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

$-\frac{1}{2} + y, -z$ and (ii) $= 2 - x, \frac{1}{2} + y, -z$. The bond length is $2 \cdot 75$ (3) Å and the angle $N(1) \cdots H(O12)-O(12)$ 171 (2)°.

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.

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) $= 2 - x,$

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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

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 $R = 0 \cdot 053$ and $R_w = 0 \cdot 074$ for 968 observed reflexions measured on a Syntex $P2_1$ automated diffractometer. The cell is orthorhombic, space group $Pnma$, with $a = 11 \cdot 394$ (4), $b = 11 \cdot 996$ (8), $c = 9 \cdot 247$ (6) Å, $V = 1264$ (1) Å^3, $Z = 4$. The six-membered ring has the envelope form.

Introduction

Knowledge of the detailed geometry of 1,4-dihydro-pyridine compounds is needed for the investigation of the structural similarities between 3-amides of type I and the reduced form of the co-enzyme NADH and because of the constantly increasing practical importance of 3,5-difunctional derivatives of type II arising from variations of the Hantzsch synthesis (Eisner & Kuthan, 1972).
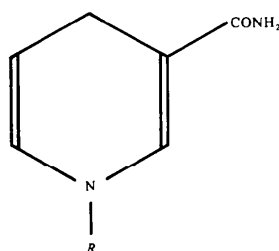
(Ia) R = n-C₃H₇
(Ib) R = C₆H₅CH₂
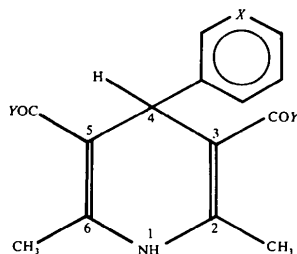
(IIa) X = N, Y = CH₃
(IIb) X = CH, Y = OC₂H₅

A characteristic feature of the molecular structure of amides (Ia,b) in crystals is the planarity of the heterocyclic ring with a rotation of the amide group from its plane by about 22 and 4° respectively (Karle, 1961; Koyama, 1963; Koyama, Robinson & Laves, 1963). Contrarily, the heterocyclic system of the 3,5-dicarbonyl derivatives (IIa,b) exhibits the boat conformation (Krajewski, Urbanczyk-Lipkowska & Gluzinski, 1977; Mishnev, Shvec, Bleidelis, Duburs, Sausina & Lusis, 1977): for the 3,5-diketone (IIa) plane C(3), C(4), C(5) makes an angle of 20·4° with plane C(2), C(3), C(5), C(6), and plane C(2), N(1), C(6) forms an angle of 12·3° with plane C(2), C(3), C(5), C(6) (Krajewski et al., 1977); for the 3,5-diester (IIb) these angles are 28·4 and 15·7° respectively (Mishnev et al., 1977). One may assume that these differences are due to the bulkiness of the substituents in positions 3, 4 and 5 in the case of compounds (IIa,b), which makes the planar conformation of the 1,4-dihydropyridine ring less advantageous from the energetic point of view. Accordingly, the EHT and CNDO/2 calculations of derivative (I) (R = CH₃) predict a minimal energy difference between the planar and boat conformations (Kuthan & Musil, 1975,

1977). In order to obtain greater insight into these factors, the title compound, which evidently exhibits smaller steric requirements for the substituents in positions 3, 4 and 5 compared to those of (IIa,b) investigated earlier, was subjected to X-ray analysis. Another remarkable feature of this compound is that it belongs to a group of analogous 3,5-dicarbonitriles characterized by intensive fluorescence in the crystal form (Kuthan & Paleček, 1974), and which are applied in scintillation techniques (Dlouhý, Kuthan, Paleček, & Šrámek, 1971).

Experimental

The title compound forms transparent crystals. The sample was prepared by Paleček & Kuthan (1976). The molecular formula was confirmed by elemental analysis and mass spectroscopy.

Crystal data

$C_{13}H_{17}N_3$, orthorhombic, $Pnma$, $a = 11\cdot394$ (4), $b = 11\cdot996$ (8), $c = 9\cdot247$ (6) Å, $V = 1264$ (1) Å³, $Z = 4$, $D_c = 1\cdot130$, $D_m = 1\cdot133$ (3) Mg m⁻³ (flotation in aqueous saccharose solution), FW 215·16, m.p. 425–426 K, $F(000) = 464$, μ(Mo $K\alpha$) = 0·0594 mm⁻¹.

The preliminary dimensions of the unit cell and the systematic absences ($0kl$: $k + l$ odd; $hk0$: h odd) were determined from oscillation and Weissenberg photographs. The possible noncentrosymmetric space group $Pna2_1$ was rejected because of the absence of optical second-harmonic generation (Dougherty & Kurtz, 1976). During the least-squares refinement $Pnma$ was confirmed, giving more realistic bond distances and valence angles.

The final unit-cell parameters (15 reflexions refined) and intensities were measured with an automatic Syntex $P2_1$ diffractometer (Mo $K\alpha$ radiation, $\lambda = 0\cdot71069$ Å, graphite monochromator). The crystal investigated ($1\cdot0 \times 1\cdot0 \times 0\cdot6$ mm) was placed on the goniometer head in a general position. Each reflexion was measured for two different ψ angles to detect and eliminate the possible influence of the Renninger effect. In the range up to $\sin\theta/\lambda = 0\cdot595$ Å⁻¹, 1177 independent reflexions were measured (θ–2θ scan); 968 were regarded as observed ($I_o > 1\cdot96\sigma_I$). No corrections for extinction or absorption were made. For the Lp correction formula and other details of measurements see Langer & Huml (1978).

Structure determination and refinement

The positions of all nonhydrogen atoms were determined simultaneously by MULTAN (Main, Woolfson, Lessinger, Germain & Declercq, 1974) and the con-

volution method (Hoppe & Paulus, 1967) with the residual analysis *CORDAL* (Kutschabsky & Reck, 1976). The subsequent difference map revealed all the H atoms.

The structure was refined using observed reflexions by the block-diagonal least-squares program *NRC*-10 (Ahmed, Hall, Pippy & Huber, 1966). The function minimized was $\sum w\Delta^2$, where $\Delta = ||F_o| - |F_c||$ and $w^{-1} = \sigma_F^2 + (kF_o)^2$. The coefficient k was finally set to 0·02 satisfying the condition of independent $w\Delta^2$ as a function of $\sin\theta$ and $|F_o|$ and giving a straight line through the origin in the normal δR plot (Abrahams & Keve, 1971).

The nonhydrogen atoms were refined anisotropically, H atoms isotropically. The atomic factors for nonhydrogen atoms were taken from *International Tables for X-ray Crystallography* (1974), those for H atoms from Stewart, Davidson & Simpson (1965). The refinement was terminated when all atomic parameter shifts dropped below 0·3 e.s.d.'s for nonhydrogen atoms and 0·6 e.s.d.'s for H atoms; the final $R = \sum \Delta/\sum |F_o| = 0·053$ and $R_w = [\sum w\Delta^2/\sum w|F_o|^2]^{1/2} = 0·074$.* The atomic parameters are given in Tables 1

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34034 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Final positional parameters and their e.s.d.'s* ($\times 10^4$) *for the nonhydrogen atoms*

	x	y	z
C(1)	362 (2)	2500	2172 (2)
C(2)	946 (1)	1487 (1)	1517 (2)
C(3)	1783 (1)	1500 (1)	479 (2)
C(4)	530 (3)	2500	3818 (3)
C(5)	−959 (2)	2500	1810 (3)
C(6)	528 (1)	439 (1)	2042 (2)
C(7)	2314 (1)	443 (1)	−89 (2)
C(8)	2966 (2)	2500	−1355 (2)
C(9)	2250 (3)	2500	−2736 (3)
N(10)	2216 (1)	2500	−55 (2)
N(11)	138 (2)	−362 (1)	2512 (2)

Table 2. *Final parameters and their e.s.d.'s for the* H *atoms*

Fractional coordinates are $\times 10^3$.

	x	y	z	B (Å²)
H(41)	26 (2)	179 (1)	423 (2)	7·8 (5)
H(42)	122 (2)	250	415 (3)	10·8 (9)
H(51)	−126 (2)	180 (1)	224 (2)	7·9 (5)
H(52)	−100 (2)	250	67 (2)	6·1 (6)
H(71)	229 (1)	37 (1)	−117 (1)	5·8 (4)
H(72)	191 (1)	−22 (1)	34 (1)	7·2 (4)
H(73)	318 (2)	39 (2)	20 (2)	8·4 (5)
H(81)	339 (1)	182 (1)	−130 (1)	5·7 (4)
H(91)	174 (1)	177 (1)	−286 (2)	7·2 (5)
H(92)	283 (2)	250	−354 (3)	10·3 (9)

and 2. The highest residual maximum on the corresponding difference map was 0·16 e Å⁻³; the minimum was −0·18 e Å⁻³.

Description of the structure

The numbering scheme with bond distances is given in Fig. 1. Valence angles are in Table 3. All the bond lengths and valence angles are close to the expected values. Only H(42) situated on the mirror plane shows a misplacement. Several attempts to set H(42) in a more convenient position during the least-squares refinement always led to the coordinates in Table 2.
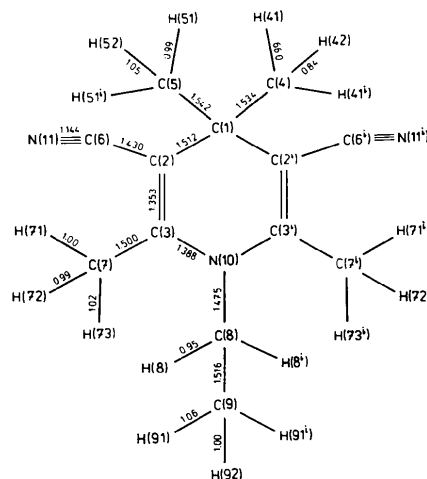

Fig. 1. Bond lengths (Å) with the numbering scheme. The e.s.d.'s of bond lengths of nonhydrogen atoms are 0·002 or 0·003 Å; those for H atoms are 0·01 or 0·02 Å [except 0·03 Å for H(42) and H(92)]. The index (i) denotes atoms in the crystallographically equivalent position x, $0·5 - y$, z. The numbering scheme was chosen to reflect the mirror symmetry of the molecule.
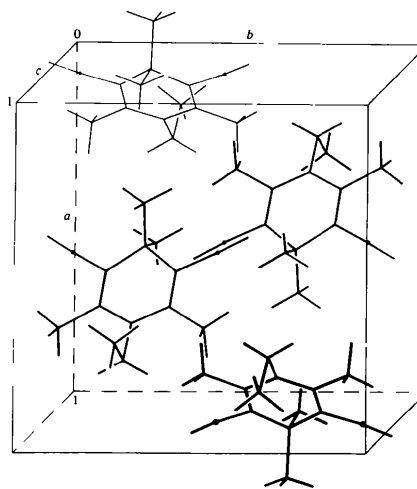

Fig. 2. Perspective view of the crystal structure of $C_{13}H_{17}N_3$.

Table 3. *Bond angles and their e.s.d.'s* (°)

C(2)–C(1)–C(2ⁱ)	106·9 (1)	C(1)–C(5)–H(51)	104 (1)
C(2)–C(1)–C(4)	110·0 (1)	C(1)–C(5)–H(52)	105 (1)
C(2)–C(1)–C(5)	110·1 (1)	H(51)–C(5)–H(51ⁱ)	115 (1)
C(4)–C(1)–C(5)	109·7 (2)	H(51)–C(5)–H(52)	113 (1)
C(1)–C(2)–C(3)	125·8 (1)	C(3)–C(7)–H(71)	114 (1)
C(1)–C(2)–C(6)	115·1 (1)	C(3)–C(7)–H(72)	110 (1)
C(3)–C(2)–C(6)	119·1 (1)	C(3)–C(7)–H(73)	110 (1)
C(2)–C(3)–C(7)	121·6 (1)	H(71)–C(7)–H(72)	108 (1)
C(2)–C(3)–N(10)	120·9 (1)	H(71)–C(7)–H(73)	106 (1)
C(7)–C(3)–N(10)	117·5 (1)	H(72)–C(7)–H(73)	107 (1)
C(2)–C(6)–N(11)	175·5 (2)	C(9)–C(8)–H(8)	109 (1)
C(9)–C(8)–N(10)	112·0 (2)	N(10)–C(8)–H(8)	105 (1)
C(3)–N(10)–C(3ⁱ)	119·6 (1)	H(8)–C(8)–H(8ⁱ)	118 (1)
C(3)–N(10)–C(8)	119·7 (1)	C(8)–C(9)–H(91)	113 (1)
C(1)–C(4)–H(41)	110 (1)	C(8)–C(9)–H(92)	106 (1)
C(1)–C(4)–H(42)	119 (2)	H(91)–C(9)–H(91ⁱ)	111 (1)
H(41)–C(4)–H(41ⁱ)	120 (2)	H(91)–C(9)–H(92)	107 (2)
H(41)–C(4)–H(42)	99 (2)		

Table 4. *Weighted mean planes*

Atoms whose deviations and e.s.d.'s ($\text{Å} \times 10^3$) are marked with an asterisk have been excluded from the plane calculation. Cartesian coordinate system: X parallel to **a**, Y parallel to **b**, Z parallel to **c**. Planarity is characterized by the χ^2 test.

Plane (I): $-0.7088X - 0.7054Z + 1.7533 = 0$
Plane (II): $-0.7025X - 0.7117Z + 1.7430 = 0$
Plane (III): $-0.7059X - 0.7083Z + 1.7491 = 0$
Plane (IV): $-0.6954X - 0.7186Z + 1.7444 = 0$
Plane (V): $-0.7011X - 0.7131Z + 1.7555 = 0$

	(I)	(II)	(III)	(IV)	(V)
C(1)	45 (4)*	24 (2)	36 (2)	15 (2)	36 (2)
C(2)	0 (3)	–13 (1)	–5 (1)	–13 (1)	–1 (1)
C(3)	1 (3)	0 (1)	1 (1)	13 (1)	15 (1)
C(6)	–5 (2)*	–24 (2)*	–13 (2)	–31 (2)*	–13 (2)
C(7)	–58 (2)*	–51 (2)*	–54 (2)*	30 (2)	–35 (2)
N(10)	–1 (3)	5 (2)	2 (2)	25 (2)	21 (2)
N(11)	3 (2)*	–21 (2)*	–7 (2)*	–34 (2)*	–11 (2)
χ^2	0·28	295	444	1274	1692

Fig. 2 gives a perspective view of the molecular packing. No contacts shorter than the sum of the van der Waals radii were found. Weighted mean planes calculated for different sets of atoms are summarized in Table 4. All their normals are parallel to within $1.1°$. The six-membered ring has a slight envelope form with C(1) deviating in the same direction as C(8) and C(9). This is in good agreement with the results of Martínez-Ripoll, Cano, García-Blanco, Martínez-Carrera & Gündel (1977), and leads to the tetragonal configuration and chemical nonequivalency of the methyl groups adjacent to C(1). The other C atoms of the ring are in the usual trigonal configuration. However, C(8) deviates from the ring plane and thus disturbs the trigonal configuration; this is perhaps due to the steric

hindrance between the ethyl substituent and the neighbouring methyl groups.

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