2-n-Propyl-7-methyl-*trans*-decahydroquinoline Hydrochloride, a Synthetic Isomer of Pumiliotoxin C
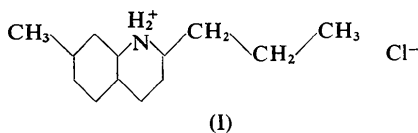
By Judith L. Flippen

Laboratory for the Structure of Matter, Naval Research Laboratory, Washington, D.C. 20375, U.S.A.

Abstract. $C_{13}H_{25}N.HCl$, monoclinic, $P2_1/c$, $a=8\cdot545$ (3), $b=7\cdot328$ (4), $c=23\cdot261$ (11) Å, $\beta=95\cdot0$ (1)°, $Z=4$ and $d_{calc}=1\cdot06$ g cm^{-3}. A system of NH$\cdots$Cl hydrogen bonds links the molecules.

Introduction. The title compound (I) was obtained as a

(I)

by-product of the synthesis of pumiliotoxin C (Kissing, 1972), a naturally occurring frog venom (Daly, Toku-yama, Habermehl, Karle & Witkop, 1969). The X-ray study was performed for the purpose of monitoring the progress of the synthesis (Habermehl & Andres, 1973). Crystals were provided by Dr B. Witkop of the National Institutes of Health. 1177 independent reflections were collected from a small crystal ($\sim 0\cdot05 \times 0\cdot10 \times 0\cdot28$ mm) on an automatic diffractometer using Cu $K\alpha$ radiation ($\lambda=1\cdot54178$ Å, Ni filter). Data were collected to a maximum 2θ of 90° beyond which the scattering was essentially zero. The θ–2θ scan mode of data collection was used. No absorption corrections were applied (max. $\mu R=0\cdot6$).

The structure was solved by routine application of the symbolic addition procedure for centrosymmetric crystals (Karle & Karle, 1966), using programs written by R. D. Gilardi, S. A. Brenner and J. H. Konnert of this laboratory. Full-matrix least-squares refinement was carried out using the program of Busing *et al.* (1971). Hydrogen atoms were added to the molecule at calculated positions and included in the final cycles of refinement as constant parameters. All data for which $|F_o| < 3\cdot0\sigma_{|F_o|}$ (327 reflections) were given zero weight for refinement purposes. The remaining reflec-

tions were weighted according to the procedure outlined by Gilardi (1973). The final R value for the data used in the refinement [the function minimized was $\sum w(|F_o| - |F_c|)^2$] was 10·7%. For the full set of data the final R value was 16·0%. R_w was 6·29% for both sets. Coordinates and thermal parameters for non-hydrogen atoms are listed in Table 1.*

Table 1. *Fractional coordinates* ($\times 10^4$) *and thermal parameters*

The thermal parameters are of the form $T = \exp[-\frac{1}{4}(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.
Standard deviations are based solely on least-squares parameters.

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cl	3361	2745	2918	3·2	4·7	6·1	0·2	1·1	−0·1
N	3713	7154	2765	2·4	10·1	2·9	−0·2	0·2	−0·8
C(2)	2315	7763	2431	3·4	5·1	4·1	−0·4	0·3	−1·7
C(3)	893	7479	2747	4·0	4·5	4·6	0·1	1·7	0·7
C(4)	1071	7919	3354	4·1	19·4	5·1	0·9	1·3	0·7
C(5)	2821	8142	4280	5·9	19·6	5·9	0·4	0·4	−2·2
C(6)	4343	7578	4605	6·5	7·3	4·2	0·1	0·7	−3·1
C(7)	5734	7840	4250	4·6	10·8	6·0	0·2	−0·3	−2·6
C(8)	5465	7219	3659	5·9	6·5	3·3	0·1	0·6	0·1
C(9)	3974	7773	3349	3·0	6·8	4·5	0·5	0·0	−1·4
C(10)	2558	7512	3681	4·1	6·5	3·3	0·3	0·5	−3·2
C(11)	7271	7385	4584	6·7	12·2	5·0	0·4	−0·2	−1·7
C(12)	2179	7169	1809	4·4	8·0	4·9	0·6	0·2	−0·0
C(13)	983	7909	1392	5·4	9·8	5·1	1·6	−0·5	−0·1
C(14)	951	7363	780	7·7	10·1	4·0	0·3	−0·9	−0·6

Average standard deviations

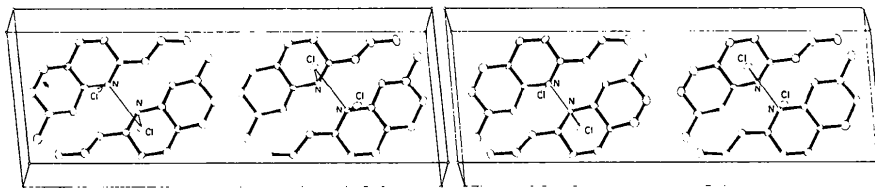|	17	38	6	0·6	0·8	0·6	0·8	0·5	0·8

Fig. 1. The contents of one unit cell. The intermolecular hydrogen bonds are shown by fine lines. The view is looking down **b** with **c**→ and **a**↑.

Discussion. The molecule is extended with a *trans* junction between the rings [average torsion angle across the ring junction is 177·5 (1·6)°]. The six-membered rings are both in a flattened chair conformation as shown by the average value for ring torsion angles, 44·0 (2·3)°, and the larger than normal ring angles [average internal ring angle is 114·7 (1·0)°]. The average C–N bond length is 1·44 (1) Å and the C–N–C angle is 117·8 (1·0)°. The average C–C bond length is 1·48 (1) Å and the average C–C–C angle is 115·6 (1·1)°.

The structure of the naturally occurring pumiliotoxin C (2-n-propyl-5-methyl-*cis*-decahydroquinoline hydrochloride) was reported earlier (Daly, Tokuyama, Habermehl, Karle & Witkop, 1969). The present molecule differs from pumiliotoxin C in the position of the methyl group [on C(5) in pumiliotoxin and on C(7) in the present molecule] and in the configuration of the junction of the fused rings (there is a *cis* junction in pumiliotoxin). The stereo configuration and molecular packing of (I) are illustrated in Fig. 1. The packing is very similar in both crystals and the hydrogen-

bonding system is the same for both molecules, linking them into zigzag columns along the **b** direction. The N···Cl distances are 3·13 and 3·18 Å in pumiliotoxin C and 3·11 (1) and 3·27 (1) Å for (I) (see Fig. 1). In both cases these are the only intermolecular approaches less than van der Waals separations.

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Cobalt Vanadate, Co₂V₂O₇, and Nickel Vanadate, Ni₂V₂O₇

BY E. E. SAUERBREI, R. FAGGIANI AND C. CALVO

Department of Physics, McMaster University, Hamilton, Ontario, Canada

Abstract. Cobalt divanadate: monoclinic, space group $P2_1/c$, $a=6\cdot594$ (2), $b=8\cdot380$ (1), $c=9\cdot470$ (9) Å, $\beta=100\cdot17$ (3)°, $Z=4$, $D_m=4\cdot29$, $D_x=4\cdot33$ g cm^{-3}. Nickel divanadate: monoclinic, space group $P2_1/c$, $a=6\cdot515$ (8), $b=8\cdot303$ (7), $c=9\cdot350$ (6) Å and $\beta=99\cdot86$ (8)°, $Z=4$, $D_m=4\cdot44$, $D_x=4\cdot41$ g cm^{-3}. The crystals were grown from the melt. The structures were refined by full-matrix least-squares methods from a model obtained from the Patterson function of Co₂V₂O₇. The divalent cations are octahedrally coordinated to oxygen atoms and the anion consists of corner-sharing VO₄ tetrahedra. The V–O–V angle is 117·5° in the cobalt salt and 117·6° in the nickel salt. The average V–O(–V) and terminal V–O bond lengths are 1·848 and 1·694 Å in Co₂V₂O₇ and 1·853 and 1·683 Å in Ni₂V₂O₇.

Introduction. A survey of the structures of stoichiometry M₂X₂O₇, with the anion based upon corner sharing XO₄ tetrahedra, by Brown & Calvo (1970), suggested that these compounds can be related to one of the known alkali metal dichromate series provided that the cation's radius exceeds a value near 1 Å and related to thortveitite below this boundary. Recent structural studies of the rare-earth disilicates, reviewed by Flesche (1973), shows that the boundary region be-

tween these two areas is rich in new structural types. At the lower end of the ionic radii scale the divanadates also show a variety of new structures as indicated by that of Mg₂V₂O₇ (Gopal & Calvo, 1974), Cu₂V₂O₇ (Calvo & Faggiani, 1974) and the present structures.

A crystal of Co₂V₂O₇ with dimensions 0·21 × 0·145 × 0·19 mm and a ground sphere of Ni₂V₂O₇ with radius 0·12 mm were used to collect 1162 and 1787 unique reflections of positive measure respectively using a Syntex P1̄ automatic diffractometer (scintillation counter; graphite monochromatized Mo Kα, $\lambda=0\cdot71069$ Å).

For Co₂V₂O₇, 990 reflexions had intensities greater than 3σ and 272 with $0<I\leq3\sigma$ were considered unobserved. For Ni₂V₂O₇ the analogous values are 1487 and 300 respectively. Reflexions $h0l$ with l odd and $0k0$ with k odd were systematically absent. The intensities were corrected for absorption, Lorentz and polarization effects. $\mu_{Co_2V_2O_7}=90\cdot7$ cm^{-1} and $\mu_{Ni_2V_2O_7}=102\cdot3$ cm^{-1}. The structure of Co₂V₂O₇ was determined from the Patterson function and both structures were refined by full-matrix least-squares methods. Atomic form factors for Ni²⁺, Co²⁺, V³⁺ and O⁻ were taken from Cromer & Waber (1965) and corrected for anomalous dispersion. Weights were chosen as $w=[3\cdot26-0\cdot15F_o+0\cdot0027F_o^2]^{-1}$ for Co₂V₂O₇ and $w=$