The bond lengths C1—C2, C3—C4, C9—C10 and C11—C12 are generally shorter than the other bonds, as can be expected from theorectical calculations (Mulliken, 1955; Hoffman, 1963). This has also been determined experimentally in the above-mentioned benzo[c]cinnolines.

As the most electronegative substituent, the F atom withdraws electrons from the γ ring and affects the bond lengths and angles of the ring, causing short bonds: C1—C2 = 1·355 (4), C2—C3 = 1·392 (5) and C3—C4 = 1·370 (4) Å; small angles: C2—C1—C14 = 117·7 (3), C2—C3—C4 = 118·3 (3), C3—C4—C5 = 119·3 (3) and C1—C14—C5 = 118·5 (3)°; and large angles: C1—C2—C3 = 124·9 (3) and C4—C5—C14 = 121·3 (3)°.

A general conclusion based on the above results is that the type and position of the substituent determines the shape of the benzo[c]cinnoline skeleton.

References

ASHBY, J., STYLES, J. A. & PATON, D. (1980). Carcinogenesis (NY), 1(1), 1–7.

DAVIES, K. (1983). SNOOPI. Program for drawing crystal and molecular diagrams. Univ. of Oxford, England.

ERLENMEYER, H. (1958). British Patent No. 794,775.

HOFFMAN, R. (1963). J. Chem. Phys. 39, 1397–1412.

HÖKELEK, T., KILIÇ, E. & TÜZÜN, C. (1991a). Acta Cryst. C47, 369–373.

HÖKELEK, T., KILIÇ, E. & TÜZÜN, C. (1991b). Acta Cryst. C47, 373–376.

HÖKELEK, T., WATKIN, D. J., KILIÇ, E. & TÜZÜN, C. (1990). Acta Cryst. C46, 1027–1029.

JAN, G. (1980). German Patent No. 2,939,259.

LEARY, J. A., LAFLEUR, A. L., LIBER, H. L. & BLEMANN, K. (1983). Anal. Chem. 55, 758–761.

MATTER, M. (1957). US Patent No. 2,778,829.

MEER, H. VAN DER (1972). Acta Cryst. B28, 367–370.

MULLIKEN, R. S. (1955). J. Chem. Phys. 23, 1833–1840.

NORTH, A. C. T., PHILLIPS, D. C. & MATHEWS, F. S. (1968). Acta Cryst. A24, 351–359.

SHELDRICK, G. M. (1976). SHELX76. Program for crystal structure determination. Univ. of Cambridge, England.

SHELDRICK, G. M. (1990). Acta Cryst. A46, 467–473.

WATKIN, D. J., CARRUTHERS, J. R. & BETTERIDGE, D. W. (1985). CRYSTALS. Program for crystal structure solution. Univ. of Oxford, England.

Structure of Two Complex Salts Formed by Diethylamine and Quinol

By M. M. MAHMOUD* AND S. C. WALLWORK

Department of Chemistry, University of Nottingham, Nottingham NG7 2RD, England

Abstract. (I), Bis(diethylammonium) 1,4-benzenediolate(2−)–1,4-benzenediol (1/1), $2C_4H_{12}N^+.C_6H_4O_2^{2-}.C_6H_6O_2$, 2DEAH$^+$.Q^{2-}.Q (DEA = diethylamine, Q = quinol), M_r = 366·5, monoclinic, C2/c, a = 12·55 (1), b = 11·87 (1), c = 16·69 (1) Å, β = 119·15 (8)°, V = 2171 Å^3, Z = 4, D_x = 1·12 Mg m^{-3}, Mo $K\alpha$ radiation, λ = 0·71069 Å, μ = 0·084 mm^{-1}, $F(000)$ = 800, room temperature, R = 0·148, wR = 0·207 for 513 reflections [$I > 2·5\sigma(I)$]. (II), Diethylammonium 1,4-benzenediolate(1−)–1,4-benzenediol (1/1), $C_4H_{12}N^+.C_6H_5O_2^-.C_6H_6O_2$, DEAH$^+$.Q$^-$.Q, M_r = 293·36, triclinic, P$\bar{1}$, a = 8·77 (1), b = 7·09 (1), c = 14·32 (1) Å, α = 91·0 (1), β = 101·2 (2), γ = 114·2 (1)°, V = 792 Å^3, Z = 2, D_m = 1·20 (3), D_x = 1·23 Mg m^{-3}, Mo $K\alpha$ radiation, λ = 0·71069 Å, μ = 0·095 mm^{-1}, $F(000)$ = 316, room temperature, R = 0·076, wR = 0·095 for 2121 reflections [$I > 3\sigma(I)$]. Both structures are extensively hydrogen bonded. (I) has chains of Q, Q^{2-}, Q', DEAH$^+$, Q^{2-}, DEAH$^+$, Q, in which Q^{2-} ions link pairs of successive chains in the b direction and Q molecules link chains in the c direction. (II) has two independent Q molecules, a Q$^-$ ion, and DEAH$^+$ ions hydrogen bonded together in a three-dimensional manner.

Introduction. As part of a series of studies of complexes of quinol (1,4-dihydroxybenzene) with nitrogen bases (cf. Mahmoud & Wallwork, 1979), crystals were prepared by adding diethylamine to solutions of quinol in ether. In different preparations, two types of crystal were obtained, the first (I) having a 1:1

* Present address: Department of Physics, Al-Mustansiriyah University, Baghdad, Iraq.

composition Q.DEA and the other (II) a 2:1 composition, 2Q.DEA. The crystal structures of both have been determined and are reported here. The results show that both are complex salts, formed by transfer of either one or two protons from quinol to diethylamine, but with neutral quinol also included in the formulae. Both salts decomposed readily in air by loss of diethylamine. For the X-ray study, they were protected with a coating of the cellulose adhesive Durofix. In spite of this, the 1:1 compound gave poor, sparse data which only refined to $R = 0\cdot148$. The 2:1 compound gave better data, refining to $R = 0\cdot076$. However, it suffered from disorder of the carbon chains in the $DEAH^+$ ions.

Experimental. D_m measured by flotation in inhibisol/xylene mixtures for (II), cell parameters for (I) from 18 reflections $(10 < \theta < 13°)$ and for (II) from 23 reflections $(13 < \theta < 15°)$ Hilger & Watts computer-controlled four-circle diffractometer, 513 unique I for (I) and 2121 for (II), Mo $K\alpha$, $\theta/2\theta$ scan, scintillation counter, $\theta_{max} = 20°$ (I) or $27°$ (II), no absorption corrections (small crystals, maximum dimensions 0·5 mm), two standard reflections for (I) and three for (II), intensity variation 12% for (I) and 5% for (II). hkl: (I) h -12 to 10, k 0 to 11, l 0 to 16; (II) h -11 to 10, k -9 to 9, l 0 to 17. Three-dimensional Patterson maps and difference syntheses for (I), direct methods ($MULTAN$; Main, Lessinger, Woolfson, Germain & Declercq, 1977) for (II); least-squares refinement with $CRYSTALS$ (Carruthers & Rollett, 1975) program: for (I) non-H atoms only, isotropic, H positions calculated and with fixed $U = 0\cdot05$ Å^2, weights from Chebychev polynomial; for (II), non-H atoms of Q anisotropic, and of $DEAH^+$ isotropic with occupation parameters refined in later stages to $\sim0\cdot4$ for C(13) to C(16) and $\sim0\cdot6$ for alternative positions C(17) to C(20), H positions calculated and isotropic U's refined, weights $1/w = 1 + [(|F_o| - 20)/42]^2$, $|F_o|$ 4·04 times absolute scale. Maximum and r.m.s. shift/e.s.d. for atomic parameters in final cycles 0·18 and 0·08 for (I), 0·55 and 0·24 for (II). Maximum heights in difference Fourier synthesis were 0·55 for (I) and 0·48 e Å^{-3} for (II). Scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV). Atomic coordinates and isotropic thermal parameters for non-H atoms are in Tables 1 and 2.* Fig. 1 shows the structure of $2DEAH^+.Q^{2-}.Q$ projected along the b axis, and Fig. 2 the structure of $DEAH^+.Q^-.Q$ projected along the b axis.

Table 1. *Atomic coordinates and isotropic thermal parameters* (Å^2) *for* (I)

|	x	y	z	U_{iso}
C(1)	0·0000	-0·001 (3)	0·2500	0·067 (9)
C(2)	0·035 (2)	0·057 (2)	0·329 (1)	0·056 (6)
C(3)	0·036 (2)	0·179 (2)	0·330 (1)	0·058 (6)
C(4)	0·0000	0·234 (2)	0·2500	0·046 (7)
C(5)	0·057 (2)	0·459 (1)	0·087 (1)	0·045 (5)
C(6)	0·125 (2)	0·492 (2)	0·049 (1)	0·048 (5)
C(7)	0·065 (2)	0·530 (1)	-0·044 (1)	0·049 (5)
C(8)	0·298 (2)	0·173 (2)	0·199 (2)	0·110 (9)
C(9)	0·256 (3)	0·191 (3)	0·107 (2)	0·13 (1)
C(10)	0·349 (3)	0·259 (3)	0·350 (2)	0·11 (1)
C(11)	0·353 (3)	0·358 (3)	0·399 (2)	0·13 (1)
O(1)	0·0000	-0·118 (2)	0·2500	0·089 (7)
O(2)	0·0000	0·349 (1)	0·2500	0·060 (5)
O(3)	0·116 (1)	0·424 (1)	0·180 (1)	0·048 (4)
N(1)	0·319 (2)	0·279 (1)	0·253 (1)	0·073 (5)

Table 2. *Atomic coordinates, isotropic* [N(1) *to* C(20)] *or equivalent isotropic* [C(1) *to* O(4)] *thermal parameters* (Å^2) *and occupation factors for* (II)

	x	y	z	U_{eq} or U_{iso}	Occ.
C(1)	0·4570 (4)	0·5279 (5)	0·7433 (2)	0·035 (2)	1·0
C(2)	0·4775 (5)	0·6840 (5)	0·6817 (3)	0·043 (2)	1·0
C(3)	0·4467 (5)	0·8541 (5)	0·7032 (3)	0·045 (2)	1·0
C(4)	0·3981 (4)	0·8763 (5)	0·7870 (3)	0·041 (2)	1·0
C(5)	0·3774 (5)	0·7235 (6)	0·8484 (3)	0·048 (2)	1·0
C(6)	0·4056 (5)	0·5500 (5)	0·8266 (3)	0·046 (2)	1·0
C(7)	0·1769 (5)	0·1088 (5)	0·5208 (3)	0·045 (2)	1·0
C(8)	0·0876 (5)	0·0229 (6)	0·4283 (3)	0·050 (2)	1·0
C(9)	0·0874 (5)	0·0845 (6)	0·5923 (3)	0·049 (2)	1·0
C(10)	0·0210 (4)	0·9615 (5)	0·9096 (2)	0·041 (2)	1·0
C(11)	0·1624 (4)	1·0647 (5)	0·9837 (3)	0·042 (2)	1·0
C(12)	-0·1405 (4)	0·8977 (5)	0·9260 (3)	0·042 (2)	1·0
O(1)	0·4881 (3)	0·3618 (3)	0·7216 (2)	0·042 (2)	1·0
O(2)	0·3647 (3)	1·0422 (4)	0·8114 (2)	0·055 (2)	1·0
O(3)	0·3513 (3)	0·2156 (4)	0·5373 (2)	0·055 (2)	1·0
O(4)	0·0354 (3)	0·9181 (4)	0·8187 (2)	0·052 (2)	1·0
N(1)	0·8203 (5)	0·4819 (6)	0·7290 (3)	0·058 (1)	1·0
C(13)	0·885 (2)	0·354 (2)	0·771 (2)	0·043 (6)	0·34 (4)
C(14)	0·885 (2)	0·394 (2)	0·875 (1)	0·060 (5)	0·43 (3)
C(15)	0·877 (2)	0·467 (2)	0·650 (1)	0·062 (5)	0·43 (3)
C(16)	0·746 (2)	0·340 (3)	0·572 (1)	0·064 (6)	0·34 (3)
C(17)	0·869 (1)	0·351 (1)	0·809 (2)	0·067 (4)	0·63 (4)
C(18)	0·813 (2)	0·373 (2)	0·903 (1)	0·075 (4)	0·55 (3)
C(19)	0·792 (2)	0·442 (2)	0·606 (1)	0·081 (5)	0·58 (4)
C(20)	0·974 (2)	0·518 (2)	0·591 (1)	0·148 (8)	0·63 (2)

Discussion. (I) contains two crystallographically independent quinol species, A lying across centres of symmetry approximately parallel to the (010) plane and B on twofold axes of symmetry at $0,y,\frac{1}{4}$ and related positions, with the ring centre at $y = 0\cdot231$. The molecular planes of A and B are almost perpendicular to each other but the hydroxyl groups O(3)H and O(3')H of A are strongly hydrogen bonded to O(2) of B with O$\cdots$O distances 2·45 (1) Å and C(5)O(3)O(2) angles 121 (1)°. O(3) also receives a hydrogen bond from N(1) of diethylamine, of length 2·81 (2) Å with a C(5)O(3)N(1) angle of 123 (1)°. N(1) is also strongly hydrogen bonded to O(1) of quinol B, with N(1)$\cdots$O(1) = 2·60 (2) Å and C(1)O(1)N(1) = 118 (1)°. Since B lies on a twofold axis of symmetry, the short hydrogen bonds O(3)$\cdots$O(2) and N(1)$\cdots$O(1) are both duplicated by

this symmetry. Their lengths show that O(1) and O(2) are probably both negatively charged, whereas the longer O(3)···N(1) suggests that O(3) is neutral. Since there are four quinols of type A, four of type B and eight diethylamines in the unit cell, these indications of charge are consistent with the transfer of protons from both O(1) and O(2) to diethylamine molecules, giving the chemical composition $2DEAH^+.Q^{2-}.Q$. This scheme also avoids the complication of duplication, by the twofold axis, of any H atoms attached to O(1) and O(2).

The hydrogen bonds form zigzag chains parallel to the a axis, linking atoms in the sequence

$$O(1')^-..HN(1)^+H..O(3)H..O(2)^-..HO(3')..HN(1')^+H..O(1')^-.$$
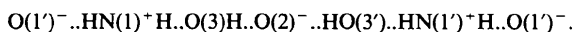
There are four such chains in the unit cell, with approximate y,z coordinates $\frac{1}{3},\frac{1}{4}; \frac{5}{6},\frac{1}{4}; \frac{1}{6},\frac{3}{4}; \frac{2}{3},\frac{3}{4}$. Pairs of chains at $y \sim \frac{1}{6}$ and $\frac{5}{6}$ or at $\frac{1}{3}$ and $\frac{2}{3}$ are spanned by quinols of type A, whereas pairs with the same z coordinate are spanned by quinols of type B. The resulting structure is a very open one, of calculated density $1.12 \, \text{Mg m}^{-3}$, even more open than $DEAH^+.Q^-.Q$, discussed below. A difference synthesis towards the end of the refinement showed no evidence for trapped or hydrogen-bonded solvent or guest molecules (maximum residual electron density

$0.55 \, \text{e} \, \text{Å}^{-3}$), though this possibility cannot be ruled out in view of the poor quality of the data.

The approximate nature of the structural results for (I) also precludes any discussion of the molecular geometry. The dimensions are all satisfactory, within the limits of error, apart from the C—C bond lengths in $DEAH^+$, which are clearly foreshortened by oscillation of C—C about the C—N bonds. [Quinol distances in Å: type B, C(1)—O(1) = 1.39 (3), C(1)—C(2) = 1.36 (2), C(2)—C(3) = 1.44 (3), C(3)—C(4) = 1.35 (2), C(4)—O(2) = 1.36 (3); type A, C(5)—O(3) = 1.41 (2), C(5)—C(6) = 1.34 (2), C(6)—C(7) = 1.44(3), C(7)—C(5') = 1.34 (2); angles in both quinols range between 118 (2) and 123 (2)°. Bond lengths and angles for diethylamine: see Table 3.] Certainly, Q and Q^{2-} cannot be distinguished in this structure on the basis of molecular dimensions, though the differences are, in fact, in the expected directions (see later).

In (II) there are three crystallographically different quinol species – type C lying across a centre of symmetry at the origin of the cell, type D lying across a centre of symmetry half way along the c axis, and type E in a general position with its centre at $x = 0.43$, $y = 0.70$, $z = 0.77$. Although positions of the H atoms have not been refined, the atoms to
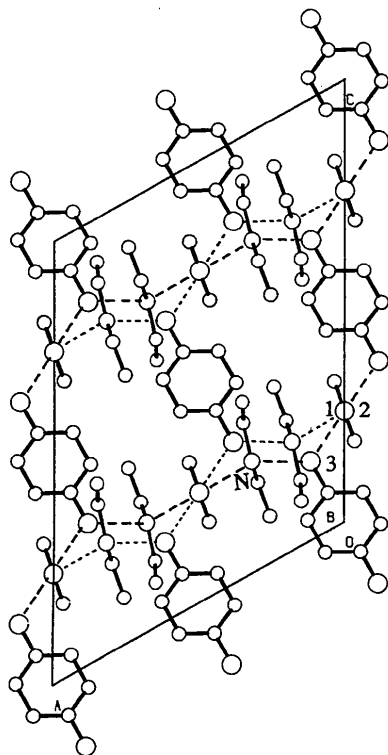

Fig. 1 The structure of $2DEAH^+.Q^{2-}.Q$ projected along **b**. ——— represents hydrogen-bond chains at $y \sim \frac{1}{3}$, $z \sim \frac{1}{4}$ and $y \sim \frac{2}{3}$, $z \sim \frac{3}{4}$, --- represents hydrogen-bond chains at $y \sim \frac{5}{6}$, $z \sim \frac{1}{4}$ and $y \sim \frac{1}{6}$, $z \sim \frac{3}{4}$. Numbers refer to O atoms.
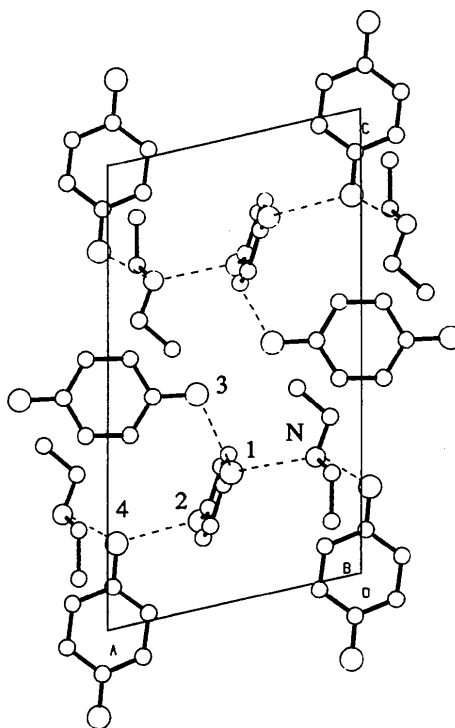

Fig. 2. The structure of $DEAH^+.Q^-.Q$ projected along **b**. ——— represents hydrogen bonds. That linking O(1) and O(2) approximately in the b direction, and the alternative positions for the ethyl chains of $DEAH^+$ are omitted for clarity. Numbers refer to O atoms.

Table 3. *Molecular geometry* (Å, °) *of* DEAH$^+$ *ions and hydrogen bonds*

DEAH$^+$ in (I)		DEAH$^+$ in (II)		(DEAH$^+$)' in (II)	
N(1)—C(8)	1·50 (3)	N(1)—C(13)	1·35 (1)	N(1)—C(17)	1·59 (2)
C(8)—C(9)	1·37 (4)	C(13)—C(14)	1·50 (3)	C(17)—C(18)	1·55 (3)
N(1)—C(10)	1·49 (3)	N(1)—C(15)	1·34 (1)	N(1)—C(19)	1·73 (2)
C(10)—C(11)	1·41 (4)	C(15)—C(16)	1·41 (3)	C(19)—C(20)	1·52 (2)
C(8)N(1)C(10)	114 (2)	C(13)N(1)C(15)	92 (1)	C(17)N(1)C(19)	129 (1)
N(1)C(8)C(9)	114 (3)	N(1)C(13)C(14)	102 (1)	N(1)C(17)C(18)	113 (1)
N(1)C(10)C(11)	114 (3)	N(1)C(15)C(16)	113 (1)	N(1)C(19)C(20)	104 (1)

Hydrogen bonds in (I)		Hydrogen bonds in (II)		Hydrogen bonds in (II)	
O(1)—N(1)	2·60 (2)	O(1)—N(1)	2·660 (4)	C(1)O(1)N(1)	110·2 (1)
O(3)—N(1)	2·81 (1)	O(4)—N(1)	2·985 (4)	C(1)O(1)O(2)	117·1 (2)
O(2)—O(3)	2·45 (1)	O(1)—O(2)	2·566 (3)	C(1)O(1)O(3)	110·3 (2)
O(1)N(1)O(3)	109 (1)	O(1)—O(3)	2·672 (4)	O(1)O(2)O(4)	115·3 (1)
C(8)N(1)O(1)	106 (1)	O(2)—O(4)	2·677 (4)	C(4)O(2)O(1)	115·4 (2)
C(8)N(1)O(3)	113 (1)			C(4)O(2)O(4)	111·3 (2)
C(10)N(1)O(1)	110 (1)	O(1)N(1)O(4)	113·2 (1)	C(7)O(3)O(1)	111·7 (2)
C(10)N(1)O(3)	105 (2)	C(13)N(1)O(1)	114·3 (8)	C(17)N(1)O(1)	101·9 (5)
N(1)O(1)N(1')	124 (1)	C(13)N(1)O(4)	109·4 (6)	C(17)N(1)O(4)	102·0 (5)
C(1)O(1)N(1)	118 (1)	C(15)N(1)O(1)	121·0 (7)	C(19)N(1)O(1)	93·8 (5)
O(3)O(2)O(3')	137 (1)	C(15)N(1)O(4)	105·0 (6)	C(19)N(1)O(4)	116·0 (5)
C(4)O(2)O(3)	111 (1)	N(1)O(1)O(2)	112·2 (1)	N(1)O(4)O(2)	112·0 (1)
N(1)O(3)O(2)	101 (1)	N(1)O(1)O(3)	101·8 (1)	C(10)O(4)N(1)	115·9 (2)
C(5)O(3)N(1)	123 (1)	O(2)O(1)O(3)	104·0 (1)	C(10)O(4)O(2)	110·7 (2)
C(5)O(3)O(2)	121 (1)				

which they are attached, and their electrical charge may be deduced unambiguously (partly from a difference synthesis but confirmed by the molecular geometries and hydrogen-bond lengths; see Table 3). Thus, quinols of types C and D are neutral species, whereas type E has lost a proton from O(1) to become a singly negatively charged species. Transfer of this proton to N(1) converts diethylamine to a positively charged ion. Each unit cell contains two DEAH$^+$ ions, and a quinol complement of 1C, 1D and 2E, giving as the overall chemical composition DEAH$^+$.Q$^-$.Q.

The structure may be described in terms of chains of hydrogen-bonded Q$^-$ ions (type E), extended along the b direction, and strings of quinol molecules of types C and D arranged alternately along the c axis, with their molecular planes roughly perpendicular to the b axis and molecular O—O axis of C roughly perpendicular to that of D, so that C and D are not directly hydrogen bonded. The Q$^-$ ions are linked into chains by strong OH···O$^-$ hydrogen bonds of length 2·566 (3) Å; the neutral quinol molecules of type C are hydrogen bonded both to the Q$^-$ chains and to the DEAH$^+$ ions, as shown in Fig. 2, whereas those of type D are hydrogen bonded only to Q$^-$. The DEAH$^+$ ions are also hydrogen bonded to the Q$^-$ chains, so there is a three-dimensional network of strong directional hydrogen bonds giving rise to an open structure of calculated density 1·23 Mg m^{-3}. [Compare the densities of the three crystalline forms of quinol: $\alpha = 1·36$ Mg m^{-3} (Wallwork & Powell, 1980), the empty clathrate cagework, $\beta = 1·22$ Mg m^{-3} (Powell, 1948; Powell & Riesz, 1948), and $\gamma = 1·38$ Mg m^{-3} (Maartmann-Moe, 1966).] No doubt the disorder of the hydrocarbon chains of the DEAH$^+$ ions results from this openness. Again, a maximum residual electron density of 0·48 e Å^{-3} found in the search for H atoms,

suggested that there were no unsuspected molecules trapped in the structure.

It is interesting that only two of the three crystallographically independent quinol OH groups [O(2) and O(4)] receive a hydrogen bond as well as donating one, whereas the negatively charged O(1) receives three hydrogen bonds and is in a roughly tetrahedral environment, suggesting a tendency towards sp^3 hybridization. The sp^3 hybridized N atom is also in a
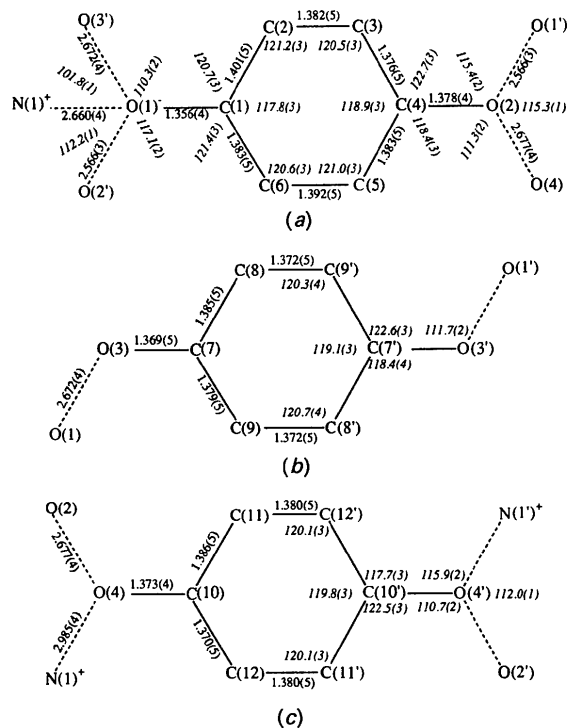

Fig. 3. Dimensions of quinol molecules and hydrogen bonds in DEAH$^+$.Q$^-$.Q: (*a*) Q$^-$ of type E, (*b*) Q of type D, (*c*) Q of type C. Distances are given in Å and angles in °.

tetrahedral environment, donating two hydrogen bonds as an $>NH_2^+$ group. All three hydrogen bonds involving the O^- atom are short: 2·566 (3) to O(2), 2·660 (4) to N(1) and 2·672 (4) Å to O(3). These distances, and the virtual equality of the CCO(1) angles [120·7 (3) and 121·4 (3)°], confirm the charged nature and lack of a proton on this atom. For each quinol OH group, the CCO angles are unequal, on account of the repulsion between the hydroxyl H atom and the CH group in the adjacent *ortho* position (see Fig. 3).

The neutral quinol molecules in (II) do not differ significantly in dimensions from each other, or from previously determined quinol dimensions (Wallwork & Powell, 1980, and references therein), or even from those of the Q^- ion. However, there is a tendency for $C-O^-$ to be shorter than $C-OH$, for the $C-C$ bonds adjacent to $C-O^-$ to be longer, and for the ring CCC angle at this position to be slightly smaller. These changes are in the same direction, but smaller, than those noted (Hough, 1976) for nitrophenolate ions compared with nitrophenols.

References

CARRUTHERS, J. R. & ROLLETT, J. S. (1975). Private communication.
HOUGH, E. (1976). *Acta Cryst.* B32, 1154–1162.
MAARTMANN-MOE, K. (1966). *Acta Cryst.* 21, 979–982.
MAHMOUD, M. M. & WALLWORK, S. C. (1979). *Acta Cryst.* B35, 2370–2374.
MAIN, P., LESSINGER, L., WOOLFSON, M. M., GERMAIN, G. & DECLERCQ, J.-P. (1977). *MULTAN77. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.
POWELL, H. M. (1948). *J. Chem. Soc.* pp. 61–73.
POWELL, H. M. & RIESZ, P. (1948). *Nature (London)*, 161, 52–53.
WALLWORK, S. C. & POWELL, H. M. (1980). *J. Chem. Soc. Perkin Trans.* 2, pp. 641–646.

Structure of Cheloviolene A from the Sponge *Chelonaplysilla violacea*
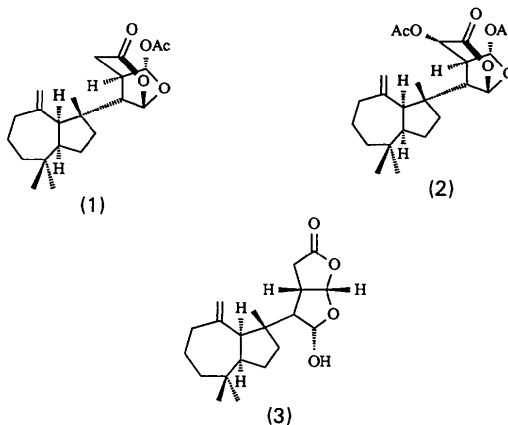
BY J. S. BUCKLETON, R. C. CAMBIE AND G. R. CLARK*

Department of Chemistry, The University of Auckland, Auckland, New Zealand

Abstract. 6-(Decahydro-1,4,4-trimethyl-8-methylene-1-azulenyl)-7-hydroxy-2,8-dioxabicyclo[3.3.0]octan-3-one, $C_{20}H_{30}O_4$, $M_r = 334\cdot46$, orthorhombic, $P2_12_12_1$, $a = 8\cdot614$ (3), $b = 13\cdot441$ (1), $c = 15\cdot948$ (2) Å, $V = 1846\cdot5$ (9) Å³, $Z = 4$, $D_m = 1\cdot17$ (1), $D_x = 1\cdot20$ g cm⁻³, Mo $K\alpha$, $\lambda = 0\cdot71069$ Å, $\mu = 0\cdot88$ cm⁻¹, $F(000) = 712$, $T = 292\cdot5$ (5) K, $R = 0\cdot047$ for 1230 observed reflections. The X-ray analysis confirms the overall structure of cheloviolene A and establishes the relative stereochemistries at the seven asymmetric centres.

Introduction. The Dendroceratid sponge *Chelonaplysilla violacea* has yielded a series of related diterpenoid compounds, including aplyviolene (1) for which we have reported a structure determined by X-ray analysis (Buckleton, Bergquist, Cambie, Clark, Karuso & Rickard, 1986). Hambley, Poiner & Taylor (1986) have also reported the structure of aplyviolene and of aplyviolacene (2) obtained from

the same source. The structures of the remaining diterpenoids have been determined from a detailed examination of ^1H and ^{13}C NMR spectra (Taylor *et al.*, unpublished). We record here confirmation of the structure of one of these compounds, cheloviolene A (3), m.p. 434–436 K, $[\alpha]_D^{17°C} = +6°$ (*c* 1·0*M*, CHCl₃), λ_{max} 1785 (γ-lactone), 1630 cm⁻¹ (C=C).

(1)

(2)

(3)