those previously reported for other highly skewed bis-exocyclic dienes, −49 and 46° for the two ring-*A* chair conformers of vitamin D_2 (Hull, Leban, Main, White & Woolfson, 1976), −53·6 and 55·2° in the corresponding α and β forms of vitamin D_3 (Trinh-Toan, DeLuca & Dahl, 1976), and 52·3° for a chiral 1,2-bis(alkylidene)diazacyclopentane derivative (Pasto & Scheidt, 1975). Steric repulsion between the C(9) methyl and C(11) methylene groups probably makes a significant contribution to the large twist of the diene system in photosantonin. The observed C(9)–C(11) contact distance is 3·320 (4) Å. The central bond, C(1)–C(2), of the diene is somewhat longer [1·505 (2) Å] than that in the two conformers of vitamin D_2 (1·44 and 1·47 Å) and vitamin D_3 [1·45 (1) and 1·45 (1) Å] perhaps indicating some lengthening of this bond in photosantonin due to ring strain as well as loss of conjugation.

The six-membered ring, which contains two trigonally hybridized C atoms, has a highly puckered chair conformation. In fact, the average endocyclic torsional bond angle is 56·7°, slightly greater than that (55·9°) in cyclohexane (Geise, Buys & Mijlhoff, 1971). The conformation of this ring is of particular interest since the diene chirality is reversed in the alternative boat or twist conformation. Although possibly present to some extent in solution, the boat conformation is probably destabilized by strong eclipsing between the H atoms of the C(5) and C(6) methylene groups.

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Diethylammonium 2,5-Dihydroxy-1,4-benzenedisulphonate

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Abstract. $2[NH_2(C_2H_5)_2]^+.C_6H_4O_8S_2^{2-}$, $M_r = 416{\cdot}5$, monoclinic, $P2_1/a$, $a = 11{\cdot}533$ (3), $b = 10{\cdot}544$ (2), $c = 8{\cdot}888$ (2) Å, $\beta = 114{\cdot}67$ (2)°, $V = 982{\cdot}2$ (7) Å^3, $Z = 2$, $D_c = 1{\cdot}41$ Mg m^{-3}. The structure was solved with the *MULTAN* system and refined by the full-matrix least-squares method. The final R value is 0·043 for 1122 observed reflections. The 2,5-dihydroxy-1,4-benzenedisulphonate ion is located on an inversion centre. The hydrogen bonds determine the packing of the ions.

Introduction. The title compound is a commercial pharmacological compound. In order to determine the geometry of the ions, the X-ray analysis was carried out.

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Colourless prismatic crystals were kindly supplied by a commercial laboratory. They were obtained by recrystallization from aqueous solution. A crystal 0·05 × 0·05 × 0·1 mm was selected for measurements on a Philips PW 1100 four-circle diffractometer. The unit cell was measured by centring 25 independent reflections and refining the orientation matrix and unit-cell parameters by least squares. Intensities were collected with Mo $K\alpha$ radiation, monochromatized by reflection from a graphite crystal. 1138 independent reflections were measured in the range $2\theta \leq 25°$; 1122 of these were considered as observed with $I > 2{\cdot}5\ \sigma(I)$.

The structure was solved with the *MULTAN* system of computer programs (Main, Woolfson, Hull, Lessinger, Germain & Declercq, 1980). An E map computed with the phases from the set with the largest combined figure of merit revealed peaks for all non-hydrogen atoms. The structure was isotropically and anisotropically refined by the least-squares method using the *SHELX* 76 program (Sheldrick, 1976). The function minimized was $w\|F_o| - |F_c\|^2$, where $w = [\sigma^2(F_o) + 0{\cdot}0003\ |F_o|^2]^{-1}$. The scattering factors were from *International Tables for X-ray Crystallography* (1974) and the anomalous-scattering factors were from Cromer & Liberman (1970). A difference synthesis at $R = 0{\cdot}062$ revealed the positions of the H atoms; these were refined isotropically, and the rest of the atoms anisotropically. The refinement was terminated at $R = 0{\cdot}043$ for all observed reflections.* The final atomic parameters are listed in Table 1. Figs. 1 and 2 show views of the 2,5-dihydroxy-1,4-benzenedisulphonate and diethylammonium ions, respectively, with the numbering of the atoms, and bond distances and angles between the non-hydrogen atoms.

Table 1. *Atomic parameters* ($\times 10^4$, *for* H $\times 10^3$) *and isotropic thermal parameters*

For non-hydrogen atoms $B_{eq} = \frac{8}{3}\pi^2 \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$.

	x	y	z	B_{eq}/B (Å^2)
C(1)	1208 (4)	4576 (5)	1049 (5)	2·5 (2)
C(2)	1088 (4)	5663 (4)	83 (6)	2·6 (2)
C(3)	−133 (4)	6061 (5)	−965 (6)	2·7 (2)
S(4)	2738 (1)	3987 (1)	2364 (2)	3·0 (1)
O(5)	2521 (3)	2976 (4)	3321 (5)	4·4 (2)
O(6)	3444 (3)	5024 (3)	3425 (4)	4·0 (2)
O(7)	3301 (3)	3561 (3)	1265 (5)	3·8 (2)
O(8)	2160 (3)	6267 (4)	205 (5)	3·7 (2)
C(9)	4466 (8)	8231 (9)	4596 (10)	6·4 (3)
C(10)	4815 (7)	7949 (6)	3203 (10)	4·8 (3)
N(11)	5333 (5)	6631 (4)	3335 (6)	3·7 (2)
C(12)	5806 (8)	6281 (7)	2084 (9)	4·7 (3)
C(13)	6343 (7)	4969 (7)	2383 (10)	5·5 (3)
H(C3)	−22 (5)	681 (5)	−158 (6)	5·7 (3)
H(O8)	197 (5)	679 (6)	44 (6)	5·7 (3)
H(C9)*A*	416 (6)	886 (6)	455 (8)	5·7 (3)
H(C9)*B*	382 (5)	763 (5)	449 (6)	5·7 (3)
H(C9)*C*	521 (6)	824 (5)	554 (7)	5·7 (3)
H(C10)*A*	412 (6)	801 (5)	222 (7)	5·7 (3)
H(C10)*B*	545 (5)	841 (5)	336 (6)	5·7 (3)
H(N11)*A*	589 (5)	659 (5)	425 (7)	5·7 (3)
H(N11)*B*	470 (5)	599 (5)	334 (6)	5·7 (3)
H(C12)*A*	516 (5)	642 (5)	118 (7)	5·7 (3)
H(C12)*B*	640 (6)	691 (5)	216 (6)	5·7 (3)
H(C13)*A*	655 (5)	480 (5)	152 (6)	5·7 (3)
H(C13)*B*	561 (5)	443 (5)	208 (6)	5·7 (3)
H(C13)*C*	702 (5)	486 (5)	364 (6)	5·7 (3)

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36335 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

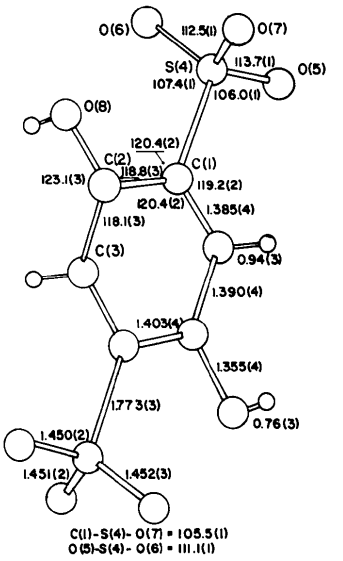

Fig. 1. View of the 2,5-dihydroxy-1,4-benzenedisulphonate ion, with the numbering of the atoms, bond distances (Å) and bond angles (°).

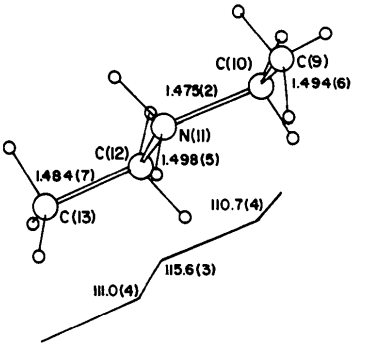

Fig. 2. View of the diethylammonium ion, with the numbering of the atoms, bond distances (Å) and bond angles (°) between non-hydrogen atoms.

Discussion. A comparative study (Table 2) shows that the geometry of the $C-SO_3^-$ group is similar to those obtained in other benzenesulphonate ions, differing clearly from those obtained in $C-SO_3-R$ groups.

The C–C [1·49 (1) Å] and C–N [1·49 (1) Å] bonds and the C–C–N [111 (1)°] and C–N–C [115·5 (3)°] angles in the diethylammonium ion are analogous to those obtained by Jérôme-Lerutte (1971) in diethylammonium tetracyanopalladate [1·47 (6), 1·49 (3) Å and 111 (2) and 114 (1)° respectively].

The packing of the ions and the hydrogen bonds are shown in Fig. 3 and Table 3. The diethylammonium ion is linked to two anions, one by a strong bond, and the second by two weak hydrogen bonds, while a strong hydrogen bond links two anions.

Table 2. *A comparative study of average geometrical values for the* $C-SO_3$ *group, the range of values also being specified*

	This work	(*A*, *B*)	(*C*, *D*)
C–S (Å)	1·773	1·77 1·764–1·774	1·74
S–O (Å)	1·451 1·450–1·452	1·46 1·453–1·466	1·41 (S=O) 1·54 (S–O) 1·40–1·42
C=S–O (°)	106·3 105·5–107·4	111·2 111·4–112·9	110 (S=O) 105 (S–O) 109–111 104–106
O–S–O (°)	112·4 111·1–113·7	112 111·9–112·7	113 (S=O) 107 (S–O) 106–120 101–113

(*A*) Hexaaquacopper(II) benzenesulphonate (Couldwell, Prout, Robey, Taylor & Rossotti, 1978). (*B*) Hexaaquacopper(II) *p*-toluenesulphonate (Couldwell, Prout, Robey, Taylor & Rossotti, 1978). (*C*) 2,4-Hexadiynylene bis(*p*-chlorobenzenesulphonate) (Mayerle & Clarke, 1978). (*D*) Dimethylammonium benzenesulphonate (Sukenik, Bonapace, Mandel, Lau, Wood & Bergman, 1977).

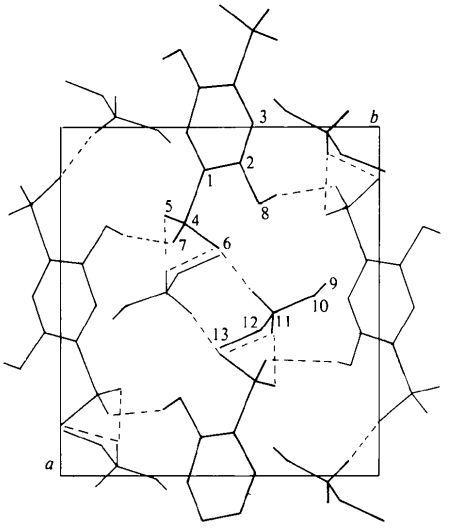

Fig. 3. Projection of the unit-cell contents down **c**.

Table 3. *Hydrogen-bond distances* (Å)

A–*B*···*C*	*AC*	*BC*
N(11)–H(N11)*A*···O(5)^{i}	2·999 (4)	2·22 (3)
N(11)–H(N11)*A*···O(6)^{i}	3·152 (4)	1·54 (3)
N(11)–H(N11)*B*···O(6)^{ii}	2·787 (4)	1·80 (3)
O(8)–H(O8)···O(7)^{iii}	2·694 (4)	1·98 (3)

Symmetry code: (i) $1-x, 1-y, 1-z$; (ii) x,y,z; (iii) $\frac{1}{2}+x, \frac{3}{2}-y, z$.

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