

The authors thank Dr K. Ulbert for valuable discussion, Mrs J. Vaňková for technical assistance and Dr V. Petříček from the Institute of Solid State Physics of the Czechoslovak Academy of Sciences for valuable consultation on the rigid-body problem.

References

- AHMED, F. R., HALL, S. R., PIPPY, M. E. & HUBER, C. P. (1966). NRC Crystallographic Programs for the IBM/360 System. *World List of Crystallographic Computer Programs*, 2nd ed., Appendix, p. 52. Utrecht: Oosthoek.
- BÄRNIGHAUSEN, H., JELLINEK, F., MUNNIK, J. & VOS, A. (1963). *Acta Cryst.* **16**, 471–475.
- CRUICKSHANK, D. W. J. (1956). *Acta Cryst.* **9**, 757–758.
- HAMILTON, W. C. (1965). *Acta Cryst.* **18**, 502–518.
- HAŠEK, J., HLAVATÁ, D. & HUML, K. (1977). *Acta Cryst.* **B33**, 3372–3376.
- HAŠEK, J., OBRDA, J., HUML, K., NEŠPŮREK, S., ŠORM, M. & CHOJNACKI, H. (1978). *Acta Cryst.* **B34**, 2756–2759.
- International Tables for X-ray Crystallography* (1974). Vol. IV, pp. 71–151. Birmingham: Kynoch Press.
- KITAIGORODSKY, A. I. (1970). *Molecular Crystals*. Moscow: Nauka.
- MITSUI, A. & EBARA, N. (1973). *Bull. Chem. Soc. Jpn.*, **46**, 327–328.
- NEŠPŮREK, S. & ŠORM, M. (1977). *Coll. Czech. Chem. Commun.* **42**, 811–818.
- PURANIK, V. & SUSCHITZKY, S. (1967). *J. Chem. Soc. C*, pp. 1006–1009.
- SABESAN, M. N. & VENKATESAN, K. (1971). *Acta Cryst.* **B27**, 986–993.
- SCHOMAKER, V. & TRUFLOOD, K. N. (1968). *Acta Cryst.* **B24**, 63–76.
- STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.
- STOUT, G. H. & JENSEN, L. H. (1968). *X-ray Structure Determination*, pp. 410–412. New York: Macmillan.

Acta Cryst. (1979). **B35**, 440–444

The Molecular and Crystal Structure of the Alkaloid Cinchonine

BY BARBARA OLEKSYN AND LUKASZ LEBIODA

Institute of Chemistry, Jagiellonian University, ul. Krupnicza 41/43, 30-060 Kraków, Poland

AND MARIA CIECHANOWICZ-RUTKOWSKA

Regional Laboratory of Physicochemical Analysis and Structural Research, ul. Krupnicza 41/43, 30-060 Kraków, Poland

(Received 15 May 1978; accepted 16 October 1978)

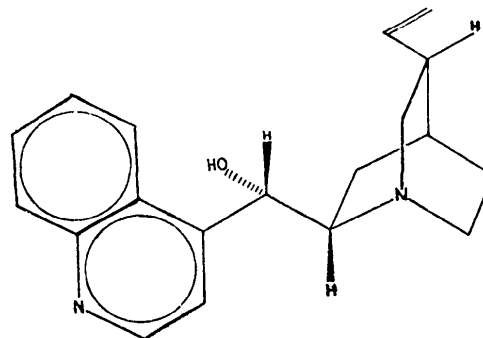
Abstract

The crystal structure of the alkaloid cinchonine, $C_{19}H_{22}N_2O$, has been solved by direct methods and refined by full-matrix least-squares computations to $R = 0.053$ for 1935 reflexions measured on a diffractometer. The monoclinic unit cell, space group $P2_1$, with $a = 10.763$ (3), $b = 7.177$ (2), $c = 11.090$ (3) Å, $\beta = 107.92$ (2)° contains two molecules. The molecules form hydrogen-bonded chains along twofold screw axes. The conformation of the free cinchonine base is the same as that found for the (cinchoninium)²⁺ cation; the differences in the bond lengths and angles are discussed.

Introduction

The molecular structure and absolute configuration of diprotonated cinchonine was determined as the result of the X-ray structure analysis of cinchoninium tetra-

chlorocadmate(II) dihydrate (Oleksyn, Stadnicka & Hodorowicz, 1978). It seemed interesting, therefore, to establish the structure of the free cinchonine base



in order to study the effect of protonation on the geometry of the molecule.

Crystal data for crystalline cinchonine were first determined by Paretzkin (1956).

Experimental

Cinchonine base was precipitated with ammonia from an aqueous solution of cinchoninium sulphate and then recrystallized from water. One of the plate-shaped crystals of maximum dimension 0.3 mm was mounted on an Enraf-Nonius CAD-4 diffractometer equipped with a graphite monochromator. The lattice parameters given by Paretzkin (1956) were confirmed and refined in the autoindexing procedure from setting angles of 15 reflexions.

Crystal data

$C_{19}H_{22}N_2O$, $M_r = 294.38$, monoclinic, $a = 10.763$ (3), $b = 7.177$ (2), $c = 11.090$ (3) Å, $\beta = 107.92$ (2)°, $V = 815.07$ Å³, $D_m = 1.20$ (6), $D_c = 1.20$ Mg m⁻³, $Z = 2$, $F(000) = 316$, space group $P2_1$, Cu $K\alpha$ radiation, $\lambda = 1.5418$ Å, $\mu(\text{Cu } K\alpha) = 0.508$ mm⁻¹.

Measurement of the intensities of 1935 independent reflexions in the range $2.0 < \theta < 80^\circ$ was performed in the $\omega/2\theta$ scanning mode with scan width: $0.80^\circ + 0.20^\circ \tan \theta$. From the collected data, 82 reflexions with net intensity < 0 were considered unobserved. In order to avoid the bias of experimental data, no other reflexions were excluded, as was recommended by Hirshfeld & Rabinovich (1973). The intensities of two control reflexions, recorded during the data collection after every 50 reflexions, remained constant to within 4%.

The data were corrected for Lorentz and polarization effects but not for absorption.

Structure determination and refinement

The structure was solved by direct methods with the *SHELX* program system (Sheldrick, 1975) by use of 322 normalized structure factors having $E > 1.2$. The origin was defined with the phases: $5,0,11$; $5,0,10$; 112 while 146 and 717 ; 644 ; $4,0,11$ were used as enantiomorph and multiresolution phases respectively. Six E maps were computed, of which the one with the best

consistency revealed the positions of 12 of the 24 non-hydrogen atoms. These positions were treated as a partial structure in the second stage of phase determination and tangent refinement. From the E map obtained at this stage the locations of the next four non-hydrogen atoms were determined. The difference Fourier synthesis phased on the 16 atoms gave the positions of the remaining eight non-hydrogen atoms ($R = 0.24$). The positions of 19 H atoms were found from the difference Fourier maps obtained at various stages of six successive cycles of full-matrix least-squares refinement with isotropic thermal parameters. For the missing three H atoms H(C9), H(1C11) and H(2C11), positions were calculated. Further refinement with anisotropic thermal parameters for the non-hydrogen atoms and isotropic for the H atoms was carried out in two partially overlapping structural segments. Refinement was terminated at $R = 0.0525$, when the shifts of atomic parameters for the non-hydrogen atoms were less than 0.1 of their standard deviations, and for the H atoms less than 0.5 of their e.s.d.'s. A final difference Fourier map showed no peaks higher than $0.18 \text{ e } \text{Å}^{-3}$.

The weighting scheme was: $w = k[\sigma^2(F_o) + gF_o^2]^{-1}$ where k and g refined to 0.9746 and 0.0034 respectively. Atomic scattering factors for O, N, C and H atoms were those of *SHELX* (Sheldrick, 1975).

Final coordinates for non-hydrogen atoms are given in Table 1 and for H atoms in Table 2.* Bond distances and angles are listed in Tables 3 and 4 respectively.

Discussion

The conformation of the cinchonine molecule (Fig. 1) is very close to that found for the (cinchoninium)²⁺ cation in its tetrachlorocadmate (Oleksyn *et al.*, 1978) and for the closely related alkaloids: (+)-10-bromo-10,11-

* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34030 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Final fractional coordinates ($\times 10^4$) for non-hydrogen atoms with estimated standard deviations in parentheses

	<i>x</i>	<i>y</i>	<i>z</i>		<i>x</i>	<i>y</i>	<i>z</i>
N(1)	8938 (2)	8151 (4)	-1587 (2)	O(12)	9007 (2)	12118 (3)	-478 (2)
C(2)	9429 (3)	9308 (6)	-2441 (3)	N(13)	5451 (3)	11724 (5)	1628 (2)
C(3)	8393 (4)	9672 (6)	-3715 (3)	C(14)	5796 (3)	12895 (6)	878 (3)
C(4)	7071 (3)	9152 (6)	-3547 (3)	C(15)	6794 (3)	12568 (5)	327 (3)
C(5)	7061 (4)	7040 (6)	-3352 (3)	C(16)	7477 (3)	10943 (4)	561 (2)
C(6)	8297 (4)	6492 (5)	-2317 (3)	C(17)	7172 (2)	9634 (5)	1398 (2)
C(7)	6944 (3)	10095 (6)	-2349 (3)	C(18)	7808 (3)	7895 (5)	1740 (3)
C(8)	7920 (3)	9171 (5)	-1193 (2)	C(19)	7436 (4)	6700 (6)	2526 (3)
C(9)	8507 (2)	10486 (4)	-77 (2)	C(20)	6416 (3)	7141 (6)	3004 (3)
C(10)	8512 (6)	11662 (8)	-4127 (5)	C(21)	5784 (3)	8795 (6)	2704 (3)
C(11)	8699 (8)	12174 (10)	-5149 (6)	C(22)	6138 (3)	10095 (5)	1900 (2)

Table 2. Fractional coordinates ($\times 10^3$) for hydrogen atoms with estimated standard deviations in parentheses

	x	y	z		x	y	z
H(1C2)	1004 (4)	871 (8)	-265 (4)	H(C9)	931 (3)	977 (6)	58 (3)
H(2C2)	986 (5)	1047 (8)	-176 (5)	H(C10)	757 (6)	1215 (13)	-465 (6)
H(C3)	853 (4)	889 (6)	-433 (4)	H(1C11)	895 (4)	1341 (7)	-536 (4)
H(C4)	638 (4)	956 (6)	-426 (4)	H(2C11)	849 (4)	1115 (7)	-592 (4)
H(1C5)	686 (5)	629 (8)	-426 (4)	H(O12)	966 (5)	1257 (8)	17 (5)
H(2C5)	625 (6)	680 (12)	-308 (5)	H(C14)	538 (4)	1405 (7)	80 (3)
H(1C6)	891 (4)	602 (6)	-281 (3)	H(C15)	701 (3)	1340 (7)	-16 (3)
H(2C6)	835 (7)	559 (10)	-161 (6)	H(C18)	865 (3)	767 (5)	151 (3)
H(1C7)	712 (3)	1142 (6)	-236 (3)	H(C19)	782 (4)	552 (7)	272 (3)
H(2C7)	601 (4)	1008 (7)	-220 (3)	H(C20)	620 (4)	621 (7)	348 (4)
H(C8)	750 (4)	822 (7)	-78 (3)	H(C21)	523 (4)	915 (7)	312 (4)

Table 3. Bond lengths (Å): (a) uncorrected, with estimated standard deviations in parentheses, (b) corrected for libration

	(a)	(b)	(a)	(b)
N(1)-C(2)	1.474 (5)	1.484	C(10)-C(11)	1.265 (10) 1.267
C(2)-C(3)	1.530 (4)	1.539	N(13)-C(14)	1.314 (5) 1.316
C(3)-C(4)	1.537 (6)	1.549	C(14)-C(15)	1.409 (5) 1.413
C(3)-C(10)	1.517 (7)	1.528	C(15)-C(16)	1.360 (5) 1.365
C(4)-C(5)	1.532 (6)	1.543	C(16)-C(17)	1.428 (4) 1.431
C(4)-C(7)	1.535 (5)	1.539	C(17)-C(18)	1.418 (5) 1.423
C(5)-C(6)	1.517 (5)	1.528	C(18)-C(19)	1.367 (5) 1.370
C(6)-N(1)	1.485 (5)	1.492	C(19)-C(20)	1.396 (6) 1.400
C(7)-C(8)	1.535 (4)	1.546	C(20)-C(21)	1.357 (6) 1.362
C(8)-N(1)	1.491 (4)	1.500	C(21)-C(22)	1.421 (5) 1.423
C(8)-C(9)	1.530 (4)	1.536	C(22)-N(13)	1.366 (5) 1.371
C(9)-O(12)	1.416 (4)	1.426	C(22)-C(17)	1.428 (4) 1.432
C(9)-C(16)	1.524 (4)	1.528		

dihydroepiquinidine (Chekhlov, Kaluski, Struchkov, Małuszyńska & Kitaigorodskii, 1974) and quinidine in its salt with (-)-1,1'-dimethyl-3-ferrocenecarboxylic acid (Carter, McPhail & Sim, 1967) as shown by comparison of the corresponding torsion angles (Table 5). This stability of the conformation in the four different crystalline environments suggests that it may well persist in other media like aqueous or lipid solutions.

The potential energy as a function of torsion angles C(15)-C(16)-C(9)-O(12), O(12)-C(9)-C(8)-C(7), C(16)-C(9)-O(12)-H(O12) was calculated in the atom-atom approximation, with the program *EENY* written by S. Motherwell, using potential constants given by Giglio (1969). Three energy minima with approximately equal values were found (Lebioda & Oleksyn, 1979). Torsion angles corresponding to one of these minima agree well with the angles observed in the structure.

The bond lengths and angles in the quinoline moiety are in good agreement with those determined recently in 2-quinolinecarboxamide (Gdaniec, Jaskolski & Kosturkiewicz, 1977), biquinolyl (Lenner & Lindgren, 1976), and 8-quinolyl cyanomethyl sulphone (Harlow & Simonsen, 1976). In all these molecules the bond angle C(14)-N(13)-C(22) is, within experimental error, 117°, the value being 5° less than the corre-

Table 4. Bond angles (°), with estimated standard deviations in parentheses

C(8)-N(1)-C(2)	110.6 (3)	C(5)-C(6)-N(1)	110.9 (3)
C(8)-N(1)-C(6)	107.1 (3)	H(1C6)-C(6)-N(1)	106.7 (21)
C(6)-N(1)-C(2)	107.5 (3)	H(1C6)-C(6)-C(5)	103.6 (18)
C(3)-C(2)-N(1)	112.7 (3)	H(2C6)-C(6)-N(1)	100.9 (39)
H(1C2)-C(2)-N(1)	109.8 (35)	H(2C6)-C(6)-C(5)	125.4 (28)
H(1C2)-C(2)-C(3)	103.7 (25)	H(2C6)-C(6)-H(1C6)	108.2 (50)
H(2C2)-C(2)-N(1)	98.3 (32)	C(8)-C(7)-C(4)	108.1 (3)
H(2C2)-C(2)-C(3)	121.9 (27)	H(1C7)-C(7)-C(4)	110.2 (22)
H(2C2)-C(2)-H(1C2)	110.4 (42)	H(1C7)-C(7)-C(8)	110.4 (17)
C(4)-C(3)-C(2)	106.6 (3)	H(2C7)-C(7)-C(4)	117.9 (20)
C(10)-C(3)-C(2)	109.5 (3)	H(2C7)-C(7)-C(8)	107.5 (20)
C(10)-C(3)-C(4)	115.6 (4)	H(2C7)-C(7)-H(1C7)	102.4 (35)
H(C3)-C(3)-C(2)	109.8 (22)	N(1)-C(8)-C(9)	112.5 (2)
H(C3)-C(3)-C(4)	107.6 (25)	C(7)-C(8)-N(1)	110.1 (2)
H(C3)-C(3)-C(10)	107.7 (28)	C(7)-C(8)-C(9)	114.5 (3)
C(5)-C(4)-C(3)	107.7 (3)	H(C8)-C(8)-C(9)	100.4 (22)
C(7)-C(4)-C(3)	109.3 (3)	H(C8)-C(8)-N(1)	105.8 (26)
C(7)-C(4)-C(5)	107.9 (3)	H(C8)-C(8)-C(7)	112.9 (19)
H(C4)-C(4)-C(3)	110.1 (27)	C(8)-C(9)-O(12)	111.0 (2)
H(C4)-C(4)-C(5)	112.7 (27)	C(16)-C(9)-C(8)	109.3 (3)
H(C4)-C(4)-C(7)	109.1 (27)	C(16)-C(9)-O(12)	111.6 (3)
C(6)-C(5)-C(4)	108.7 (3)	C(8)-C(9)-H(C9)	107.5 (23)
H(1C5)-C(5)-C(4)	111.2 (30)	H(C9)-C(9)-O(12)	107.8 (23)
H(1C5)-C(5)-C(6)	116.1 (26)	C(16)-C(9)-H(C9)	109.6 (22)
H(2C5)-C(5)-C(4)	104.6 (47)	C(11)-C(10)-C(3)	126.5 (6)
H(2C5)-C(5)-C(6)	111.5 (32)	H(C10)-C(10)-C(8)	108.9 (5)
H(2C5)-C(5)-H(1C5)	104.2 (46)	H(C10)-C(10)-C(11)	78.5 (5)
H(1C11)-C(11)-C(10)	127.8 (7)	C(22)-C(17)-C(18)	118.0 (3)
H(2C11)-C(11)-C(10)	116.8 (7)	C(19)-C(18)-C(17)	120.7 (3)
H(2C11)-C(11)-H(1C11)	115.2 (7)	H(C18)-C(18)-C(17)	117.5 (21)
H(O12)-O(12)-C(9)	109.3 (37)	H(C18)-C(18)-C(19)	120.9 (20)
C(22)-N(13)-C(14)	116.6 (3)	C(20)-C(19)-C(18)	121.3 (4)
C(15)-C(14)-N(13)	124.7 (4)	H(C19)-C(19)-C(18)	121.5 (28)
H(C14)-C(14)-N(13)	114.1 (27)	H(C19)-C(19)-C(20)	117.1 (28)
H(C14)-C(14)-C(15)	120.9 (27)	C(21)-C(20)-C(19)	119.9 (4)
C(16)-C(15)-C(14)	120.0 (3)	H(C20)-C(20)-C(19)	114.7 (30)
H(C15)-C(15)-C(14)	122.2 (28)	H(C20)-C(20)-C(21)	125.3 (29)
H(C15)-C(15)-C(16)	117.8 (27)	C(22)-C(21)-C(20)	121.2 (4)
C(17)-C(16)-C(15)	118.0 (3)	H(C21)-C(21)-C(20)	119.0 (31)
C(15)-C(16)-C(9)	121.6 (3)	H(C21)-C(21)-C(22)	119.0 (32)
C(17)-C(16)-C(9)	120.4 (3)	C(21)-C(22)-N(13)	118.0 (3)
C(18)-C(17)-C(16)	124.4 (3)	C(21)-C(22)-C(17)	118.9 (3)
C(22)-C(17)-C(16)	117.6 (3)	C(17)-C(22)-N(13)	123.1 (3)

sponding angle in diprotonated cinchonine (Oleksyn *et al.*, 1978). This angle deformation, accompanied by the increase of the two adjacent angles C(15)-C(14)-N(13) and C(15)-C(22)-N(13), can be attributed to a repulsive interaction between the free electron pair at N(13) and the N(13)-C(22) and N(13)-C(14) bond electrons. Similar effects were reported by Gieren & Schanda (1977). The quinoline system is planar within experimental error, as shown in Table 6.

No important difference has been found between the bond lengths corrected for thermal motion and those

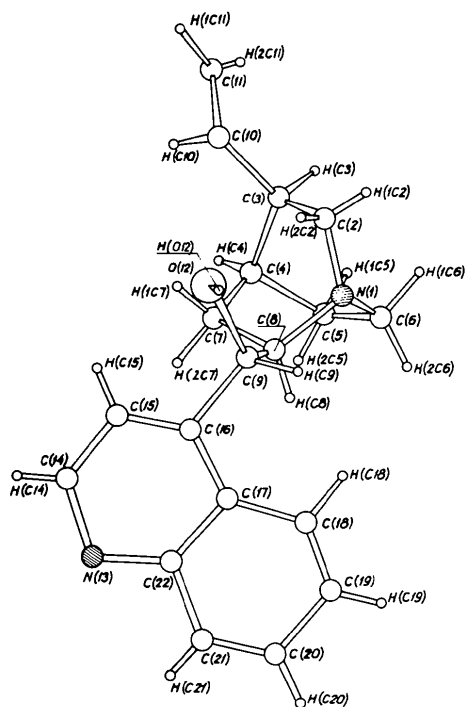


Fig. 1. A molecule of cinchonine showing the conformation and atom-numbering scheme.

Table 5. Comparison of selected torsion angles in the title compound (A), (cinchoninium)²⁺ cation (B), (+)-10-bromo-10,11-dihydroepiquinidine (C), and the quinidine salt of (-)-1,1'-dimethyl-3-ferrocene-carboxylic acid (D)

	(A)	(B)	(C)	(D)
(a) About the C(9)–C(8) bond				
C(16)–C(9)–C(8)–N(1)	–160.3	–167.3	–171.6	171.4
C(16)–C(9)–C(8)–C(7)	73.0	69.8	65.5	49.4
O(12)–C(9)–C(8)–C(7)	–50.6	–48.4	–167.9	–73.8
O(12)–C(9)–C(8)–N(1)	76.1	74.5	–45.0	48.3
O(12)–C(9)–C(8)–H(C8)	–171.8	–175.3	–	–
H(C9)–C(9)–C(8)–N(1)	–41.5	–49.8	–	–
H(C9)–C(9)–C(8)–H(C8)	70.5	60.4	–	–
C(16)–C(9)–C(8)–H(C8)	–48.3	–57.1	–	–
H(C9)–C(9)–C(8)–C(7)	–168.7	–172.7	–	–
(b) About the C(9)–C(16) bond				
O(12)–C(9)–C(16)–C(17)	–158.7	–158.8	–37.6	–166.4
O(12)–C(9)–C(16)–C(15)	23.4	23.2	137.9	17.8
H(C9)–C(9)–C(16)–C(15)	142.7	142.7	–	–
H(C9)–C(9)–C(16)–C(17)	–39.4	–39.4	–	–
C(8)–C(9)–C(16)–C(15)	–99.8	–97.0	–101.8	–109.2
C(8)–C(9)–C(16)–C(17)	78.1	80.9	82.7	66.5
(c) About the line C(4)–N(1)				
C(3)–C(4)–N(1)–C(2)	9.1	12.5	10.8	9.5
C(3)–C(4)–N(1)–C(8)	132.0	136.2	133.4	135.8
C(3)–C(4)–N(1)–C(6)	–110.0	–107.5	–107.9	–110.9
C(7)–C(4)–N(1)–C(8)	11.0	14.0	12.1	14.9
C(7)–C(4)–N(1)–C(6)	129.0	129.3	130.7	128.1
C(7)–C(4)–N(1)–C(2)	–111.9	–109.7	–110.6	–111.4
C(5)–C(4)–N(1)–C(6)	9.1	12.5	10.6	6.8
C(5)–C(4)–N(1)–C(2)	128.2	130.9	129.3	127.3
C(5)–C(4)–N(1)–C(8)	–108.9	–105.3	–108.0	–106.4

References: (A) This work. (B) Oleksyn *et al.* (1978). (C) Chekhlov *et al.* (1974). (D) Carter *et al.* (1967).

determined in the protonated quinuclidine (Oleksyn *et al.*, 1978). The more significant changes of bond angles are consistent with the change of repulsive interaction between the free pair at N(1) and electrons in the N(1)–C(2), N(1)–C(8) and N(1)–C(6) bonds. A co-operative effect is connected with the change of the electron density along these bonds. The free electron pair at N(1) diminishes the electron density in the vicinity of N(1) thus reducing the repulsion between the electrons of the bonds. This leads to a more tetrahedral arrangement of the bonds around N(1) in comparison to the slightly flattened tetrahedron observed in the protonated quinuclidine.

The results of a rigid-body-motion analysis, carried out by the method of Schomaker & Trueblood (1968), for a model comprising the whole molecule and for the quinoline and quinuclidine moieties vibrating independently are reported in Table 7. The results show that the whole molecule cannot be regarded as rigid because of strong internal libration of the quinuclidine around the C(8)–C(9) bond and independent vibrations of the vinyl group C(10)–C(11). An estimate of the tensor of internal vibration was found by subtraction of the

Table 6. Deviations (Å) of the atoms from the least-squares plane in the quinoline moiety

The equation of the plane is $4.7030x + 3.0731y + 6.8561z = 7.2830$. Coordinates x, y, z refer to crystal axes a, b, c .

N(13)	–0.0008	C(18)	0.0085
C(14)	0.0074	C(19)	0.0051
C(15)	–0.0017	C(20)	–0.0113
C(16)	–0.0188	C(21)	–0.0060
C(17)	0.0087	C(22)	0.0088

Table 7. The results of the rigid-body-motion analysis

Least-squares fit to rigid-body motion for cinchonine (A), and the quinoline (B) and quinuclidine (C) moieties

	R.m.s. $U_{ij} - U_{ijRBM}^2$	$\langle \sigma(U_{ij}) \rangle$	$R = (\sum U_{ij} - U_{ijRBM}^2) / \sum U_{ij}^2$
(A)	0.0089 Å ²	0.0018 Å ²	0.1721
(B)	0.0024	0.0015	0.0449
(C)	0.0019	0.0016	0.0361

Rigid-body T and L elements referred to the axes a^*, b, c . (Elements of the S matrix were zero within 2σ range.)

	T × 10 ⁴ (Å ²)			L (deg ²)		
(A)	391 (33)	–27 (26)	–49 (22)	8.5 (1.0)	0.0 (0.7)	–2.6 (1.3)
		401 (28)	23 (20)		6.6 (1.0)	2.0 (1.0)
			411 (21)			18.4 (2.6)
(B)	457 (12)	–5 (10)	–14 (10)	6.6 (1.0)	3.3 (0.7)	–0.7 (0.7)
		485 (10)	–24 (9)		6.6 (1.3)	–3.3 (1.0)
			380 (10)			14.8 (1.3)
(C)	427 (10)	–30 (9)	30 (8)	7.5 (1.0)	2.0 (1.0)	2.6 (1.3)
		444 (10)	28 (8)		17.4 (1.3)	11.8 (1.3)
			392 (8)			35.8 (2.0)

Eigenvalues and eigenvectors for the tensor $L_c - L_a$ (value for the a_{11} element was taken as zero)

24.5 deg ²	0.471	0.590	0.808
4.3	–0.342	–0.751	0.565
–0.7	0.938	–0.303	0.166

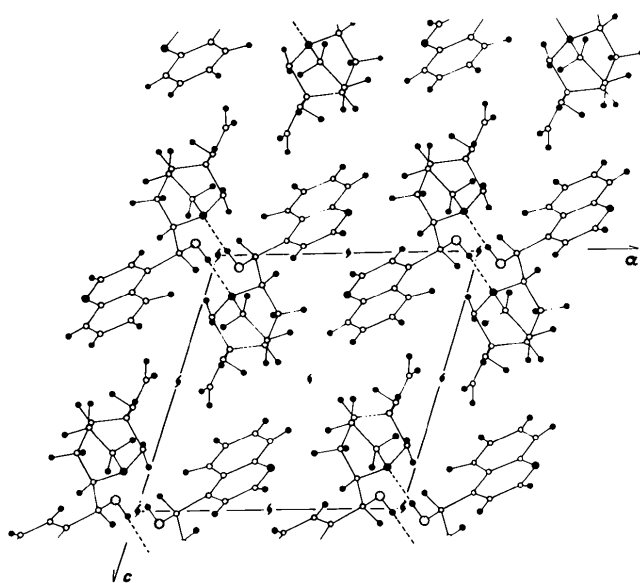


Fig. 2. The packing of the molecules viewed along the *b* axis.

whole molecule tensor from that for the quinuclidine. The angle between the eigenvector corresponding to the maximal eigenvalue and the C(8)–C(9) bond is 16° .

The packing of molecules in the structure is depicted in Fig. 2. Along twofold screw axes, chains of hydrogen-bonded molecules can be seen. The neighbouring chains are held together only by van der Waals forces. Each molecule of a chain interacts with two others forming hydrogen bonds: $N(1) \cdots H(O12^i) - O(12^i)$ and $(N1^{ii}) \cdots H(O12) - O(12)$ where $(i) = 2 - x$,

$-\frac{1}{2} + y, -z$ and $(ii) = 2 - x, \frac{1}{2} + y, -z$. The bond length is $2.75(3) \text{ \AA}$ and the angle $N(1) \cdots H(O12) - O(12)$ $171(2)^\circ$.

Thus, in terms of the classification given by Leiserowitz & Weinstein (1975), the structure of cinchonine can be described as the chiral packing arrangement of one-dimensional chiral hydrogen-bonded arrays.

References

- CARTER, O. L., MCPHAIL, A. T. & SIM, G. A. (1967). *J. Chem. Soc. A*, pp. 365–373.
- CHEKHLOV, A. N., KALUSKI, Z., STRUCHKOV, YU. T., MALUSZYŃSKA, G. & KITAIGORODSKII, A. I. (1974). *J. Struct. Chem. (USSR)*, **15**, 780–784.
- GDANIEC, M., JASKOLSKI, O. & KOSTURKIEWICZ, Z. (1977). *Acta Cryst.* **B33**, 2284–2286.
- GIEREN, A. & SCHANDA, F. (1977). *Acta Cryst.* **B33**, 2554–2559.
- GIGLIO, E. (1969). *Nature (London)*, **222**, 339–341.
- HARLOW, R. L. & SIMONSEN, S. H. (1976). *Acta Cryst.* **B32**, 2690–2693.
- HIRSHFELD, F. L. & RABINOVICH, D. (1973). *Acta Cryst.* **A29**, 510–513.
- LEBIODA, L. & OLEKSYN, B. (1979). To be published.
- LEISEROWITZ, L. & WEINSTEIN, M. (1975). *Acta Cryst.* **B31**, 1463–1466.
- LENNER, M. & LINDGREN, O. (1976). *Acta Cryst.* **B32**, 1903–1905.
- OLEKSYN, B. J., STADNICKA, K. M. & HODOROWICZ, S. H. (1978). *Acta Cryst.* **B34**, 811–816.
- PARETZKIN, B. (1956). *Acta Cryst.* **9**, 201–202.
- SCHOMAKER, V. & TRUEBLOOD, K. N. (1968). *Acta Cryst.* **B24**, 63–76.
- SHELDRIK, G. M. (1975). *SHELX*. Program for crystal structure determination. Univ. of Cambridge, England.

Acta Cryst. (1979). **B35**, 444–447

Structure of 1-Ethyl-2,4,4,6-tetramethyl-1,4-dihydro-3,5-pyridinedicarbonitrile

BY K. HUML AND J. JEČNÝ

Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences, 162 06 Praha 6, Czechoslovakia

AND L. KUTSCHABSKY AND G. RECK

Zentralinstitut für Physikalische Chemie, Akademie der Wissenschaften der DDR, 1199 Berlin-Adlershof, German Democratic Republic

(Received 19 September 1978; accepted 24 October 1978)

Abstract

The structure of $C_{13}H_{17}N_3$ has been determined simultaneously by direct methods and the convolution method with residual analysis. Block-diagonal least-squares refinement led to $R = 0.053$ and $R_w = 0.074$

for 968 observed reflexions measured on a Syntex *P2*₁ automated diffractometer. The cell is orthorhombic, space group *Pnma*, with $a = 11.394(4)$, $b = 11.996(8)$, $c = 9.247(6) \text{ \AA}$, $V = 1264(1) \text{ \AA}^3$, $Z = 4$. The six-membered ring has the envelope form.

0567-7408/79/020444-04\$01.00

© 1979 International Union of Crystallography