

thermal parameters for the H atoms were fixed throughout all subsequent refinements. Least-squares refinement converged to final  $R = 0.044$ ,  $wR = 0.048$ ,  $S = 1.416$ . At this point all subsequent shifts were found to be  $< 0.001\sigma$ . A single prominent peak is evident on the difference electron density map measuring  $0.67 e \text{ \AA}^{-3}$  in the immediate vicinity of Br. Otherwise, all remaining difference peaks were found to be  $< 0.39 e \text{ \AA}^{-3}$ . Anomalous scattering of Br and S atoms was employed for verification of the proper choice of enantiomeric configuration, following the statistical criterion proposed by Hamilton (1965). The opposite enantiomorph refined to final reliability indices of  $R = 0.051$ ,  $wR = 0.057$ . Scattering factors for neutral atoms and anomalous-scattering parameters for Br and S atoms were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). All calculations were performed on a PDP 11/60 utilizing the *SDP-Plus* package (Frenz, 1978).

**Discussion.** Refined positional parameters for all atoms and equivalent isotropic  $B$  values are supplied in Table 1. Atom numbering follows the scheme indicated in Fig. 1. Fig. 2 shows a stereo *ORTEP* (Johnson, 1976) representation of the molecule. Interatomic bonding distances and angles are supplied in Table 2.\* Bond distances and angles are, generally, as expected. The one exception to this is

\* Lists of structure factors, complete bond distances and angles, and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55634 (18 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: CR1012]

the exocyclic C—O bond at C1 in the pyranose ring. At  $1.37 \text{ \AA}$ , this bond is significantly shorter than anticipated, but is consistent with previously reported structures with pyranose substituents (Birnbaum, Roy, Brisson & Jennings, 1987; Kim & Jeffrey, 1967; Berman, Chu & Jeffrey, 1967) in which an O atom is attached at one of the anomeric positions. As is often the case, e.s.d.'s in atomic positions generally worsen in direct proportion to distance from the heavy atoms (Br and S) in the structure. The pyranose ring exists in the chair conformation with all substituents, except for the methoxy group at C1 (one of the anomeric C atoms), in equatorial positions. The phenyl C atoms of the tosyl and benzoyl substituents are approximately planar within the limitations of the data exhibiting minimal overlap (closest contact being that between atoms Cb2 and C13, with a non-bonded distance of  $3.62 \text{ \AA}$ ). The planes described by these two rings intersect at an angle of  $13.5^\circ$ .

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*Acta Cryst.* (1993). **C49**, 483–486

## A Chloride of a Substituted Heterocyclic Analogue of Chrysene: $C_{19}H_{17}N_2O^+ \cdot Cl^-$

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**Abstract.** 12-Amino-6-hydroxyethylbenzo[*i*]phenanthridinium chloride,  $C_{19}H_{17}N_2O^+ \cdot Cl^-$ ,  $M_r = 324.83$ , monoclinic,  $P2_1/n$ ,  $a = 18.554 (3)$ ,  $b = 10.466 (2)$ ,  $c = 7.959 (4) \text{ \AA}$ ,  $\beta = 91.78 (3)^\circ$ ,  $V = 1545 (1) \text{ \AA}^3$ ,  $Z = 4$ ,

$D_x = 1.40 \text{ g cm}^{-3}$ ,  $\lambda(\text{Cu } K\alpha) = 1.5418 \text{ \AA}$ ,  $\mu = 22.43 \text{ cm}^{-1}$ ,  $F(000) = 680$ ,  $T = 298 \text{ K}$ ,  $R = 0.034$ ,  $wR = 0.037$ , for 1115 reflections with  $I > 3\sigma(I)$ . The polynuclear framework is remarkably planar with the largest inter-ring-plane angle,  $A/C = 4^\circ$ . Bay-region dimensions, with beach bond C—C =  $1.450 (6) \text{ \AA}$  and beach C—C—C bond angles close to

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122°, are as in chrysenes and phenanthrenes without a bay substituent. The hydroxyethyl group lies out of the molecular plane with a close approach between its hydroxyl H atom and the Cl ion.

**Introduction.** Substituted chrysenes (or benzo[*a*]phenanthrenes), which occur widely in smokes, exhausts and coal-liquefaction products, exhibit a range of carcinogenic activity (Berger & Seybold, 1979; Melikian, LaVoie, Hecht & Hoffmann, 1983) and appear to be more flexible than benzo[*a*]anthracenes (Kashino, Zacharias, Prout, Carrell, Glusker, Hecht & Harvey, 1984; Zacharias, Kashino, Glusker, Harvey, Amin & Hecht, 1984; Briant, Jones & Shaw, 1985). The substituted benzo[*i*]phenanthridines (or benzazaphenanthrenes) include potential DNA-intercalating anti-cancer drugs (Wilson, Keel, Jones & Mosher, 1982; Henry, 1982) but have received less crystallographic study. We report here the structure of an inactive salt analogue of chrysene with substituents away from the bay region: 12-amino-6-hydroxyethylbenzo[*i*]phenanthridinium chloride (HABIC). The crystallographic numbering is shown in Fig. 1.

**Experimental.** Crystals were obtained as yellow-brown translucent plates (Dr D. W. Henry & M. W. Lerrom *via* Dr C. W. Mosher, SRI International) elongated along *c*. Absences from photographic measurements indicated space group *P*2<sub>1</sub>/*n*. A crystal of dimensions 0.50 × 0.25 × 0.09 mm was used to refine cell dimensions (25 reflections, 24 < 2θ < 48°) and for intensity data collection on an Enraf-Nonius CAD-4 diffractometer with Cu Kα radiation (Biophysics, Leeds University), using ω/2θ scans of variable scan rate (maximum time for final scan 50 s) over 2θ range 1–70° and index range *h* ± 22, *k* ± 12, *l* – 9/0. Intensity standard 542 (117 measurements) and orientation reflections 262 and 922, checked hourly, showed 9% decay. 6417 measured reflections yielded 4115 reflections with |*F*| > 3σ(|*F*|) of which

2317 were unique. Merging *R* = 0.016. Structure solution used *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980) with the SUNY Buffalo (1970) program system including *LINUS* (Coppens & Hamilton, 1970), *JIMDAP* and *ORFFE* (Busing, Martin & Levy, 1964) at the University of Aarhus (with assistance of Drs A. C. Hazell and R. G. Hazell). The most favourable phase set arising from input to *MULTAN* of an 18-atom benzophenanthridine fragment gave a hexagonal array. Within this array (apart from the Cl<sup>-</sup>) were two molecular clusters close to the *ac* plane and separated by a bond vector; the mean position was taken for full-matrix isotropic least-squares (LS) refinement of C and N atoms of the nucleus, and Cl. After further LS refinements on *F*, Fourier synthesis (*JIMDAP*) revealed the amino N and an ethyl C atom, a difference Fourier (Δ*F*) at *R* = 0.23 located the remaining hydroxyethyl C and O atoms (and showed the position of the phenanthridine N atom), and (at *R* = 0.072) a further Δ*F* synthesis indicated 16 of the 17 H atoms (the hydroxyl H atom emerged on a difference map at the *R* = 0.035 stage). There was only slight improvement (*R* = 0.034, *wR* = 0.037) after the final anisotropic (isotropic for H atoms) LS refinements [40 atoms, 277 parameters, 1115 observed reflections, *I* > 3σ(*I*)] following reweighting,  $w^{-1} = [(1 + 0.01)|F_o|^2 + \sigma(F_o)^2]^{1/2} - |F_o|$ , and adjustment of a Lorentzian type-I isotropic secondary-extinction parameter 0.115 (17) × 10<sup>-2</sup>. A final Δ*F* synthesis showed only randomly distributed peaks < |0.15| e Å<sup>-3</sup>. Scattering factors were taken from Stewart, Davidson & Simpson (1965) for H atoms and Cromer & Mann (1968) for C, N, O and Cl atoms. No correction for absorption was made.

**Discussion.** Final fractional coordinates of C, N and Cl atoms with equivalent isotropic temperature factors are given in Table 1,\* bond lengths for non-H atoms in the cation and corresponding bond angles are listed in Table 2. Overall, the chrysene-like nucleus, in the absence of substituents at either of the bay regions C(4) to C(11) and C(8) to C(15), is highly planar, with a minimum angle between mean ring planes of 4° (between unsubstituted ring *A* and heterocyclic ring *C*); mean deviations of the non-H atoms from the individual ring planes are < 0.01 Å. At the bay regions, torsion angles C(4)–C(5)–C(10)–C(11) and C(8)–C(9)–C(14)–C(15) are

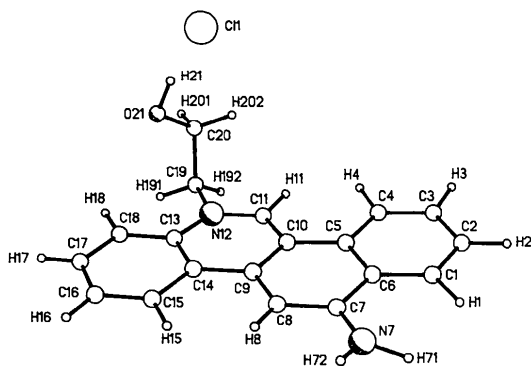


Fig. 1. View of HABIC showing substituents and crystallographic numbering scheme.

\* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, and bond lengths and angles involving H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55565 (10 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: MU0287]

Table 1. Fractional atomic coordinates ( $\times 10^5$ ) and average equivalent isotropic thermal parameters ( $\text{\AA}^2 \times 10^4$ )

$$U_{eq} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j.$$

|       | x           | y           | z          | $U_{eq}$ |
|-------|-------------|-------------|------------|----------|
| C(1)  | -9146 (30)  | -21125 (50) | 45975 (65) | 480 (34) |
| C(2)  | -5400 (32)  | -31466 (55) | 52477 (68) | 537 (37) |
| C(3)  | 1926 (34)   | -32936 (51) | 49730 (71) | 525 (38) |
| C(4)  | 5569 (32)   | -24021 (49) | 40432 (71) | 477 (33) |
| C(5)  | 1917 (26)   | -13240 (44) | 33532 (60) | 387 (30) |
| C(6)  | -5492 (25)  | -11864 (46) | 36491 (59) | 378 (30) |
| C(7)  | -9239 (26)  | -496 (46)   | 30194 (61) | 397 (31) |
| C(8)  | -5498 (27)  | 8685 (49)   | 21564 (66) | 407 (32) |
| C(9)  | 1725 (26)   | 7466 (43)   | 18376 (58) | 371 (30) |
| C(10) | 5604 (26)   | -3553 (42)  | 24014 (64) | 371 (30) |
| C(11) | 12728 (27)  | -4758 (48)  | 20163 (65) | 407 (33) |
| N(12) | 16392 (20)  | 4029 (35)   | 11617 (49) | 398 (26) |
| C(13) | 13009 (27)  | 15380 (43)  | 6157 (62)  | 395 (31) |
| C(14) | 5692 (25)   | 16997 (42)  | 9153 (58)  | 361 (29) |
| C(15) | 2289 (30)   | 28192 (45)  | 2963 (62)  | 445 (34) |
| C(16) | 6168 (32)   | 37138 (53)  | -5588 (71) | 502 (36) |
| C(17) | 13423 (33)  | 35451 (53)  | -8252 (72) | 513 (38) |
| C(18) | 16930 (30)  | 24697 (51)  | -2364 (67) | 467 (34) |
| C(19) | 24111 (28)  | 1393 (58)   | 8749 (75)  | 467 (37) |
| C(20) | 28771 (32)  | 4519 (56)   | 24082 (83) | 575 (41) |
| O(21) | 28176 (20)  | 17735 (35)  | 28016 (52) | 615 (27) |
| N(7)  | -16313 (25) | 1201 (51)   | 33024 (65) | 509 (32) |
| Cl(1) | 29863 (8)   | 19403 (13)  | 65979 (19) | 571 (9)  |

Table 2. Bond lengths ( $\text{\AA}$ ) and angles ( $^\circ$ )

|                  |           |                   |           |
|------------------|-----------|-------------------|-----------|
| C(1)—C(2)        | 1.378 (7) | C(11)—N(12)       | 1.341 (6) |
| C(2)—C(3)        | 1.392 (7) | N(12)—C(13)       | 1.406 (6) |
| C(3)—C(4)        | 1.381 (7) | C(13)—C(14)       | 1.396 (9) |
| C(4)—C(5)        | 1.418 (7) | C(14)—C(9)        | 1.452 (6) |
| C(5)—C(6)        | 1.409 (6) | C(14)—C(15)       | 1.412 (6) |
| C(6)—C(1)        | 1.414 (7) | C(15)—C(16)       | 1.374 (7) |
| C(6)—C(7)        | 1.459 (6) | C(16)—C(17)       | 1.381 (7) |
| C(7)—N(7)        | 1.350 (6) | C(17)—C(18)       | 1.375 (7) |
| C(7)—C(8)        | 1.381 (7) | C(18)—C(13)       | 1.404 (7) |
| C(8)—C(9)        | 1.378 (7) | N(12)—C(19)       | 1.483 (6) |
| C(9)—C(10)       | 1.425 (6) | C(19)—C(20)       | 1.510 (8) |
| C(10)—C(5)       | 1.450 (6) | C(20)—O(21)       | 1.423 (6) |
| C(10)—C(11)      | 1.372 (7) |                   |           |
| C(6)—C(1)—C(2)   | 119.6 (5) | C(10)—C(9)—C(14)  | 117.1 (4) |
| C(1)—C(2)—C(3)   | 120.8 (6) | C(9)—C(10)—C(11)  | 119.0 (5) |
| C(2)—C(3)—C(4)   | 120.4 (6) | C(10)—C(11)—N(12) | 123.9 (5) |
| C(3)—C(4)—C(5)   | 120.6 (6) | C(11)—N(12)—C(13) | 120.5 (4) |
| C(4)—C(5)—C(6)   | 118.3 (5) | C(11)—N(12)—C(19) | 117.2 (4) |
| C(5)—C(6)—C(1)   | 120.3 (5) | C(13)—N(12)—C(19) | 122.2 (4) |
| C(4)—C(5)—C(10)  | 122.1 (5) | N(12)—C(13)—C(14) | 118.5 (4) |
| C(1)—C(6)—C(7)   | 120.7 (5) | C(9)—C(14)—C(13)  | 120.9 (5) |
| C(6)—C(5)—C(10)  | 119.6 (4) | N(12)—C(13)—C(18) | 120.2 (5) |
| C(5)—C(6)—C(7)   | 118.9 (4) | C(9)—C(14)—C(15)  | 121.2 (4) |
| C(6)—C(7)—C(8)   | 119.8 (5) | C(18)—C(13)—C(14) | 121.3 (5) |
| C(6)—C(7)—N(7)   | 120.3 (5) | C(13)—C(14)—C(15) | 117.9 (5) |
| C(8)—C(7)—N(7)   | 119.8 (5) | C(14)—C(15)—C(16) | 120.2 (5) |
| C(7)—C(8)—C(9)   | 122.3 (5) | C(15)—C(16)—C(17) | 121.1 (6) |
| C(8)—C(9)—C(10)  | 120.1 (5) | C(16)—C(17)—C(18) | 120.4 (6) |
| C(8)—C(9)—C(14)  | 122.7 (5) | C(17)—C(18)—C(13) | 119.1 (5) |
| C(5)—C(10)—C(9)  | 119.3 (4) | N(12)—C(19)—C(20) | 111.5 (5) |
| C(5)—C(10)—C(11) | 121.7 (5) | C(19)—C(20)—O(21) | 110.0 (5) |

only 4.7 (7) and 0.3 (7) $^\circ$ . The beach C—C bonds of 1.450 (6)  $\text{\AA}$  and C—C—C angles of  $\sim 122^\circ$  (e.s.d. 0.5 $^\circ$ ) in the two bays are similar to each other and to corresponding dimensions in the bays of phenanthrenes (Johnson, Jones & Shaw, 1991) and chrysenes (Glusker, 1985; Zacharias, Prout, Myers & Glusker, 1991; Bulgarovskaya, Zavodnik & Vozzhennikov, 1987). Several C—C bonds in HABIC are as short as 1.37–1.38  $\text{\AA}$ , although the substituted K-region C(7)—C(8) bond [1.381 (7)  $\text{\AA}$ ] is longer than the analogous bond in 5-methylbenz-[a]anthracene (Jones, Shaw & Briant, 1990).

The three bond angles at the amino substitution point, C(7), are almost identical, but N(12)—C(19) leans slightly away [C—N—C angles 117.2 (4), 122.2 (4) $^\circ$ ] from the bay region, as with non-ortho substituents in some other polycyclics (Briant, Johnson, Jones & Shaw, 1991); C(7)—N(7) = 1.350 (6)  $\text{\AA}$  is moderately short. With torsion angles C(11)—N(12)—C(19)—C(20) =  $-80^\circ$  and C(13)—N(12)—C(19)—C(20) =  $98^\circ$ , the hydroxyethyl group stands perpendicular to the 'chrysenes' plane, as in 6-N,N-diacetylaminochrysenes (Wieckowski & Krygowski, 1981); the hydroxyl O atom is *gauche* to the quaternary N atom [torsion angle N(12)—C(19)—C(20)—O(21) =  $-61^\circ$ ]. The Cl $^-$  ion is located above the molecular plane (Fig. 1), weakly linked to the hydroxyl group [3.03 (1)  $\text{\AA}$  from O(21) and 2.02 (7)  $\text{\AA}$  from H(21)].

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*Acta Cryst.* (1993). **C49**, 486–489

## Structure du 11,11'-Bi[3-éthylènedioxy-17β-cyano-5-hydroxy-17α-triméthylsiloxy-19-nor-5α-androst-9(10)-ène] Monohydrate

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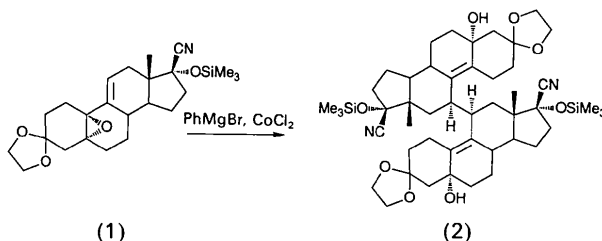
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(Reçu le 11 février 1992, accepté le 25 juin 1992)

**Abstract.** 3,3'-Di(ethylenedioxy)-5,5'-dihydroxy-17α,17α'-bis(trimethylsiloxy)-11,11'-bi[19-nor-5α-androst-9(10)-ène]-17β,17β'-dicarbonitrile monohydrate, C<sub>48</sub>H<sub>72</sub>N<sub>2</sub>O<sub>8</sub>Si<sub>2</sub>.H<sub>2</sub>O, *M<sub>r</sub>* = 879.3, orthorhombic, *P*2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>, *a* = 31.201 (12), *b* = 13.789 (6), *c* = 11.620 (5) Å, *V* = 4999.3 Å<sup>3</sup>, *Z* = 4, *D<sub>x</sub>* = 1.168 Mg m<sup>-3</sup>, λ(Cu Kα) = 1.5418 Å, μ = 1.05 mm<sup>-1</sup>, *F*(000) = 1904, *T* = 295 K, *R*(*F*) = 0.08 for 2961 reflexions. The structure consists of two steroid skeletons linked at β by their C(11) atoms. The superposition of these steroids shows that they have very similar conformations. The above relatively high *R* value is probably the consequence of a continuous crystal degradation induced by the escape of a water molecule.

**Introduction.** Le 11,11'-bi[3-éthylènedioxy-17β-cyano-5-hydroxy-17α-triméthylsiloxy-19-nor-5α-androst-9(10)-ène] monohydrate (2), ci-après désigné par 'bistéroïde', a été obtenu par l'addition à 273 K de l'époxyde (1) (1,65 g, 3,84 mM) à une solution 0,85 M de bromure de phénylmagnésium dans le THF (14 mL, 11,9 mM) en présence de chlorure de cobalt(II) anhydre (50 mg, 0,38 mM), avec un rendement de 66%. Les caractéristiques physiques pouvaient correspondre à un dimère ayant une liaison C—C entre les carbones 11 et 11'. Le produit a été cristallisé dans l'éther isopropylique, mais le point de

fusion s'étalant sur une trop longue plage de température n'a pu être déterminé. (α)<sub>D</sub> = -15 (1)° (*c* = 1%, CHCl<sub>3</sub>). RMN <sup>1</sup>H (δ): 0,22 (*s*, 9H, OSiMe<sub>3</sub>), 1,16 (*s*, 3H, Me-18), 3,37 (*m*, 1H, H-11) et 3,97 (*s*, 4H, cétal). Microanalyse pour C<sub>48</sub>H<sub>72</sub>N<sub>2</sub>O<sub>8</sub>Si<sub>2</sub> calculé C 66,93, H 8,43, N 3,25%; observé C 67,3, H 8,5, N 2,9%. L'encombrement stérique particulièrement important autour des positions 11β confère un intérêt particulier à la détermination de la structure tridimensionnelle de ce produit.



**Partie expérimentale.** Cristal incolore, 0,4 × 0,5 × 0,2 mm, paramètres cristallins obtenus sur diffractomètre Philips PW 1100 (anticathode au Cu) avec 25 réflexions 15,2 < θ < 17,6°. Mesure des intensités par *flying stepscan* (Logiciel Philips), angle de balayage de 1,60°, vitesse de scanning de 0,025 s par pas de 2/100° en θ, domaine d'exploration de 2θ ≤ 121° (0 ≤ *h* ≤ 34, 0 ≤ *k* ≤ 15, 0 ≤ *l* ≤ 12). Réflexions