Structural Analysis of Picene, $C_{22}H_{14}$

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Abstract. $M_r = 278.35$, monoclinic, $P2_1$, $a = 8.480$ (2), $b = 6.154$ (2), $c = 13.515$ (3) Å, $\beta = 90.46$ (1)°, $V = 705.27$ (3) Å^3, $Z = 2$, $D_m = 1.324$, $D_x = 1.311$ Mg m^{-3}, $\lambda(\text{Cu } K\alpha) = 1.5418$ Å, $\mu = 0.53$ mm^{-1}, $F(000) = 292$, $T = 297$ K, $R = 0.062$ for 759 observed reflections. The molecule is slightly distorted from a planar structure owing to intramolecular overcrowding. The distances between the overcrowded H atoms are 1.87, 1.88 and 1.89 Å, about 0.5 Å less than the usual van der Waals distance.

Introduction. The physiological and chemical properties of the polycyclic aromatic hydrocarbons have been studied extensively and they are known to display a wide range of carcinogenic activity (Hartwell, 1951; Shubik & Hartwell, 1957, 1969). In addition these polycyclic aromatic hydrocarbons contain the skeleton of a large class of natural compounds – sterols, related bile acids and oestrogenic hormones (Bernal & Crowfoot, 1935).

Picene exists in two distinct crystalline forms, monoclinic and orthorhombic. Preliminary data for the orthorhombic form had been given by Bernal & Crowfoot (1935). Values for the cell dimensions given by them differ considerably from ours. The present structural investigation has been undertaken to provide more accurate stereochemical information on the polycyclic aromatic hydrocarbon picene in the monoclinic form.

Experimental. Crystals from chloroform. Initial cell parameters and symmetry from oscillation and Weissenberg photographs. Systematic absences: $0k0$, $k \neq 2n$. Crystal size $0.20 \times 0.25 \times 0.23$ mm. Cell parameters refined by least-squares fit of 25 high-angle reflections ($14° \leq \theta \leq 18°$). Intensity data measured on an Enraf–Nonius CAD-4 diffractometer using graphite-monochromatized Cu $K\alpha$ radiation. 1157 unique reflections measured ($h = -9$ to 9, $k = 0$ to 6, $l = 0$ to 15; $2° \leq \theta \leq 60°$). 759 observed reflections with $I \geq 3\sigma(I)$. Lp correction, absorption ignored. Correction for variation ($< 1.5\%$) of intensity. Structure solved by direct methods (*MULTAN*78, Main, Hull,

Lessinger, Germain, Declercq & Woolfson, 1978). Block-diagonal least-squares refinement on F for non-H atoms; H atoms (located from ΔF synthesis) not refined. $R = 0.062$ (observed reflections), $wR = 0.037$, $w = 1/\sigma^2(|F_o|)$, $R(\text{all reflections}) = 0.11$. Max. $\Delta/\sigma < 0.05$. Peak heights in the range -0.17 to $+0.15$ e Å^{-3} in final ΔF synthesis. No secondary-extinction correction. Scattering factors for non-H atoms from Cromer & Waber (1965), for H from Stewart, Davidson & Simpson (1965).

Discussion. A projection of the crystal structure, together with the atom-numbering scheme, viewed down the b axis is illustrated in Fig. 1. The final atomic parameters are listed in Table 1 while the intramolecular bond distances and angles are listed in Table 2.†

The structure may be compared with those of phenanthrene (Trotter, 1963), chrysene (Iball, 1934) and 7H-benzo[h,i]chrysen-7-one (α form) (Fujisawa, Sato & Saito, 1981). The C–C bond distances range from 1.358 (9) to 1.479 (8) Å, values similar to those found in all these structures. For the present structure the bond distances in the two outer rings are 1.358 (9),

† Lists of structure factors, anisotropic thermal parameters, H-atom parameters and least-squares-planes' data have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42008 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
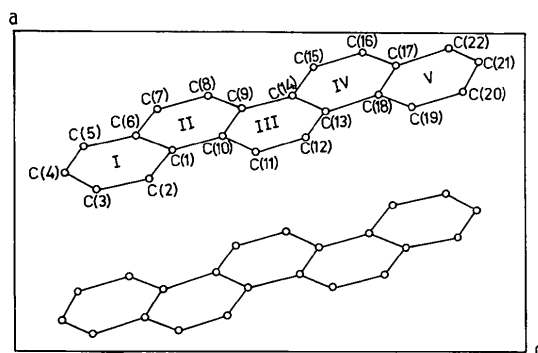

Fig. 1. Projection of the crystal structure of picene down the b axis.

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1·369 (8), 1·374 (11) and 1·365 (10) Å for C(3)—C(4), C(4)—C(5), C(20)—C(21) and C(21)—C(22), respectively. This is probably due to the large thermal motion at both ends of the long molecule.

The bond distances 1·459 (8), 1·479 (8) and 1·430 (7) Å for C(1)—C(10), C(13)—C(18) and C(9)—C(14), respectively, in the central rings are large and

compatible with the analogous bond distances in the structure of 5,6-dihydrodibenz[a,j]anthracene (Wei, 1972) and 5,6-dihydrodibenz[a,h]anthracene (Wei & Einstein, 1972).

The three extra-annular C—C—C angles at C(1), C(9) and C(18) are large [ranging from 122·3 (6) to 123·9 (6)°]. This is probably due to the overcrowding of the attached H atoms. Similar distortions have also been observed in phenanthrene (Trotter, 1963), 5,6-dihydrodibenz[a,h]anthracene (Wei & Einstein, 1972) and 5,6-dihydrodibenz[a,j]anthracene (Wei, 1972).

The shifts of the C atoms from the mean plane through all the atoms* indicate that the molecule as a whole is almost planar. The dihedral angle between the two outermost rings (I) and (V) is 3·72°. Rings (I), (II), (III), (IV) and (V) are all nearly planar, the maximum deviations from the corresponding best planes being 0·019, 0·024, 0·015, 0·010 and 0·004 Å respectively. The slight non-planarity of the molecule appears to be signficant since this is probably the result of minimizing the overall molecular strains. However, the individual ring in the molecule still remains planar. The dihedral angles between the planes of rings (I) and (II) are 1·86 (0·17), (II) and (III) are 1·08 (0·17), (III) and (IV) are 0·98 (0·18), and (IV) and (V) are 0·65 (0·17)°.

The packing of the molecule is shown in Fig. 1. Intermolecular C···C distances less than 3·7 Å are C(2)···C(7) 3·56 (1), C(8)···C(11) 3·58 (1), C(12)··· C(15) 3·50 (1), C(16)···C(19) 3·59 (1) (the second atom of each pair is in the molecule at $x, y - 1, z$) and C(10)···C(12) 3·57 (1) Å (second atom in the molecule at $-x + 1, y + \frac{1}{2}, -z + 1$).

In the present polycyclic aromatic hydrocarbon system, the H(12)···H(19), H(2)···H(11) and H(15)··· H(8) distances are 1·87, 1·88 and 1·89 Å respectively. These distances are much shorter than the accepted van der Waals contacts of 2·4 Å (Pauling, 1960). In the reinvestigated structure of phenanthrene (Kay, Okaya & Cox, 1971) the deviations of the rings from coplanarity have been considered in terms of molecular distortion caused by the overcrowded H atoms. In several polycyclic aromatic hydrocarbons such steric effects caused by the overcrowded H atoms have been investigated by Coulson & Haigh (1963). In this structure such steric effects can be considered to be mainly responsible for the significant deviations of the three extra-annular C—C—C angles, which is described above.

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters (Hamilton, 1959) with e.s.d.'s in parentheses*

	x	y	z	$B_{eq}(\text{Å}^2)$
C(1)	0·6308 (6)	0·2155 (11)	0·3028 (4)	3·81
C(2)	0·5434 (7)	0·0449 (14)	0·2607 (4)	5·09
C(3)	0·5065 (8)	0·0458 (15)	0·1589 (5)	6·38
C(4)	0·5598 (7)	0·2070	0·0993 (4)	5·77
C(5)	0·6449 (7)	0·3808 (13)	0·1336 (4)	5·52
C(6)	0·6770 (6)	0·3848 (12)	0·2370 (4)	4·04
C(7)	0·7645 (7)	0·5541 (13)	0·2787 (4)	4·30
C(8)	0·8023 (7)	0·5686 (13)	0·3771 (4)	4·50
C(9)	0·7633 (6)	0·3992 (11)	0·4439 (4)	3·45
C(10)	0·6767 (6)	0·2256 (11)	0·4069 (4)	3·75
C(11)	0·6269 (6)	0·0540 (13)	0·4713 (4)	3·89
C(12)	0·6705 (7)	0·0510 (14)	0·5719 (4)	4·86
C(13)	0·7599 (7)	0·2316 (12)	0·6073 (4)	4·41
C(14)	0·8062 (6)	0·4012 (10)	0·5464 (4)	3·51
C(15)	0·8942 (6)	0·5739 (12)	0·5864 (4)	3·59
C(16)	0·9380 (7)	0·5804 (13)	0·6838 (4)	4·72
C(17)	0·8987 (7)	0·4088 (12)	0·7500 (4)	4·33
C(18)	0·8090 (7)	0·2358 (12)	0·7125 (4)	4·02
C(19)	0·7686 (7)	0·0728 (14)	0·7781 (4)	4·55
C(20)	0·8190 (7)	0·0829 (15)	0·8776 (4)	5·60
C(21)	0·9074 (8)	0·2556 (14)	0·9106 (4)	6·03
C(22)	0·9491 (7)	0·4218 (12)	0·8492 (4)	5·48

Table 2. *Bond distances (Å) and angles (°) with e.s.d.'s in parentheses*

C(1)—C(2)	1·403 (10)	C(12)—C(13)	1·426 (10)
C(2)—C(3)	1·409 (9)	C(13)—C(14)	1·388 (9)
C(3)—C(4)	1·358 (9)	C(14)—C(9)	1·430 (7)
C(4)—C(5)	1·369 (8)	C(14)—C(15)	1·404 (9)
C(5)—C(6)	1·422 (8)	C(15)—C(16)	1·366 (8)
C(6)—C(1)	1·426 (9)	C(16)—C(17)	1·426 (10)
C(6)—C(7)	1·395 (10)	C(17)—C(18)	1·401 (9)
C(7)—C(8)	1·369 (8)	C(18)—C(13)	1·479 (8)
C(8)—C(9)	1·420 (9)	C(18)—C(19)	1·384 (10)
C(9)—C(10)	1·387 (9)	C(19)—C(20)	1·409 (8)
C(10)—C(1)	1·459 (8)	C(20)—C(21)	1·374 (11)
C(10)—C(11)	1·434 (9)	C(21)—C(22)	1·365 (10)
C(11)—C(12)	1·406 (8)	C(22)—C(17)	1·406 (8)

C(2)—C(1)—C(6)	116·2 (6)	C(12)—C(13)—C(14)	122·7 (6)
C(2)—C(1)—C(10)	123·9 (6)	C(12)—C(13)—C(18)	118·7 (6)
C(1)—C(2)—C(3)	120·4 (6)	C(13)—C(14)—C(9)	119·8 (5)
C(2)—C(3)—C(4)	120·6 (6)	C(14)—C(9)—C(10)	119·0 (5)
C(3)—C(4)—C(5)	123·2 (6)	C(9)—C(14)—C(15)	120·7 (5)
C(4)—C(5)—C(6)	116·3 (6)	C(14)—C(13)—C(18)	118·6 (5)
C(5)—C(6)—C(1)	123·3 (6)	C(13)—C(18)—C(17)	120·6 (6)
C(5)—C(6)—C(7)	120·5 (6)	C(13)—C(18)—C(19)	122·3 (6)
C(1)—C(6)—C(7)	116·2 (6)	C(18)—C(17)—C(16)	117·7 (6)
C(6)—C(7)—C(8)	124·1 (6)	C(17)—C(16)—C(15)	121·4 (6)
C(7)—C(8)—C(9)	121·1 (6)	C(16)—C(15)—C(14)	122·2 (6)
C(8)—C(9)—C(10)	117·5 (5)	C(15)—C(14)—C(13)	119·5 (5)
C(8)—C(9)—C(14)	123·4 (5)	C(18)—C(19)—C(20)	120·3 (6)
C(9)—C(10)—C(1)	121·1 (5)	C(19)—C(20)—C(21)	120·3 (7)
C(1)—C(10)—C(11)	118·5 (5)	C(20)—C(21)—C(22)	121·7 (7)
C(10)—C(1)—C(6)	119·9 (5)	C(21)—C(22)—C(17)	117·3 (6)
C(9)—C(10)—C(11)	120·4 (5)	C(22)—C(17)—C(18)	123·2 (6)
C(10)—C(11)—C(12)	121·4 (6)	C(17)—C(18)—C(19)	117·1 (6)
C(11)—C(12)—C(13)	116·7 (6)	C(16)—C(17)—C(22)	119·1 (6)

* See deposition footnote.

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Structures of Tifluadom [5-(2-Fluorophenyl)-1-methyl-2-(3-thenoyl-aminomethyl)-2,3-dihydro-1H-1,4-benzodiazepine] Hydrochloride, $C_{22}H_{21}FN_3OS^+.Cl^-$, and of (+)-Tifluadom p-Toluenesulphonate, $C_{22}H_{21}FN_3OS^+.C_7H_7O_3S^-$, and the Absolute Configuration of the Latter

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Abstract. $C_{22}H_{21}FN_3OS^+.Cl^-$: $M_r = 429.9$, orthorhombic, $P2_12_12_1$, $a = 21.362$ (13), $b = 14.919$ (3), $c = 6.484$ (1) Å, $V = 2066$ Å^3, $Z = 4$, $D_x = 1.38$ g cm^{-3}, Cu $K\alpha$ radiation, graphite monochromator, $\lambda = 1.54178$ Å, $\mu = 28.7$ cm^{-1}, $F(000) = 896$, room temperature, $R = 0.051$, 2146 significant reflections, orange parallelepipeds from ethanol. (+)-$C_{22}H_{21}FN_3OS^+.C_7H_7O_3S^-$: $M_r = 565.7$, orthorhombic, $P2_12_12_1$, $a = 10.319$ (6), $b = 10.824$ (5), $c = 24.537$ (13) Å, $V = 2741$ Å^3, $Z = 4$, $D_x = 1.37$ g cm^{-3}, Cu $K\alpha$ radiation as above, $\mu = 22.5$ cm^{-1}, $F(000) = 1184$, room temperature, $R = 0.041$, 2428 significant reflections, deep-yellow prisms from acetone. The absolute configuration is 2S, using standard chemical numbering. In both structures, the 2-substituent is axially placed on the diazepine ring. In (+)-tifluadom, this ring is in a twist-boat conformation with symmetry axis passing through C(5a), whereas in the hydrochloride the ring is a boat with a symmetry plane passing through C(3). The conformations are otherwise very similar in the two crystal structures, including the presence of two intermolecular hydrogen bonds from N(4) and the amide group of the 2-substituent to the anion. Bond distances and angles are normal.

Introduction. Tifluadom [KC 5103, (I)] is a novel opioid drug, selective for opiate κ-receptors (Römer et al., 1982a) and almost devoid of affinity for benzodiazepine binding sites (Römer et al., 1982b).

(I) (+)-(2S)-Tifluadom
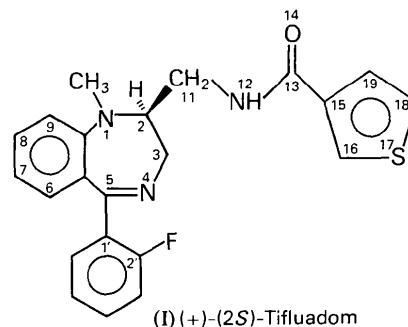
The crystal structure analysis of the racemic hydrochloride (which crystallizes in the noncentrosymmetric space group $P2_12_12_1$ so that individual crystals contain exclusively one or the other enantiomer) was undertaken to compare the conformation with those of classical opiates. After resolution of the racemate had shown that analgesic activity resides principally in the