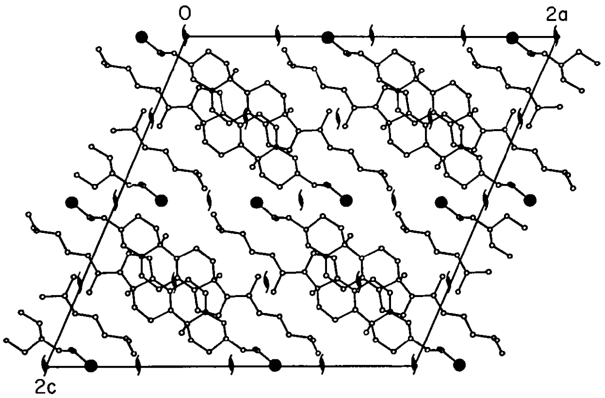

Fig. 2. Partial packing diagram of cholesteryl chloroformate.

local packing conditions. It has now been found in an extended configuration in this structure, in cholesteryl iodide (Carlisle & Crowfoot, 1945) and in 7-bromocholesteryl chloride (Burki & Nowacki, 1956) and in a relatively contracted state caused by the synclinal conformation about C(22)—C(23) [*i.e.* cholesteryl myristate molecule *A* (Craven & DeTitta, 1976) and cholesterol monohydrate molecule *A* (Craven, 1976)]. The conformation about C(23)—C(24) will of course have less of an effect upon the total length of the tail.

A packing diagram is shown in Fig. 2. The plane of the rings is parallel to the *ac* plane with the entire molecule oriented parallel to the [$\bar{1}$02] direction. Viewed down the screw axis, there is some overlap of the *B*, *C*, and *D* rings in a manner similar to the *B* form of cholesteryl iodide (Carlisle & Crowfoot, 1945). A search for intermolecular contacts found no close encounters of any kind. This appears to be one of the few reported cases of a steroid-type structure stabilized entirely by weak van der Waals forces.

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The Structure of Pyridinium 1-Amino-4-bromo-9,10-dioxoanthracene-2-sulphonate

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Abstract. $C_{19}H_{13}BrN_2O_5S$, triclinic, $P\bar{1}$, $a = 12·493$ (3), $b = 9·784$ (3), $c = 7·895$ (1) Å, $\alpha = 101·38$ (2), $\beta = 85·14$ (2), $\gamma = 108·61$ (2)°; $Z = 2$; $V = 895·94$ Å^3; $D_m = 1·692$, $D_x = 1·719$ g cm^{-3}; $\mu r = 0·6$. Diffractometer data collected with monochromatic Cu *Kα* radiation consisted of 1628 independent reflexions with $I > 1·96\sigma(I)$. The structure was solved by direct methods and refined by a full-matrix least-squares procedure to the final *R* value of 0·033. The anion (excluding the SO_3 group) and the cation are both planar. They are linked in pairs by N—H···O hydrogen bonds (2·759 Å).

Introduction. A crystal structure analysis of the title compound was undertaken to solve some problems connected with the synthesis of one of the anthrapyridone dyes. The crystals were supplied by Dr J. Omąkowska from the Institute of Chemistry, University of Łódź.

Crystals of the title compound were triclinic, equidimensional in habit and black in colour. A crystal with dimensions 0·2 × 0·2 × 0·3 mm was used for data collection. Intensities were collected on a Syntex $P2_1$ four-circle diffractometer equipped with a graphite monochromator using Cu $K\alpha$ radiation. 1722 independent reflexions were measured to the limit $2\theta = 100°$ by a θ–2θ scan. 1628 of them, with $I > 1·96\sigma(I)$, were classified as observed. Accurate cell constants were obtained by the least-squares method from diffractometer measurements.

No absorption correction was applied due to the low linear absorption coefficient for Cu $K\alpha$ radiation and the intensities were converted to $|F|^2$ in the usual way.

The statistics of the normalized structure factors (E) suggested a centrosymmetric space group, which was subsequently confirmed by the successful refinement of the structure in the space group $P\bar{1}$. The crystal structure was solved by a symbolic addition procedure. Phases for 159 reflexions with $E > 1·6$ were determined. These formed the basis for the determination of the phases of 400 reflexions with $E > 1·22$ used for computing E maps. The positions of all non-hydrogen atoms of the anion and the position of the nitrogen atom of the cation were located on one of these maps. The resulting structure factor calculation gave a value of $R = 0·28$.

Table 1. *Fractional coordinates and, for* H *atoms, isotropic thermal parameters, with standard deviations in parentheses*

	x	*y*	*z*	*B* (Å^2)
Br	0·62234 (5)	0·85200 (6)	0·52030 (8)	
C(1)	0·2577 (4)	0·5285 (5)	0·3860 (6)	
C(2)	0·2814 (4)	0·6578 (5)	0·5140 (6)	
C(3)	0·3894 (4)	0·7440 (5)	0·5453 (6)	
C(4)	0·4813 (4)	0·7070 (5)	0·4608 (6)	
C(5)	0·4639 (4)	0·5769 (5)	0·3429 (6)	
C(6)	0·5615 (4)	0·5270 (5)	0·2588 (6)	
C(7)	0·5370 (4)	0·3912 (5)	0·1286 (6)	
C(8)	0·6276 (5)	0·3461 (6)	0·0502 (7)	
C(9)	0·6051 (7)	0·2164 (8)	−0·0686 (8)	
C(10)	0·4968 (7)	0·1353 (7)	−0·1110 (8)	
C(11)	0·4061 (5)	0·1769 (6)	−0·0373 (7)	
C(12)	0·4276 (5)	0·3087 (5)	0·0858 (6)	
C(13)	0·3300 (5)	0·3536 (5)	0·1680 (6)	
C(14)	0·3510 (4)	0·4874 (5)	0·3005 (6)	
N(1)	0·1505 (4)	0·4485 (6)	0·3490 (8)	
S	0·1699 (1)	0·7103 (1)	0·6415 (2)	
O(1)	0·2342 (3)	0·2778 (4)	0·1231 (5)	
O(2)	0·6582 (3)	0·5937 (4)	0·3013 (5)	
O(3)	0·1188 (3)	0·5930 (4)	0·7390 (5)	
O(4)	0·2241 (3)	0·8483 (4)	0·7505 (5)	
O(5)	0·0916 (3)	0·7156 (5)	0·5208 (5)	
C(21)	−0·0370 (10)	0·2601 (13)	0·8580 (11)	
C(22)	−0·0825 (8)	0·1181 (17)	0·8773 (13)	
C(23)	−0·0300 (11)	0·0221 (9)	0·7974 (14)	
C(24)	0·0623 (9)	0·0663 (10)	0·7050 (13)	
C(25)	0·1044 (6)	0·2057 (10)	0·6909 (12)	
N(21)	0·0552 (6)	0·3001 (6)	0·7631 (9)	
H(N21)	0·093 (6)	0·404 (9)	0·744 (9)	5·70
H(C21)	−0·076 (7)	0·310 (9)	0·909 (11)	7·34
H(C22)	−0·150 (8)	0·088 (9)	0·929 (11)	8·00
H(C23)	−0·062 (7)	−0·071 (10)	0·798 (11)	7·31
H(C24)	0·087 (8)	0·011 (10)	0·667 (12)	6·80
H(C25)	0·159 (7)	0·234 (9)	0·642 (11)	5·94
H(C3)	0·404 (5)	0·822 (6)	0·622 (7)	2·49
H(C8)	0·704 (5)	0·401 (7)	0·095 (8)	3·74
H(C9)	0·656 (6)	0·193 (8)	−0·099 (7)	4·38
H(C10)	0·479 (6)	0·056 (8)	−0·185 (9)	4·77
H(C11)	0·321 (5)	0·125 (7)	−0·073 (8)	4·09
H1(N1)	0·131 (6)	0·383 (8)	0·273 (9)	4·70
H2(N1)	0·089 (6)	0·475 (7)	0·395 (9)	4·70

A three-dimensional Fourier map revealed the positions of the remaining non-hydrogen atoms. The R value was 0·19 at this stage.

The structure was refined by the full-matrix least-squares method. Cruickshank's weighting scheme, $w^{-1} = A + BF_o + CF_o^2$, was used with values of A, B, C calculated after each cycle by the method of Lee (1974). The first three cycles with isotropic thermal parameters reduced the R factor to 0·105 and the next three cycles with anisotropic thermal parameters gave $R = 0·044$.

Positions of 12 of the hydrogen atoms were derived from the difference electron density map. Their isotropic parameters were assumed to be the same as the average isotropic parameters of the atoms to which they were attached. The refinement of atomic parameters was continued with the temperature factors of hydrogen atoms treated isotropically but not being refined. After two cycles of refinement a new difference map was calculated which revealed the positions of the remaining hydrogen atoms.

The final R values after the next three cycles of refinement were $R = 0·033$ and $R_w = 0·036$. Final atomic parameters are listed in Table 1 with their standard deviations. Scattering factors were taken from *International Tables for X-ray Crystallography* (1962). All calculations were carried out on an ODRA 1305 computer with the local version of the NRC crystallographic system (Ahmed, Hall, Pippy & Huber, 1966), *ORFLS* (Busing, Martin & Levy, 1962) and a Fourier synthesis program written by M. Cygler, 1975.*

Discussion. The title compound exists in crystals in the form of a salt with a 1-amino-4-bromo-9,10-dioxoanthracene-2-sulphonate anion and a pyridinium cation.

The planarity of the anion carbon rings varies: the C ring is planar within the limits of experimental error while in the rings B and A the deviations from the best plane are more significant (Table 2). The angles between

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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 33581 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Deviations of atoms* (Å) *from the least-squares planes of the anion carbon rings*

x, y and z are fractional coordinates.

Ring *A*. $3{\cdot}2068x - 6{\cdot}8112y + 6{\cdot}6387z = -0{\cdot}1918$

C(1)	−0·019	C(4)	−0·021
C(2)	0·026	C(5)	0·027
C(3)	−0·007	C(14)	−0·007

Ring *B*. $2{\cdot}5454x - 6{\cdot}7845y + 6{\cdot}6503z = -0{\cdot}4336$

C(5)	−0·019	C(12)	−0·002
C(6)	0·008	C(13)	−0·008
C(7)	0·002	C(14)	0·019

Ring *C*. $2{\cdot}4081x - 6{\cdot}6588y + 6{\cdot}7213z = -0{\cdot}4499$

C(7)	0·003	C(10)	−0·001
C(8)	−0·005	C(11)	−0·001
C(9)	0·004	C(12)	0·000

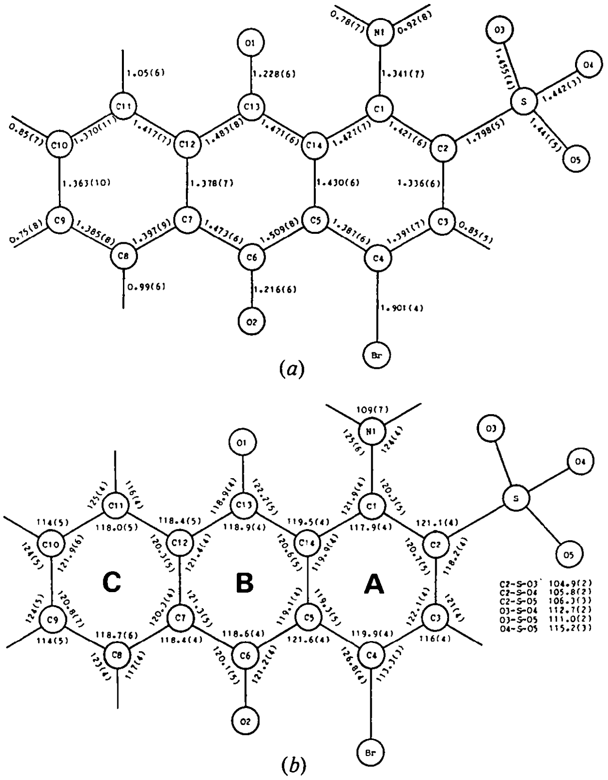

Fig. 1. Intramolecular geometry for the 1-amino-4-bromo-9,10-dioxoanthracene-2-sulphonate anion. (*a*) Interatomic distances (Å). (*b*) Bond angles (°).

the ring planes are: $\angle A,B = 3{\cdot}61$, $\angle B,C = 0{\cdot}76$, $\angle A,C = 4{\cdot}33°$. The degree of aromaticity of the rings diminishes in the order *C*, *B*, *A*. It was interesting to compare the bond lengths of the title compound (Fig. 1) with the bond lengths of anthraquinone (Lonsdale, Milledge & El Sayed, 1966) which is the analogous non-substituted compound. The greatest differences in the lengths of analogous bonds in both compounds involve C(2)–C(3) 1·336 (1·384 in anthraquinone), C(1)–C(2) 1·421 (1·382), C(1)–C(14) 1·427 (1·396), C(7)–C(12) 1·378 (1·412), C(6)–O(2) 1·216 (1·243 Å). The remaining bond lengths in the two compounds differ by less than 0·025 Å.

The anions form parallel layers 3·4 Å apart. The equation of the 'best' plane for the 14 carbon atoms of the anion is: $2{\cdot}7168x - 6{\cdot}7440y + 6{\cdot}6791z - 0{\cdot}3168 = 0$, where x, y and z are fractional coordinates. Atoms C(2) and C(4) deviate from this plane by 0·078 and −0·065 Å respectively. Deviations of the remaining atoms are smaller. The length of C(1)–N(1) indicates its partially double-bond character. An intramolecular hydrogen bond N(1)–H···O(1), where the distance O(1)···H is 2·05 Å and the N(1)–H–O(1) angle is

Table 3. *Deviations of atoms* (Å) *from the least-squares plane of the pyridinium cation*

C(21)	0·003	C(24)	−0·003
C(22)	0·003	C(25)	0·009
C(23)	−0·003	N(21)	−0·009

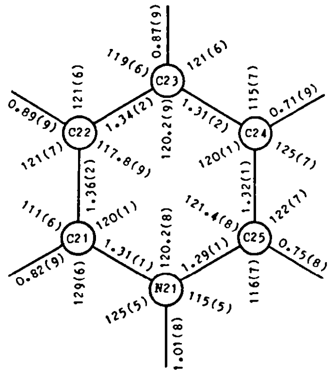

Fig. 2. Bond distances (Å) and angles (°) for the pyridinium cation.

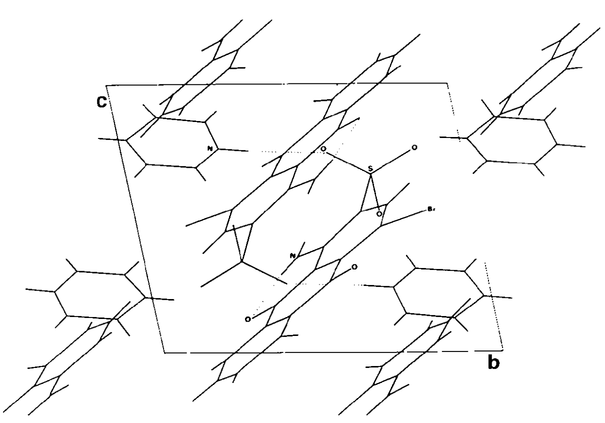

Fig. 3. Drawing of the structure viewed along *a*. Dotted lines represent hydrogen bonds.

equal to 126°, contributes to the formation of a quasi-aromatic ring. This indicates sp^2 configuration of the amine N atom.

The equation of the 'best' plane for the pyridinium cation is: $7{\cdot}2958x - 1{\cdot}4437y + 6{\cdot}6054z - 5{\cdot}0191 = 0$. The deviations of the cation non-hydrogen atoms from this plane are listed in Table 3. The anion and cation planes form a dihedral angle of 25·5°.

Bond lengths in the cation (Fig. 2) are somewhat shortened with respect to those described in the literature (Serewicz, Robertson & Meyers, 1965). This shortening is probably because the correction for the librational movement of the whole cation was not applied. The anion is connected to the cation by a strong hydrogen bond N(21)—H···O(3) where the distances N(21)···O(3) and H···O(3) are 2·759 and 1·79 Å respectively and the N(21)—H···O(3) angle is 161°. Remaining intermolecular distances are greater than the sum of their respective van der Waals radii. Weak intermolecular interactions explain the fragility and softness of the crystals.

The projection of the structure along the x axis is shown in Fig. 3.

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1:1 Complex of Indan-1,2,3-trione 2-(*N*-Benzoyl-*N*-phenylhydrazone) with Indan 1,2,3-trione 2-(*N*-Phenylhydrazone)

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Abstract. $C_{22}H_{14}N_2O_3.C_{15}H_{10}N_2O_2$, $M_r = 604{\cdot}25$, orthorhombic, space group $P2_12_12_1$, $a = 12{\cdot}701\ (4)$, $b = 6{\cdot}986\ (2)$, $c = 33{\cdot}314\ (9)$ Å, $V = 2955{\cdot}9 \times 10^{-24}$ cm^3, $Z = 4$, $D_c = 1{\cdot}358$ g cm^{-3}, $\mu(\text{Cu } K\alpha) = 7{\cdot}6$ cm^{-1}. The X-ray analysis ($R = 0{\cdot}053$ on 2490 reflections) shows that the complex is held together mainly by van der Waals interactions.

Introduction. In the course of studies (Puckett, Greensley, Paul & Curtin, 1977; Puckett, Paul & Curtin, 1976) on indan-1,2,3-trione 2-(*N*-benzoyl-*N*-phenylhydrazone) derivatives (1), an orange crystalline solid was obtained from indan-1,2,3-trione 2-(*N*-phenylhydrazone) (2) on treatment with benzoyl chloride. This solid was shown to be a 1:1 complex of (1) and (2) (Puckett, 1975). In order to provide more data for a systematic survey of the conformations of molecules related to (1), and to probe the types of intermolecular interactions in the complex, an X-ray structural analysis was undertaken. The cell data (given in the abstract) were obtained by a least-squares fit to the 2θ settings for ten reflections on a Picker FACS-1 diffractometer (Cu $K\alpha$, $\lambda = 1{\cdot}54178$ Å) at ambient room temperature. Intensity data were measured using a 2θ continuous scan method out to a maximum 2θ of 130° (Cu $K\alpha$). Out of 2927 independent reflections measured, a total of 2490 were considered significant at the $2\sigma(I)$ level; the values of $\sigma(I)$ were calculated from the equation of Corfield, Doedens & Ibers (1967). No corrections for extinction or absorption were applied. The structure was solved using the *MULTAN* direct-methods program (Germain, Main & Woolfson, 1971). All hydrogen atoms were clearly located from difference maps. The structure was refined by a full-matrix least-squares method with positional and anisotropic thermal parameters for all non-hydrogen atoms and positional and isotropic thermal parameters for the hydrogen atoms being varied. The largest peak on a