# Crystal structure of (−)-$\Delta^{16(17)}$-dehydrolupaninium perchlorate from sealed-tube and synchrotron X-ray diffraction data

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## Abstract

Two independent X-ray structure determinations on the same crystal sample of the lupine alkaloid (—)-$\Delta^{16(17)}$-dehydrolupaninium perchlorate, $[C_{15}H_{23}N_2O]^+ \cdot ClO_4^-$, were carried out, one using a laboratory 4-circle diffractometer equipped with a sealed X-ray tube, and the other, a 6-circle diffractometer installed at the Swiss-Norwegian beam line at the ESRF in Grenoble. The same crystal sample was used but different setting angles for positioning reflections were applied. The measurements provide the most precise dimensions obtained so far for the immonium group. Both determinations reveal consistent details of the dehydrolupaninium cation structure and of $ClO_4^-$ anion distortions. The cation rings A, B, C and D assume distorted half-chair, chair, distorted sofa, and chair conformations, respectively. No short electrostatic interactions between the immonium group and the perchlorate anion are observed, in contrast to all previous studies. © 1998 Elsevier Science B.V. All rights reserved.

*Keywords:* Crystal structure; (—)-$\Delta^{16(17)}$-Dehydrolupaninium perchlorate; Sealed-tube and synchrotron X-ray diffraction data

## 1. Introduction

Lupine alkaloids have been intensively studied for decades [1, 2], mainly for their biological, biochemical and agricultural significance. Sparteines are the main representatives of these alkaloids; they are built of two quinolizidine moieties and exhibit a variety of stereochemical properties [3]. Over one hundred crystal structures of sparteine derivatives have been determined [4, 5], among them a series of immonium salts of sparteine which are substrates in stereospecific syntheses and transformations of cyclic amines [1, 2, 6] and in the biosyntheses of alkaloids [7]. The

immonium salts of sparteine investigated with X-rays include: $\Delta^{1(6)}$-dehydro-17-oxosparteinium perchlorate [8], $\Delta^{1(6)}$-dehydrosparteinium perchlorate [9] and diperchlorate [10], $\Delta^{1(6),11(16)}$-didehydrosparteinium diperchlorate [11], $\Delta^{11(16)}$-dehydrolupaninium perchlorate monohydrate [12], $\Delta^{1(2)}$-dehydro-2-methylsparteinium diperchlorate monohydrate [13], and $\Delta^{1(2)}$-dehydro-2-phenylsparteinium diperchlorate [14]. In the cations of these salts the immonium bond was located either between the fused piperidinium rings A and B, or between rings C and D, or in the outer ring A. All these structures exhibited some kind of disorder of the bulky perchlorate anions and of the labile terminal atoms of the outer piperidinium rings [15]. In the presently investigated structure of $\Delta^{16(17)}$-dehydrolupaninium perchlorate (denoted **I**), the immonium bond is located in the

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Table 1
Crystal data and structure refinement details for two structural determinations of (−)-$\Delta^{16(17)}$-dehydrolupaninium perchlorate

| Empirical formula | | $[C_{15}H_{23}N_{20}]^+ \cdot ClO_4^-$ | |
|---|---|---|---|
| Formula weight | | 346.80 | |
| Temperature (K) | | 293(2) | |
| Crystal system | | Monoclinic | |
| Space group | | $P2_1$ | |
| Z | | 2 | |
| F(000) (e) | | 368 | |
| Crystal size (mm) | | 0.2 × 0.2 × 03 | |
| Refinement method | | Full-matrix least-squares on $F^2$ | |
| X-ray source monochromator | | Sealed X-ray tube graphite | Synchrotron/Si |
| Diffractometer | | KM-4 | KM-6 CH |
| Setting angles | | κ-natural [16] | Bisecting |
| Monochromator | | Pyrolitic graphite | Double Si crystal |
| Beam divergence (deg) | | About 0.3 | 0.01 |
| Wavelength (Å) | | 0.71069 | 0.65522 |
| Unit cell dimensions | $a$ (Å) | 7.582(2) | 7.5919(10) |
| | $b$ (Å) | 10.479(2) | 10.4741(9) |
| | $c$ (Å) | 10.813(2) | 10.8041(11) |
| | $\beta$ (°) | 109.72(3) | 109.685(12) |
| | $V$ (Å$^3$) | 808.7(3) | 808.7(2) |
| Density (calculated) (g/cm$^{-3}$) | | 1.424 | 1.424 |
| Absorption coefficient (mm$^{-1}$) | | 0.264 | 0.264 |
| $\Theta$ range for data (°) | | 2.00 ≤ 26.06 | 2.57 ≤ 25.06 |
| Index ranges for h, k, l | | 0/9, −12/12, −13/13 | 0/9, −13/13, −13/13 |
| Reflections collected | | 3212 | 3818 |
| Independent reflections | | 3196 ($R_{int}$ = 0.0089) | 3561 ($R_{int}$ = 0.0169) |
| Data/restraints/parameters | | 3196/1/209 | 3548/1/301 |
| Goodness-of-fit on F$^2$ | | 1.089 | 1.095 |
| Final R1 and wR2 indices | I > 2σ$_I$ | 0.0349, 0.0887 | 0.0372, 0.1016 |
| | All data | 0.0469, 0.0942 | 0.0411, 0.1455 |
| Absolute structure parameter | | −0.09(9) | 0.05(6) |
| Extinction coefficient | | 0.027(4) | 0.26(3) |
| Largest difference Fourier map peak and hole (e Å$^{-3}$) | | 0.213 and −0.201 | 0.340 and −0.215 |

inner ring C of the cation. The main purpose of this study was to provide structural information on the conformation of the cation and on its interionic interactions, to determine precise dimensions of the immonium group, and to compare these data with those from structures investigated previously. Moreover, the diffraction measurements were independently carried out using a laboratory 4-circle diffractometer equipped with a sealed X-ray tube and a graphite monochromator, and a 6-circle diffractometer installed at the BM-1 synchrotron beam, monochromated with double Si crystals, of the European synchrotron radiation facility (ESRF) in Grenoble. A comparison of the results of these experiments is presented.

## 2. Experimental

The crystals of **I** were obtained by slow evaporation from aqueous solution; they were colourless prisms with well-developed faces. The same crystal sample was used for both laboratory and synchrotron measurements as we were interested in testing the performance of the new six-circle KM-6CH diffractometer and in comparing the experimental techniques. To obtain more reliable structural results free of systematic errors related to the crystal shape, different modes of diffractometers operation were used: the bisecting mode for KM-6CH and natural κ-mode of diffractometer setting angles for KM-4 [16]. The details of the measurements are listed in Table 1.

Table 2

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($A^2 \times 10^3$) for **I**. Anisotropic thermal parameters ($A^2 \times 10^3$) for non-hydrogen, and isotropic thermperature factors for H-atoms. The temperature factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11} + \ldots + 2hka^*b^*U_{12}]$

| | $x$ | $y$ | $z$ | $U_{11}/U_{iso}$ | $U_{22}$ | $U_{33}$ | $U_{23}$ | $U_{13}$ | $U12$ |
|---|---|---|---|---|---|---|---|---|---|
| Cl | 7360(1) | 4473(1) | 2340(1) | 37(1) | 41(1) | 45(1) | 6(1) | 9(1) | −3(1) |
| O(1) | 5531(2) | 3937(2) | 1766(2) | 37(1) | 60(1) | 60(1) | 6(1) | 7(1) | −3(1) |
| O(2) | 8646(3) | 3469(2) | 2910(2) | 44(1) | 57(1) | 90(1) | 0(1) | −1(1) | 7(1) |
| O(3) | 7864(4) | 5087(5) | 1363(3) | 76(2) | 235(5) | 98(2) | 87(3) | 7(2) | −53(2) |
| O(4) | 7409(4) | 5312(3) | 3387(4) | 89(2) | 90(2) | 134(2) | −62(2) | 24(2) | −2(2) |
| N(1) | 9430(2) | −48(2) | 1961(2) | 30(1) | 58(1) | 30(1) | 1(1) | 9(1) | 12(1) |
| C(2) | 10987(3) | 588(3) | 1957(2) | 30(1) | 86(2) | 38(1) | 27(2) | 14(1) | 6(1) |
| O(2) | 12537(2) | 289(4) | 2712(2) | 28(1) | 156(3) | 69(1) | 27(2) | 9(1) | 7(1) |
| C(3) | 10731(4) | 1695(4) | 1021(3) | 43(1) | 90(2) | 63(2) | 8(2) | 27(1) | −6(1) |
| C(4) | 9065(4) | 1607(4) | −193(3) | 59(2) | 87(2) | 41(1) | 14(1) | 29(1) | 7(1) |
| C(5) | 7359(3) | 1310(2) | 182(2) | 38(1) | 56(1) | 32(1) | 6(1) | 9(1) | 7(1) |
| C(6) | 7598(3) | 65(2) | 920(2) | 33(1) | 45(1) | 25(1) | −6(1) | 5(1) | 6(1) |
| C(7) | 6036(2) | −155(2) | 1514(2) | 27(1) | 43(1) | 28(1) | −5(1) | 0(1) | −5(1) |
| C(8) | 6249(4) | −1455(2) | 2155(2) | 52(1) | 37(1) | 43(1) | −10(1) | 7(1) | −16(1) |
| C(9) | 8088(3) | −1435(2) | 3290(2) | 47(1) | 30(1) | 41(1) | 1(1) | 11(1) | 5(1) |
| C(10) | 9695 (4) | −1202(3) | 2769(2) | 51(1) | 55(1) | 46(1) | 5(1) | 19(1) | 25(1) |
| C(11) | 8014(2) | −482(2) | 4323(2) | 28(1) | 37(1) | 29(1) | 3(1) | 6(1) | −1(1) |
| C(12) | 7085(4) | −978(3) | 5278(2) | 48(1) | 53(1) | 41(1) | 14(1) | 1 6(1) | 2(1) |
| C(13) | 7102(4) | 0(3) | 6306(2) | 49(1) | 82(2) | 37(1) | 9(1) | 22(1) | 8(1) |
| C(14) | 618(1)4 | 1226(3) | 5665(3) | 56(1) | 72(2) | 43(1) | 2(1) | 27(1) | 13(1) |
| C(15) | 7040(4) | 1714(2) | 4681(2) | 66(1) | 42(1) | 43(1) | −11(1) | 28(1) | −2(1) |
| N(16) | 7014(2) | 702(1) | 3718(1) | 28(1) | 30(1) | 32(1) | −3(1) | 12(1) | −3(1) |
| C(17) | 6123(2) | 845(2) | 2504(2) | 22(1) | 36(1) | 34(1) | 3(1) | 10(1) | 0(1) |
| | | | | | | | | | |
| H(3A) | 10551(59) | 2446(44) | 1491(41) | 86(12) | | | | | |
| H(3B) | 11964(65) | 1627(44) | 860(40) | 95(13) | | | | | |
| H(4A) | 9112(54) | 880(42) | −776(39) | 83(11) | | | | | |
| H(4B) | 8807(59) | 2304(44) | −690(41) | 86(12) | | | | | |
| H(5A) | 7263(37) | 1993(27) | 700(26) | 39(6) | | | | | |
| H(5B) | 6350(40) | 1303(27) | −522(29) | 44 (7) | | | | | |
| H( 6) | 7591(31) | −430(27) | 269(23) | 34(5) | | | | | |
| H(7) | 4837(32) | −93(21) | 746(22) | 28(5) | | | | | |
| H( 8A) | 6157(42) | −2165(32) | 1507(30) | 56(8) | | | | | |
| H( 8B) | 5360(44) | −1571(31) | 2455(29) | 51(8) | | | | | |
| H( 9) | 8175(43) | −2342(31) | 3687(28) | 55(8) | | | | | |
| H(1OA) | 10871(48) | −1008(31) | 3469(32) | 57(8) | | | | | |
| H(1OB) | 9825(45) | −1991(35) | 2239(31) | 62(9) | | | | | |
| H(1)1) | 9262(33) | −186(21) | 4852(23) | 32(6) | | | | | |
| H(12A) | 5703(53) | −1149(35) | 4731(34) | 72(10) | | | | | |
| H(12B) | 7718(45) | −1760(35) | 5689(31) | 60(8) | | | | | |
| H(13A) | 8308(50) | 69(35) | 6815(32) | 63(9) | | | | | |
| H(13B) | 6572(48) | 411(38) | 6898(33) | 70(9) | | | | | |
| H(14A) | 4989(59) | 1083(36) | 5244(36) | 69 (10) | | | | | |
| H(14B) | 6365(58) | 1906(44) | 6406(39) | 85(11) | | | | | |
| H(15A) | 6516(51) | 2485(36) | 4225(35) | 71(10) | | | | | |
| H(15B) | 8387(52) | 1807(35) | 5178(32) | 68(9) | | | | | |
| H(17) | 5571(38) | 1604(29) | 2196(26) | 44(7) | | | | | |

Table 3
Bond lengths (Å) and angles (°) from two structural determination of (−)-$\Delta^{16(17)}$-dehydrolupaninium perchlorate

| | Lab/graphite | Synchrotron/Si |
|---|---|---|
| Cl–O(1) | 1.426(3) | 1.431(2) |
| Cl–O(2) | 1.423(3) | 1.426(2) |
| Cl–O(3) | 1.396(4) | 1.395(3) |
| Cl–O(4) | 1.425(4) | 1.423(3) |
| N(1)–C(2) | 1.357(5) | 1.358(3) |
| N(1)–C(10) | 1.458(5) | 1.465(3) |
| N(1)–C(6) | 1.465(4) | 1.469(2) |
| C(2)–O(2) | 1.231(4) | 1.225(3) |
| C(2)–C(3) | 1.501(6) | 1.507(4) |
| C(3)–C(4) | 1.491(5) | 1.486(4) |
| C(4)–C(5) | 1.509(5) | 1.513(3) |
| C(5)–C(6) | 1.503(5) | 1.507(3) |
| C(6)–C(7) | 1.544(4) | 1.544(3) |
| C(7)–C(17) | 1.472(4) | 1.483(3) |
| C(7)–C(8) | 1.513(5) | 1.512(3) |
| C(8)–C(9) | 1.518(5) | 1.516(3) |
| C(9)–C(11) | 1.515(5) | 1.512(3) |
| C(9)–C(10) | 1.518(5) | 1.526(3) |
| C(11)–N(16) | 1.485(4) | 1.486(2) |
| C(11)–C(12) | 1.523(4) | 1.524(3) |
| C(12)–C(13) | 1.504(6) | 1.508(4) |
| C(13)–C(14) | 1.513(6) | 1.513(4) |
| C(14)–C(15) | 1.513(5) | 1.511(3) |
| C(15)–N(16) | 1.475(4) | 1.480(2) |
| N(16)–C(17) | 1.268(4) | 1.265(2) |
| | | |
| O(3)–Cl–O(2) | 110.0(3) | 110.1(2) |
| O(3)–Cl–O(4) | 112.2(4) | 112.2(3) |
| O(2)–Cl–O(4) | 106.2(2) | 106.4(2) |
| O(3)–Cl–O(1) | 109.4(2) | 109.1(2) |
| O(2)–Cl–O(1) | 108.7(2) | 108.70(12) |
| O(4)–Cl–O(1) | 110.3(2) | 110.4(2) |
| C(2)–N(1)–C(10) | 117.9(3) | 117.5(2) |
| C(2)–N(1)–C(6) | 123.4(3) | 124.0(2) |
| C(10)–N(1)–C(6) | 115.6(3) | 115.3(2) |
| O(2)–C(2)–N(1) | 120.5(4) | 121.0(3) |
| O(2)–C(2)–C(3) | 121.2(4) | 121.3(3) |
| N(1)–C(2)–C(3) | 118.2(3) | 117:07(2) |
| C(4)–C(3)–C(2) | 115.2(4) | 115.0(3) |
| C(3)–C(4)–C(5) | 108.6(3) | 109.1(2) |
| C(6)–C(5)–C(4) | 111.4(3) | 111.0(2) |
| N(1)–C(6)–C(5) | 113.0(3) | 112.9(2) |
| N(1)–C(6)–C(7) | 109.1(2) | 109.4(2) |
| C(5)–C(6)–C(7) | 112.2(3) | 112.1(2) |
| C(17)–C(7)–C(8) | 109.(3)(2) | 109.4(2) |
| C(17)–C(7)–C(6) | 110.0(2) | 109.9(2) |
| C(8)–C(7)–C(6) | 110.6(3) | 110.3(2) |
| C(7)–C(8)–C(9) | 106.1(3) | 106.6(2) |
| C(11)–C(9)–C(10) | 113.5(3) | 113.6(2) |
| C(11)–C(9)–C(8) | 110.6(6) | 110.6(2) |
| C(10)–C(9)–C(8) | 110.0(3) | 109.7(2) |
| N(1)–C(10)–C(9) | 113.0(3) | 112.7(2) |
| N(16)–C(11)–C(9) | 111.3(2) | 111.53(14) |
| N(16)–C(11)–C(12) | 107.5(3) | 107.3(2) |
| C(9)–C(11)–C(12) | 114.7(3) | 114.6(2) |
| C(13)–C(12)–C(11) | 112.1(3) | 112.1(2) |
| C(12)–C(13)–C(14) | 110.5(3) | 110.6(2) |
| C(15)–C(14)–C(13) | 111.4(3) | 111.5(2) |
| N(16)–C(15)–C(14) | 110.1(3) | 110.2(2) |
| C(17)–N(16)–C(15) | 121.(3) | 121.3(2) |
| C(17)–N(16)–C(11) | 124.2(3) | 124.7(2) |
| C(15)–N(16)–C(11) | 113.8(2) | 113.9(2) |
| N(16)–C(17)–C(7) | 123.6(3) | 122.9(2) |

The structure was solved from the laboratory data by direct methods [17], and the nonhydrogen atoms were refined with anisotropic thermal parameters. The hydrogen-atom positions were then calculated from the cation geometry and a riding model with thermal parameters $U_{iso} = 1.5U_{eq}$ of their carriers was used in subsequent refinements. Synchrotron radiation permitted the observation of a larger fraction of significant reflections and thus allowed the refinement of all H-atoms positions and of their isotropic thermal parameters. Attempts to refine the H-atoms from the laboratory data resulted in larger e.s.d. values and $R$ factors. The function minimized was $\Sigma w(|F_o|^2-|F_c|^2)^2$ with weights $w = \sigma_I^{-2}$. All the structure refinements were performed with SHELXL-93 package [18], and further calculations concerning disorder of the $ClO_4^-$ anion with with POP-97 [19]; the structures were drawn with the program XP from Siemens. Only the final atomic coordinates refined from the synchrotron data are listed in Table 2 (see the discussion in Section 3). The absolute configuration of the cation has been determined in both experiments as C(6)$R$, C(7)$S$, C(9)$S$ and C(11)$S$ (Table 3), which corresponds to that found in many naturally occurring sparteines [20]. The specific rotation of I dissolved in water has been measured as $[\alpha]_D^{20} = -113.6°$.

## 3. Results and discussion

### 3.1. Immonium group dimensions

Until recently little information was available on the geometry of the immonium group. The first immonium salt determined by X-rays as N,N-dimethyliso-propylideniminium perchlorate [21]; however due to
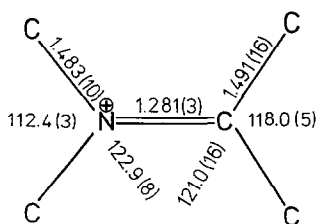
Fig. 1. Schematic drawing of the immonium fragment with average dimensions calculated from the dimensions observed in $\Delta^{1(6)}$-dehydrosparteinium diperchlorate, $\Delta^{1(6)}$-dehydro-17-oxosparteinium perchlorate and $\Delta^{1(6),11(16)}$-didehydrosparteinium diperchlorate.

the disorder of the structure the dimensions of the cation were biased. Nevertheless, the dimensions were used in theoretical calculation of the charge distribution in the cation [21], and were cited in review literature on enamines [22]. A series of structural studies on the immonium salts of sparteine alkaloids listed above [8–14] revealed that the dimensions of the immonium group were considerably different from those reported previously [21]. The average dimensions of the immonium group obtained from those data [8–14] are shown in Fig. 1. It is characteristic of the dehydrosparteinium perchlorate crystals that their structures are partly disordered, due to the rotations of the perchlorate anions and due to the conformational disorder of the terminal piperidinium rings. Therefore, Fig. 1 shows the dimensions of the immonium group averaged only from the most precisely determined structures of $\Delta^{1(6)}$-dehydro-17-oxosparteinium perchlorate, $\Delta^{1(6)}$-dehydrosparteinium diperchlorate and $\Delta^{1(6),11(16)}$-didehydrosparteinium diperchlorate [8, 10, 11]. It was found characteristic that the $C-N^+-C$ valency angle opposite to the $^+N=C$ bond is nearly 112°, markedly smaller than 120° as would be expected for an $sp^2$ atom, and that the C–C–C bond opposite the immonium bond is less sharpened to about 118°. The accuracy of the other results is relatively low, due to disorder of perchlorate anions and terminal piperidinium rings. Therefore, one of the main aims of this study was to provide more accurate dimensions of the immonium group. They are listed in Table 3. The $N^+=C$ bond in **I** of 1.265(2) Å is shorter than observed previously,while other features of the immonium group, such as reduction of the $C-N^+-C$ angle, in **I** to 113.9(2)°, have been confirmed. A sharpening of the valency angles

Table 4

Selected endo- and exocyclic torsion angles (°) in the $(-)\Delta^{16(17)}$-dehydrolupaninium cation, as determined in two structural studies

| Data set | LAB/graphite | Synchrotron/Si |
|---|---|---|
| **Ring A** | | |
| N(1)–C(2)–C(3)–C(4) | − 27.6(5) | − 28.3(4) |
| C(2)–C(3)–C(4)–C(5) | 49.4(5) | 50.2(4) |
| C(3)–C(4)–C(5)–C(6) | − 59.5(5) | − 59.7(3) |
| C(4)–C(5)–C(6)–N(1) | 47.0(4) | 46.4(3) |
| C(5)–C(6)–N(1)–C(2) | − 24.7(4) | − 24.8(3) |
| C(6)–N(1)–C(2)–C(3) | 14.6(5) | 15.2(3) |
| **Ring B** | | |
| N(1)–C(6)–C(7)–C(8) | − 58.2(3) | − 58.2(2) |
| C(6)–C(7)–C(8)–C(9) | 63.9(3) | 64.1(2) |
| C(7)–C(8)–C(9)–C(10) | − 61.2(2) | − 60.9(4) |
| C(8)–C(9)–C(10)–N(1) | 54.5(3) | 54.3(4) |
| C(9)–C(10)–N(1)–C(6) | − 49.8(2) | − 49.6(4) |
| C(10)–N(1)–C(6)–C(7) | 50.5(2) | 50.2(4) |
| **Ring C** | | |
| C(7)–C(8)–C(9)–C(11) | 65.3(4) | 64.9(2) |
| C(8)–C(9)–C(11)–N(16) | − 40.2(4) | − 39.9(2) |
| C(9)–C(11)–N(16)–C(17) | 8.4(4) | 8.6(2) |
| C(11)–N(16)–C(17)–C(7) | − 2.6(4) | − 2.7(3) |
| N(16)–C(17)–C(7)–C(8) | 28.2(4) | 28.0(2) |
| C(17)–C(7)–C(8)–C(9) | − 57.2(3) | − 56.9(2) |
| **Ring D** | | |
| C(11)–N(16)–C(15)–C(A) | − 58.2(4) | − 58.0(2) |
| N(16)–C(15)–C(14)–C(13) | 54.0(4) | 53.6(3) |
| C(15)–C(14)–C(13)–C(12) | − 53.8(4) | − 53.5(3) |
| C(14)–C(13)–C(12)–C(11) | 56.2(4) | 56.1(3) |
| C(13)–C(12)–C(11)–N(16) | − 57.1(3) | − 57.2(2) |
| C(12)–C(1(1))–N(16)–C(15) | 58.6(3) | 58.7(2) |
| **Exocyclic torsion angles** | | |
| C(10)–N(1)–C(2)–O(2) | − 7.7(6) | − 8.0(4) |
| C(6)–N(1)–C(2)–O(2) | − 166.8(4) | − 166.6(3) |
| C(10)–N(1)–C(2)–C(3) | 173.8(3) | 173.8(2) |
| C(10)–N(1)–C(6)–C(5) | 175.8(3) | 176.1(2) |
| C(4)–C(5)–C(6)–C(7) | 170.9(3) | 170.5(2) |
| C(5)–C(6)–C(7)–C(17) | − 63.4(3) | − 63.5(2) |
| C(2)–N(1)–C(10)–C(9) | 149.6(3) | 149.7(2) |
| C(1(1))–C(9)–C(10)–N(1) | − 70.3(4) | − 69.9(2) |
| C(10)–C(9)–C(11)–C(12) | − 153.7(3) | − 153.8(2) |
| C(9)–C(11)–C(12)–C(13) | 178.6(3) | 178.4(2) |
| C(14)–C(15)–N(16)–C(17) | 118.5(3) | 118.5(2) |
| C(15)–N(16)–C(17)–C(7) | − 178.9(3) | − 178.9(2) |
| C(6)–C(7)–C(17)–N(16) | − 93.4(3) | − 93.3(2) |

opposite a double bond is also characteristic of the structures of ethylene (117°) and allene (115.8°) [23]. The immonium group in **I** is located in the inner ring C, while in the previously determined
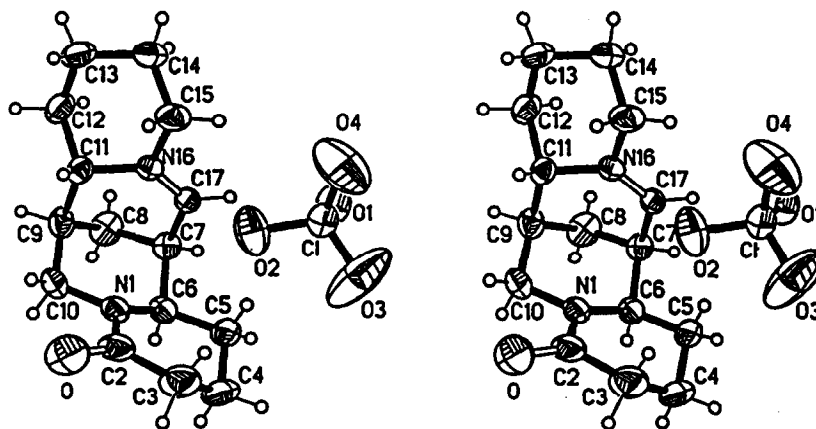
Fig. 2. ORTEP stereodrawing of the ionic pair of $\Delta^{16(17)}$-dehydrolupaninium perchlorate. The thermal ellipsoids are drawn at 50% probability level.

structures it was located in either terminal ring A or at the junctions of the terminal rings. It appears that the longer immonium bonds in the structures reported previously result from their location in the cation, although accuracy of those data is too low for detailed comparisons. For example, the somewhat longer $N^+{=}C$ bond of 1.307(10) Å in $\Delta^{1(2)}$-2-methylsparteinium diperchlorate monohydrate [13] may be due to the effect of hyperconjugation, which is suggested by a shortening of the C(2)–C(Me) bond and positions of the methyl H-atoms. In all cases the immonium groups form a planar system within a few degrees of the $C{-}N^+{=}C{-}C$ torsion angles.
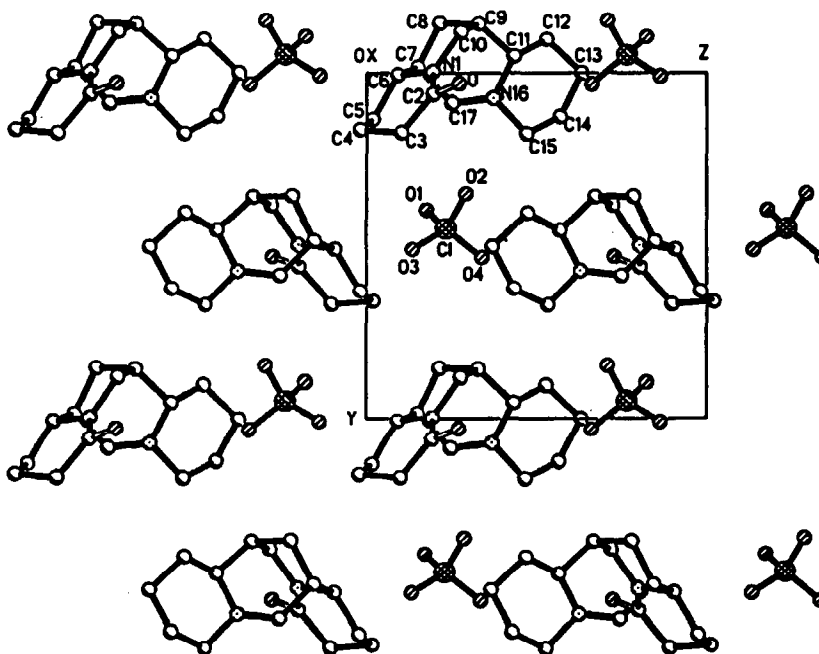


Fig. 3. Crystal packing of $\Delta^{16(17)}$-dehydrolupaninium perchlorate viewed along [x]. Hydrogen atoms are omitted for clarity.
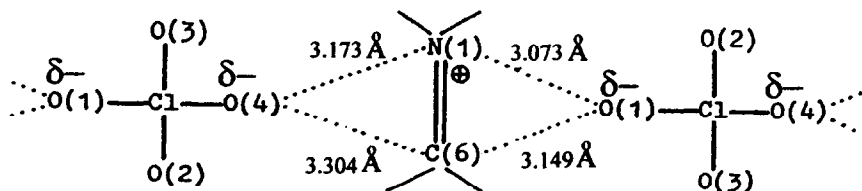
Fig. 4. Interionic short contacts in the crystal of $\Delta^{1(6)}$-dehydro-17-oxosparteinium perchlorate [8].

## 3.2. Conformation of the cation

A stereoscopic view of the ionic pair of **I** is shown in Fig. 2, and the torsion angles are listed in Table 4. The piperidone ring A of the cation has the conformation of a distorted half-chair due to the lactarn group, piperidine ring B is a chair sharpened at C(8) and flattened at N(1), piperidinium ring C is a distorted sofa, and ring D is a chair. The ring junctions A/B and C/D have quasi-*trans* and quasi-*cis* configurations, respectively. Owing to the immonium bond involving the N(16) atom, the cation cannot undergo transformations of the quinolizidine C/D.

## 3.3. Interactions of immonium groups

The crystal packing of **I** is shown in Fig. 3. It was found inherent to the series of previously investigated dehydrosparteinium perchlorates that the immonium groups were located close to the perchlorate anions; this was consistent with the concept of the crystal packing minimizing the energy of electrostatic interactions in these ionic crystals. Such an arrangement is illustrated in Fig. 4, showing the short interionic contacts between the ions in the structure of $\Delta^{1(6)}$-dehydro-17-oxosparteinium perchlorate along the crystal direction [y]. As similar arrangements were present also in other immonium salts, including N,N-dimethylpropylideniminium perchlorate [21], it was concluded that the electrostatic interactions govern the ionic packing in this group of crystals. However in **I**, where the immonium group is located in the inner ring C, no such close contacts to the perchlorate anions have been found. On the other hand, short contacts C(17)···O' of 2.865(3) Å and N(16)···O' of 3.229(2) Å (primes denote the atoms transformed by symmetry operation x-1, y, z) to the electronegative oxygen of the lactarn group are present. A C(17)H···O' hydrogen bond can be ruled

out, as the H(17)···O' distance equals 2.895(12) Å, and the C–H···O angle is smaller than 90°. The shortest interionic contacts of the perchlorate oxygens to the cation atoms in **I** are: C(6)···O(1″) of 3.288(3), C(12)···O(2″) of 3.223(2), C(11)···O(2″) of 3.385(3), C(4)···O(3″) of 3.400(3) and C(14)···O(4″) of 3.358(3) Å. It appears that in **I** this arrangement, favouring shorter contacts of the immonium group to the lactam oxygen than to the bulky $ClO_4^-$ anion, are due to the close packing requirements, as described by Kitaygorodsky [24].

## 3.4. Comparison of the X-ray tube and synchrotron data

Several systematic comparisons of crystal-structure models of the same compound independently determined by diffraction methods have been reported. Such studies were primarily undertaken to assess the accuracy of structural parameters, the reliability of their estimated standard deviations, and to detect systematic errors in the data. Independent diffraction studies on the same substance were arranged, e.g. Refs. [25, 26], or coincided accidentally, e.g. Refs. [27, 28]. In most cases they concerned data collections performed with diffractometers equipped with sealed X-ray tubes. More recently, similar diffraction measurements, employing conventional X-ray tubes and synchrotron beams, performed on simple compounds have been compared [29]. Apart from the considerable increase in intensity, synchrotron beams usually offer much lower divergence [30] than the graphite-monochromated beams from X-ray tubes [31]. The narrow profile of the reflection shown in Fig. 5(a) testifies to the low mosaicity of the sample of **I**. Such low mosaicity of the crystal is not common for organic crystals. In two other tests on organic crystals, a complex reflection shape testified to a shattered structure of the samples (two independent
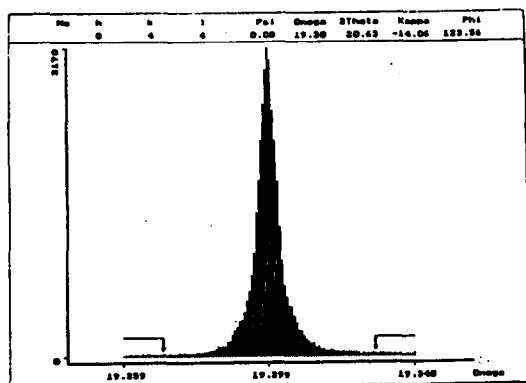
(a)
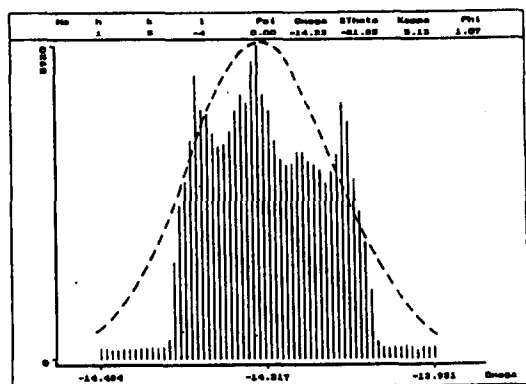


(b)
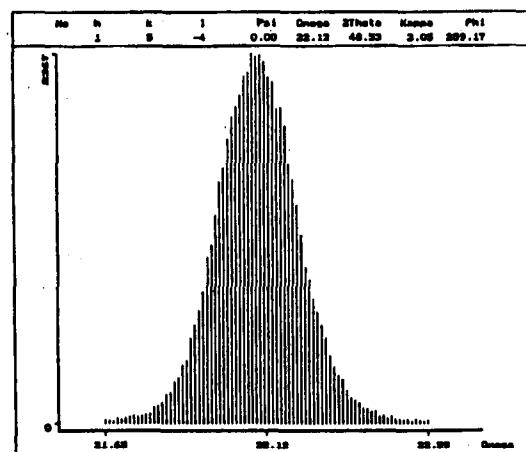


(c)

samples were tested for each of the substances). Fig. 5(b) shows a (15$\bar{4}$) reflection for the crystal of $N$-phthaloyl-L-alanyl-L-valine methyl ester. When rescaled, the full width at half maximum (FWHM) of the (044) reflection of **I** [Fig. 5(a)] would correspond to about 0.5 mm in Fig. 5(b). The two 'shattered' crystals were routinely measured in the laboratory using a KUMA-4 diffractometer equipped with a sealed tube and a graphite monochromator, and no indication of their lower quality was detected, except for somewhat broadened reflections [see Fig. 5(c)]. Both these structures refined to low $R$-factors and low standard deviations of atomic parameters [32].

The structure of **I** is more complex than the samples used in previous tests [29]. We chose this sample crystal for several reasons; it is noncentrosymmetric and mainly composed of light elements, so it was possible to assess the feasibility of determining absolute configuration and accuracy of locating H-atoms. Additionally, the crystal contains a bulky perchlorate anion, which is often orientationally disordered in immonium salts, due to the absence of hydrogen bonds, while the orientation of the cation is usually well defined. We were interested in the dimensions of such a perchlorate anion in two independent determinations. The synchrotron data are superior to those measured in the laboratory; the unit-cell dimensions are measured more precisely, more intensities could be collected with a higher accuracy, which is reflected in more accurate final atomic positions and thermal parameters, and in the more reliable absolute configuration determination. This is a combined effect of the equipment and X-ray beams which were used. The lower divergence of the synchrotron radiation, along with the extremely precise crystal positioning by the

Fig. 5. Reflection (044) profile of the $\Delta^{16(17)}$-dehydrolupaninium perchlorate crystal scanned in $\omega$-2$\Theta$ mode using the low divergence synchrotron beam, Si-monochromated and without focusing mirrors, at ESRF in Grenoble (a). Reflection (15$\bar{4}$) of the $N$-phtha-loyl-L-alanyl-L-valine methyl ester sample recorded at the same conditions at ESRF (b); and the same reflection recorded at laboratory using a KUMA-4 diffractometer equipped with a sealed Mo tube and a graphite monochromator. Note the scale difference between these plots: the full width at half maximum (FWHM) of the reflection from sample **I** shown in (a) corresponds to 0.5 mm when rescaled to (b), and to less than 0.3 mm when rescaled to (c). The dashed line in (b) outlines the profile of the reflection shown in (c).

KM-6 diffractometer, produced more accurate unit-cell parameters, although a similar set of reflections was used. The more intense synchrotron beam allowed more reflections to be measured in a shorter time and with better statistics than in the laboratory and consequently produced more accurate atomic parameters and absolute configuration determination [33]. Nevertheless, the two structures are in excellent agreement. Therefore, only the atomic coordinates determined from the synchrotron data are listed in Table 2. An intriguing result concerns the dimensions of the perchlorate anion, which is often considered to be a regular tetrahedron, with any differences in its bond lengths and valency angles attributed to experimental errors due to its disorder. The distortions in the geometry of the anion are reproduced in the two independent measurements (see Table 3), which indicates that they may be either real distortions, or that they may result from discrepancies between the disordered anion and the model refined in the least-squares procedure.

## Acknowledgements

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