der Waals radii in this structure.

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## 7-Chloromethyl-12-methylbenz[a]anthracene

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**Abstract.** C<sub>20</sub>H<sub>15</sub>Cl, *M<sub>r</sub>* = 290.8, monoclinic, *P*2<sub>1</sub>/*c*, *a* = 20.449 (4), *b* = 11.473 (2), *c* = 13.025 (2) Å, β = 108.91 (1)°, *V* = 2890.9 Å<sup>3</sup>, *Z* = 8, *D<sub>x</sub>* = 1.336 g cm<sup>-3</sup>, λ(Cu Kα) = 1.5418 Å, μ = 21.14 cm<sup>-1</sup>, *F*(000) = 1216, *T* = 294 K, *R* = 0.045, *wR* = 0.049, for 3471 diffractometer data [*I<sub>o</sub>* ≥ 3σ(*I*)]. The ring system is puckered as a result of the bulkiness of the 12-methyl group.

**Introduction.** 7-Chloromethyl-12-methylbenz[a]anthracene (7-CIME-12-MBA) has been found to exhibit both carcinogenic and antitumor activity (Peck, Tan & Peck, 1976), and is more carcinogenic than its non-methylated analog, 7-chloromethylbenz[a]anthracene. The crystal-structure determination of 7-CIME-12-MBA was undertaken in order to obtain reliable atomic parameters so that the structural

features of various benzanthracenes might be compared (Glusker, Zacharias & Carrell, 1976).

**Experimental.** Crystals of 7-CIMe-12-MBA were provided by Dr Peck (Peck, Tan & Peck, 1976). The intensity data were measured on a Syntex *P1* four-circle diffractometer using the  $\theta$ - $2\theta$  variable-scan-rate technique where the scan rate ranged from 2 to  $24^\circ \text{ min}^{-1}$  depending on the intensity of the reflection being measured. The radiation used was  $\text{Cu K}\alpha$  employing a graphite monochromator. Of the 5378 independent data measured (out to  $\sin\theta/\lambda = 0.603 \text{ \AA}^{-1}$ ;  $0 \leq h \leq 24$ ,  $0 \leq k \leq 13$ ,  $-15 \leq l \leq 14$ ), 1907 data had  $I < 3\sigma(I)$  and were judged to be below the threshold of measurement, where  $\sigma(I)$  was determined using counting statistics. The cell parameters were obtained from 15 well centered reflections between  $50$  and  $70^\circ 2\theta$ . The data were corrected for Lorentz and polarization factors and a spherical absorption correction was applied [ $r = 0.014 \text{ cm}$ ,  $\mu(\text{Cu K}\alpha) = 21.14 \text{ cm}^{-1}$ ] since the crystal used was equidimensional:  $0.28 \text{ mm}$  on an edge. Absorption correction factors ranged between 1.51 and 1.56. The three monitor reflections indicated that there was no crystal deterioration during the course of the measurement of the data.

The structure was solved by direct methods (Germain, Main & Woolfson, 1971*a,b*; Stewart, Kruger, Ammon, Dickinson & Hall, 1972). Of the 42 non-H atoms, 40 were readily found as peaks in the initial *E* map. The remaining atoms were located in an electron density map, the phases for which were

Table 1. Final atomic coordinates and equivalent isotropic displacement parameters ( $\text{\AA}^2$ )

$U_{\text{eq}} = 1/3(U_{11} + U_{22} + U_{33})$ . The temperature factor is of the form  $T_{hkl} = \exp[-2\pi^2(h^2 a^{*2} U_{11} + \dots + 2hka^*b^* U_{12} + \dots)]$ .

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq}}$
C1A	0.69939 (3)	0.49530 (8)	0.43139 (6)	0.0786 (4)
C1A	0.3545 (1)	0.3067 (3)	0.1901 (2)	0.064 (2)
C2A	0.3002 (1)	0.3313 (3)	0.0986 (3)	0.077 (2)
C3A	0.2912 (1)	0.4427 (4)	0.0549 (2)	0.080 (2)
C4A	0.3395 (1)	0.5271 (3)	0.1007 (2)	0.075 (2)
C5A	0.4507 (1)	0.5854 (3)	0.2323 (2)	0.064 (2)
C6A	0.5086 (1)	0.5605 (2)	0.3130 (2)	0.059 (1)
C7A	0.5772 (1)	0.4318 (2)	0.4604 (2)	0.050 (1)
C8A	0.6462 (1)	0.2984 (3)	0.6059 (2)	0.067 (2)
C9A	0.6504 (2)	0.2038 (3)	0.6692 (3)	0.081 (2)
C10A	0.5930 (2)	0.1320 (3)	0.6519 (3)	0.084 (2)
C11A	0.5326 (2)	0.1537 (3)	0.5707 (3)	0.075 (2)
C12A	0.4638 (1)	0.2773 (2)	0.4150 (2)	0.055 (1)
C13A	0.4613 (1)	0.3702 (2)	0.3444 (2)	0.049 (1)
C14A	0.4031 (1)	0.3932 (2)	0.2441 (2)	0.054 (1)
C15A	0.3968 (1)	0.5023 (3)	0.1937 (2)	0.058 (1)
C16A	0.5175 (1)	0.4536 (2)	0.3728 (2)	0.048 (1)
C17A	0.6340 (1)	0.5200 (2)	0.4942 (2)	0.057 (1)
C18A	0.5840 (1)	0.3279 (2)	0.5212 (2)	0.054 (1)
C19A	0.5258 (1)	0.2533 (2)	0.5012 (2)	0.057 (1)
C20A	0.4013 (1)	0.2040 (3)	0.4109 (3)	0.073 (2)
C1B	-0.19494 (3)	0.00046 (8)	0.21661 (6)	0.0789 (4)
C1B	0.1435 (1)	0.1993 (3)	0.3319 (2)	0.060 (2)
C2B	0.1977 (1)	0.1781 (3)	0.2935 (2)	0.078 (2)
C3B	0.2083 (1)	0.0708 (3)	0.2577 (2)	0.091 (2)
C4B	0.1623 (1)	-0.0151 (3)	0.2553 (2)	0.080 (2)
C5B	0.0534 (1)	-0.0850 (3)	0.2788 (2)	0.066 (2)
C6B	-0.0048 (1)	-0.0633 (3)	0.3011 (2)	0.057 (2)
C7B	-0.0762 (1)	0.0624 (2)	0.3767 (2)	0.048 (1)
C8B	-0.1470 (1)	0.1928 (3)	0.4517 (2)	0.075 (2)
C9B	-0.1511 (2)	0.2868 (3)	0.5118 (3)	0.097 (2)
C10B	-0.0953 (2)	0.3606 (3)	0.5526 (3)	0.094 (2)
C11B	-0.0351 (2)	0.3404 (3)	0.5335 (2)	0.075 (2)
C12B	0.0353 (1)	0.2213 (2)	0.4487 (2)	0.047 (1)
C13B	0.0393 (1)	0.1297 (2)	0.3802 (2)	0.044 (1)
C14B	0.0972 (1)	0.1108 (2)	0.3377 (2)	0.050 (1)
C15B	0.1054 (1)	0.0025 (3)	0.2931 (2)	0.060 (2)
C16B	-0.0156 (1)	0.0436 (2)	0.3512 (2)	0.044 (1)
C17B	-0.1326 (2)	-0.0260 (3)	0.3486 (2)	0.059 (2)
C18B	-0.0842 (1)	0.1652 (2)	0.4311 (2)	0.055 (1)
C19B	-0.0268 (1)	0.2420 (2)	0.4713 (2)	0.054 (1)
C20B	0.0966 (1)	0.2966 (4)	0.5062 (3)	0.063 (2)

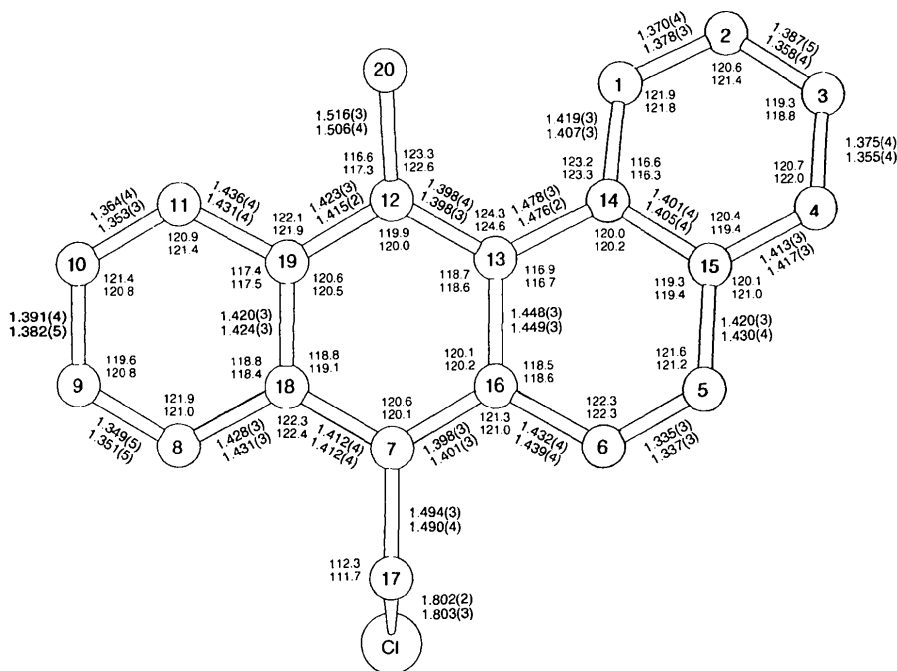


Fig. 1. Bond distances and angles. The values for molecule *A* are above those for molecule *B*. The bond angle e.s.d.'s range from 0.01 to 0.03°.

determined by the 40 known atoms. The structure was then refined by full-matrix least squares with isotropic temperature factors to  $R = 0.14$ . The atoms were then refined with anisotropic thermal parameters, one molecule at a time, to  $R = 0.06$ . The H atoms were located in a difference electron density map and the molecules were again refined separately, with isotropic thermal parameters for the H atoms and anisotropic thermal parameters for the non-H atoms, to  $R = 0.045$  and  $wR = 0.049$ . In all, 3471 non-zero-weight reflections were used for the refinement. The quantity refined was  $\sum w[K(|F_o| - |F_c|)]^2$  where  $w = 1/\sigma^2(F)$ .  $\sigma(F)$  was obtained from the relation:  $\sigma(F) = (F/2)\{[\sigma^2(I/I^2) + \delta^2]\}^{1/2}$ , where  $\delta$  is the measured instrumental uncertainty, obtained by repetitive measurement of our check reflections. A value of  $\delta = 0.017$  was found for this experiment. The e.s.d.'s were normalized to account for the fact that only one half of the structure was refined in any cycle.  $(\Delta/\sigma)_{\max} = 0.1$ ;  $-0.15 \leq \Delta\rho \leq 0.1 \text{ e \AA}^{-3}$  in the final difference map.

The final atomic parameters are listed in Table 1.\* The full-matrix least-squares program of Gantzel, Sparks, Long & Trueblood (1969) as modified by the author (Carrell, 1975) was used for the refinement. The atomic scattering factors for C and Cl atoms were taken from *International Tables for X-ray Crystallography* (1962, Vol. III, pp. 201–207) while the values used for H atoms were those of Stewart, Davidson & Simpson (1965). The real component of anomalous dispersion for Cl ( $f' = 0.348$ ) of Cromer & Mann (1968) was used.

**Discussion.** The bond lengths and bond angles found in this study of 7-ClMe-12-MBA are shown in Fig. 1. A comparison of the two independent molecules reveals that within experimental e.s.d. the two molecules are virtually the same. The largest differences in bond lengths are found at C(2)—C(3) and C(3)—C(4) where the differences are 0.029 ( $\Delta/\sigma \approx 6$ ) and 0.020 Å ( $\Delta/\sigma \approx 5$ ) respectively. Thermal ellipsoids (Davies, 1983) are shown in Fig. 2.

This study reveals that molecules of 7-ClMe-12-MBA are quite non-planar although the individual rings are approximately planar. The 'fold' angles between the outer rings are 20.8° in molecule *A* and 21.8° in molecule *B*. These values illustrate the high degree of non-planarity of the molecules. By comparison, all the rings in molecules of 7-ClMBA (Zacharias, 1977) are approximately coplanar. The presence of the methyl group at C(12) introduces

overcrowding which is compensated for by the 'bending' of the molecule. A stereoview of one of the two molecules is shown in Fig. 3 (Carrell, 1977).

The crystallographically independent molecules of 7-ClMe-12-MBA are packed in the crystal in segregated manner. Molecules of *A* associate with other *A* molecules, and *B* with *B*. The molecules pack as stacked 'dimers' related to other dimeric pairs in the familiar 'herringbone' arrangement. The only interaction between molecules is a 'herringbone' packing arrangement between *A* and *B* molecules. One of the main features of this packing arrangement is that the molecules exhibit columnar stacking of the rings with a small amount of molecular overlap as illustrated in Fig. 4.

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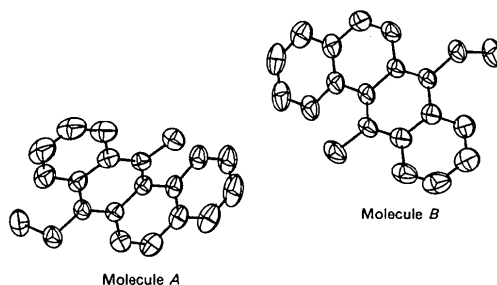


Fig. 2. Thermal ellipsoids drawn at 50% probability.

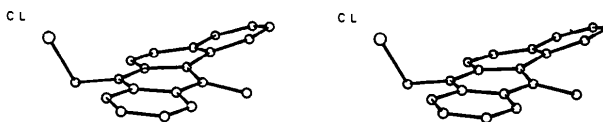


Fig. 3. Stereoview of the molecule showing the large 'fold' angle between the outer rings.

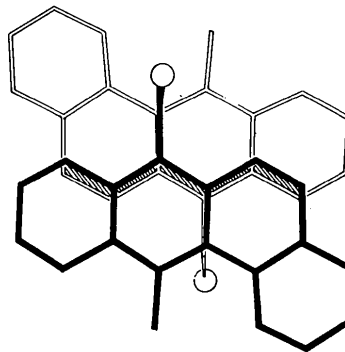


Fig. 4. Overlap of the ring systems.

\* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55633 (24 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: CR0405]

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## Structure of 4,7-Bis(4-mercaptobenzoyl)-1-tosyl-1,4,7-triazacyclononane

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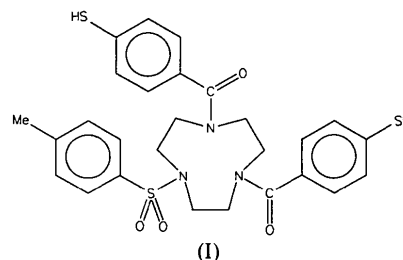
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**Abstract.** 4,7-Bis(4-mercaptobenzoyl)-1-tosyl-1,4,7-triazacyclononane-*n*-hexane (2/1),  $C_{27}H_{29}N_3O_4S_3 \cdot 0.5C_6H_{14}$ ,  $M_r = 598.8$ , monoclinic,  $P2_1/3$ ,  $a = 24.113$  (5),  $b = 11.020$  (5),  $c = 12.065$  (4) Å,  $\beta = 100.07$  (2)°,  $V = 3156.7$  Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.260$  g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71069$  Å,  $\mu = 2.6$  cm<sup>-1</sup>,  $F(000) = 1268$ ,  $T = 293$  K,  $R = 0.085$  for 2493 observed reflections. The triazacyclononane ring has a 'twist-chair-chair' conformation, with a pseudotwofold symmetry axis in the ring. Two of the substituent groups are directed to opposite sides of the ring, the third is more equatorially orientated; all are at approximately  $sp^2$ -hybridized N atoms. The two thiol groups form S—H···O hydrogen bonds connecting molecules in chains.

**Introduction.** Recently we synthesized the novel tridentate trithiol, 1,4,7-tris(4-mercaptobenzoyl)-1,4,7-triazacyclononane, which acts as a tripodal ligand to Fe<sub>4</sub>S<sub>4</sub> metal clusters generating a site-differentiated Fe site (Evans, Leigh & Santana, 1991; Evans, Garcia, Leigh, Newton & Santana, 1992). As a minor product in the preparation of this molecule, we obtained crystals of the title compound (I). Presumably a small amount of 1-tosyl-1,4,7-triazacyclononane had been present in the 1,4,7-tri-

azacyclononane starting material used in the synthesis. We describe below a two-step synthesis to the title compound; the spectroscopic properties of this material are identical to those of the crystals used in the structural determination.



**Experimental.** The title molecule was prepared in two steps, but the protected-thiol intermediate was also isolated and characterized.

4,7-Bis[4-(acetylthio)benzoyl]-1-tosyl-1,4,7-triazacyclononane. To a slurry of 1,4,7-triazacyclononane trihydrochloride (157 mg, 0.66 mmol) and triethylamine (0.40 g, 0.55 cm<sup>3</sup>, 3.94 mmol) in dichloromethane (25 cm<sup>3</sup>), was added solid 4-toluenesulfonyl chloride (125 mg, 0.66 mmol). After stirring for 2 min, 4-(acetylthio)benzoyl chloride (283 mg,