synthesis calculated with reflexions having $\sin\theta/\lambda < 0.5$ Å^{-1} showed all H atoms as highest peaks of the map; final refinement with fixed isotropic temperature factors for H atoms and unit weights led to $R = 0.051$; max. and average shift/error in final LS cycle 2.68 and 0.21 (including H atoms); final difference synthesis had no electron density > 0.31 and < -0.28 e Å^{-3}. No correction for secondary extinction. Most of the calculations performed with *XRAY*76 (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976).

Discussion. Table 1* contains the final atomic parameters; Fig. 1 (Johnson, 1965) shows the geometry of the structure and the atom labelling. Bond lengths and angles together with their e.s.d.'s are in Table 2.

Two asymmetrically bifurcated hydrogen bonds of the type reported by Monge, Martínez-Ripoll & García-Blanco (1978) have been located. The geometrical features of the hydrogen-bond network, calculated with *PARST*5 (Nardelli, Musatti, Domiano & Andreetti, 1965), are shown in Fig. 2.

* Lists of structure amplitudes, anisotropic thermal parameters, H-atom parameters and bond lengths and angles involving H atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39832 (42 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

As was expected, the initial pyrazole ring has experienced an expansion in the course of the reaction leading to a dihydropyrimidine derivative.

Through the crystal-structure determination it has been established that of the two diastereoisomers, (*RR,SS*) and (*RS,SR*), that isolated as the salt was the (*RS,SR*).

References

ELGUERO, J., DE LA HOZ, A. & PARDO, C. (1984). Private communication.

International Tables for X-ray Crystallography (1974). Vol. IV, pp. 72–98. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.

MAIN, P., LESSINGER, L., WOOLFSON, M. M., GERMAIN, G. & DECLERCQ, J.-P. (1977). *MULTAN*77. *A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.

MONGE, A., MARTÍNEZ-RIPOLL, M. & GARCÍA-BLANCO, S. (1978). *Acta Cryst.* B**34**, 2847–2850.

NARDELLI, M., MUSATTI, A., DOMIANO, P. & ANDRETTI, G. D. (1965). *Ric. Sci.* **35**, 807–810.

STEWART, J. M., MACHIN, P. A., DICKINSON, C. W., AMMON, H. L., HECK, H. & FLACK, H. (1976). The *XRAY*76 system. Tech. Rep. TR-446. Computer Science Center, Univ. of Maryland, College Park, Maryland.

Acta Cryst. (1985). C**41**, 411–413

Structure of Diethyl 1,4-Dihydro-2,4,6-trimethyl-3,5-pyridinedicarboxylate, $C_{14}H_{21}NO_4$

BY S. FORTIER, M. E. FRASER, N. J. MOORE, Y. S. PARK AND R. A. WHITNEY

Department of Chemistry, Queen's University, Kingston, Canada K7L 3N6

AND G. S. MARKS

Department of Pharmacology and Toxicology, Queen's University, Kingston, Canada K7L 3N6

(*Received* 22 *June* 1984; *accepted* 17 *October* 1984)

Abstract. $M_r = 267.3$, monoclinic, $P2_1/a$, $a = 16.921$ (3), $b = 7.483$ (2), $c = 11.429$ (2) Å, $\beta = 94.24$ (2)°, $V = 1443.2$ Å^3, $Z = 4$, $D_x = 1.230$ g cm^{-3}, λ(Cu $K\alpha$) = 1.54184 Å, $\mu = 7.01$ cm^{-1}, $F(000) = 576$, $T = 293$ K, final $R = 0.056$ for 1371 observed reflections. The dihydropyridine ring adopts a flat-boat conformation. The C(4) methyl substituent is approximately perpendicular to the dihydropyridine ring. The two ethoxycarbonyl groups are twisted in opposite directions so that the molecule does not have mirror symmetry.

Introduction. In recent years 1,4-dihydro-3,5-pyridinedicarboxylates have become of great interest due to their biological activity. The 4-aryl derivatives represent a new class of highly active calcium antagonists (Bossert, Meyer & Wehinger, 1981) while the 4-alkyl derivatives exhibit porphyrinogenic activity in a variety of animals (Marks, 1978). In this latter case the nature of the biological activity observed is dependent on the structure of the 4-alkyl group (Augusto, Beilan & Ortiz de Montellano, 1982). Since it is known that 1,4-dihydro-3,5-pyridinedicarboxylates can adopt a ring

0108-2701/85/030411-03$01.50

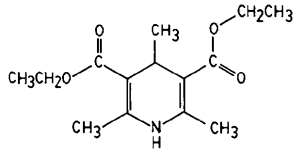
© 1985 International Union of Crystallography

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters for the non-*H *atoms with e.s.d.'s in parentheses*

$B_{eq} = \frac{4}{3}\sum_i\sum_j\beta_{ij}(\mathbf{a}_i.\mathbf{a}_j)$.

	x	y	z	B_{eq}(Å^2)
O(1)	0·3161 (2)	0·4077 (4)	0·4131 (3)	8·46 (8)
O(2)	0·3075 (2)	0·6896 (4)	0·3558 (2)	7·02 (7)
O(3)	0·1352 (2)	0·9136 (3)	0·0350 (2)	5·55 (6)
O(4)	0·0766 (1)	0·7290 (3)	−0·0968 (2)	4·82 (5)
N(1)	0·1656 (2)	0·2964 (3)	0·1055 (3)	4·49 (6)
C(2)	0·1352 (2)	0·4324 (4)	0·0347 (3)	3·93 (7)
C(3)	0·1459 (2)	0·6037 (4)	0·0718 (3)	3·67 (6)
C(4)	0·1836 (2)	0·6439 (4)	0·1929 (3)	4·05 (7)
C(5)	0·2307 (2)	0·4861 (5)	0·2446 (3)	4·14 (7)
C(6)	0·2166 (2)	0·3197 (4)	0·2032 (3)	4·24 (7)
C(7)	0·2523 (2)	0·1479 (5)	0·2492 (3)	5·63 (9)
C(8)	0·0941 (2)	0·3635 (5)	−0·0772 (3)	5·27 (9)
C(9)	0·1203 (2)	0·7622 (4)	0·0036 (3)	3·99 (7)
C(10)	0·0465 (2)	0·8812 (5)	−0·1642 (3)	4·85 (8)
C(11)	0·0051 (2)	0·8140 (5)	−0·2742 (3)	5·79 (9)
C(12)	0·1204 (2)	0·6988 (5)	0·2758 (3)	5·59 (9)
C(13)	0·2881 (2)	0·5178 (5)	0·3452 (3)	5·14 (8)
C(14*A*)	0·3578 (4)	0·762 (1)	0·4596 (5)	5·8 (2)
C(15*A*)	0·4261 (6)	0·804 (2)	0·4189 (8)	10·0 (3)
C(14*B*)	0·3647 (8)	0·702 (1)	0·4461 (9)	11·0 (3)
C(15*B*)	0·3948 (7)	0·893 (1)	0·4529 (8)	10·2 (3)

conformation that varies from planar, as in the case of diethyl 2,6-dihydro-3,5-pyridinedicarboxylate (Lenstra, Petit, Dommisse & Alderweireldt, 1979), to a boat conformation in which the C(4) substituent is nearly perpendicular to the dihydropyridine ring, as in the case of diethyl 1,4-dihydro-2,6-dimethyl-4-phenyl-3,5-pyridinedicarboxylate (Hempel & Gupta, 1978), it is of interest to study the effect of C(4) alkyl substituents on the ring conformation. In the present study the title compound (I), having a C(4) methyl substituent, has been examined.



(I)

Experimental. Colourless, plate-shaped crystal, specimen 0·33 × 0·25 × 0·07 mm; Enraf–Nonius CAD-4 diffractometer, graphite-monochromatized Cu $K\alpha$; cell parameters from least squares applied to 24 reflections with $12{\cdot}6 < \theta < 24{\cdot}8°$; 2131 unique reflections, 1371 considered observed at $3\sigma(I)$ level, h 0→18, k 0→8, l −12→12, $\theta < 60°$, ω–2θ scans; three standard reflections monitored after every 7200 s of exposure, max. variation in intensity −9·9%; Lp correction, decay correction, absorption ignored. Initial attempts to solve the structure, using *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980), failed. The density map gave a so-called chicken-wire solution. As this suggested that the molecule was properly oriented but incorrectly located in the unit cell, the space group was relaxed to $P1$. A ten-atom fragment was used for Karle recycling and a further E map showed the four molecules. From those, it was then possible to determine the correct position of the molecule in space group $P2_1/a$. Difference Fourier maps revealed positions of 14 H atoms, remaining ones calculated. Full-matrix least-squares refinement minimizing $\sum w||F_o| - |F_c||^2$, where $w = 4F^2/[\sigma^2(F^2) + (0{\cdot}06F^2)^2]$, anisotropic temperature factors for non-H atoms. H atoms, assigned isotropic temperature factors equal to 1·2 times equivalent isotropic value of parent atom, included in calculations but not refined. Scattering factors those of Cromer & Waber (1974). Correction for isotropic secondary-extinction effect included in refinement, $g = 1{\cdot}78 \times 10^{-6}$. Final $R = 0{\cdot}056$, $R_w = 0{\cdot}074$, $S = 1{\cdot}79$ for all observed reflections; final max. Δ/σ 0·07, final max. and min. $\Delta\rho$ excursions 0·24 and −0·20 e Å^{-3}; calculations performed on a PDP 11/23 computer using Enraf–Nonius *SDP* (Frenz, 1979) and *ORTEP* (Johnson, 1965).

Discussion. The atomic parameters are given in Table 1,* and a view of the molecule is shown in Fig. 1. Bond lengths and angles are given in Table 2.

Orientational disorder was observed in one of the two ethoxycarbonyl groups. Two positions for the corresponding C_2H_5 [C(14*A*)–C(15*A*) and C(14*B*)–C(15*B*)] were refined, each being assigned an occupancy of 0·50. Pertinent torsional angles are listed in Table 2. The 1,4-dihydropyridine ring adopts a flat-boat conformation. The dihedral angles between the plane defined by atoms C(2)–C(3)–C(5)–C(6) and the planes defined by C(2)–N(1)–C(6) and by C(3)–C(4)–C(5) are 8·9 (5) and 17·2 (5)° respectively. The conformation observed was also reported for 1,4-dihydro-*N*-phenylnicotinamide (Karle, 1961), 3,5-diacetyl-1,4-dihydro-2,6-dimethyl-4-(3-pyridyl)-pyridine (Krajewski, Urbańczyk-Lipkowska &

* Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39839 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

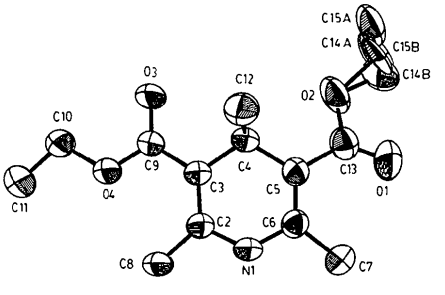


Fig. 1. *ORTEP* diagram (Johnson, 1965) and atom-numbering scheme. Ellipsoids are drawn at the 50% probability level.

Table 2. *Bond distances* (Å), *bond angles* (°) *and selected torsion angles* (°)

O(1)–C(13)	1·205 (3)	C(3)–C(4)	1·510 (3)
O(2)–C(13)	1·330 (4)	C(3)–C(9)	1·467 (3)
O(2)–C(14*A*)	1·510 (13)	C(4)–C(5)	1·519 (4)
O(2)–C(14*B*)	1·37 (2)	C(4)–C(12)	1·537 (4)
O(3)–C(9)	1·210 (3)	C(5)–C(6)	1·347 (4)
O(4)–C(9)	1·341 (3)	C(5)–C(13)	1·468 (4)
O(4)–C(10)	1·446 (3)	C(6)–C(7)	1·499 (4)
N(1)–C(2)	1·376 (3)	C(10)–C(11)	1·481 (4)
N(1)–C(6)	1·371 (3)	C(14*A*)–C(15*A*)	1·32 (2)
C(2)–C(3)	1·358 (3)	C(14*B*)–C(15*B*)	1·52 (2)
C(2)–C(8)	1·501 (4)		
C(13)–O(2)–C(14*A*)	122·8 (6)	C(4)–C(5)–C(13)	118·5 (2)
C(13)–O(2)–C(14*B*)	107·1 (8)	C(6)–C(5)–C(13)	120·9 (3)
C(9)–O(4)–C(10)	117·4 (2)	N(1)–C(6)–C(5)	119·2 (2)
C(2)–N(1)–C(6)	124·8 (2)	N(1)–C(6)–C(7)	112·9 (2)
N(1)–C(2)–C(3)	118·6 (2)	C(5)–C(6)–C(7)	127·8 (2)
N(1)–C(2)–C(8)	112·1 (2)	O(3)–C(9)–O(4)	121·1 (2)
C(3)–C(2)–C(8)	129·3 (2)	O(3)–C(9)–C(3)	123·5 (2)
C(2)–C(3)–C(4)	120·8 (2)	O(4)–C(9)–C(3)	115·3 (2)
C(2)–C(3)–C(9)	124·7 (2)	O(4)–C(10)–C(11)	108·1 (2)
C(4)–C(3)–C(9)	114·5 (2)	O(1)–C(13)–O(2)	121·3 (3)
C(3)–C(4)–C(5)	112·0 (2)	O(1)–C(13)–C(5)	126·9 (3)
C(3)–C(4)–C(12)	110·6 (2)	O(2)–C(13)–C(5)	111·8 (3)
C(5)–C(4)–C(12)	109·7 (2)	O(2)–C(14*A*)–C(15*A*)	105·4 (9)
C(4)–C(5)–C(6)	120·5 (2)	O(2)–C(14*B*)–C(15*B*)	109 (2)
C(6)–N(1)–C(2)–C(3)	−10·5 (5)	C(3)–C(4)–C(5)–C(6)	−20·5 (4)
C(2)–N(1)–C(6)–C(5)	9·7 (5)	C(4)–C(5)–C(6)–N(1)	7·2 (5)
C(2)–C(3)–C(4)–C(5)	19·7 (4)	C(2)–C(3)–C(4)–C(12)	−103·0 (4)
N(1)–C(2)–C(3)–C(4)	−5·7 (5)	C(12)–C(4)–C(5)–C(6)	102·8 (4)
C(4)–C(3)–C(9)–O(4)	−170·7 (5)	C(4)–C(5)–C(13)–O(2)	−18·5 (5)

Gluziński, 1977) and diethyl 1,4-dihydro-2,6-dimethyl-4-phenyl-3,5-pyridinedicarboxylate (Hempel & Gupta, 1978). The two ethoxycarbonyl groups are twisted in opposite directions so that the molecule does not have a mirror symmetry. The C(4) methyl substituent is approximately perpendicular to the dihydropyridine ring.

Financial assistance in operating and equipment grants from the Natural Sciences and Engineering Research Council of Canada is gratefully acknowledged.

References

AUGUSTO, O., BEILAN, H. S. & ORTIZ DE MONTELLANO, P. R. (1982). *J. Biol. Chem.* **257**, 11288–11295.

BOSSERT, F., MEYER, H. & WEHINGER, E. (1981). *Angew. Chem. Int. Ed. Engl.* **20**, 762–769.

CROMER, D. T. & WABER, J. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV. Birmingham: Kynoch Press.

FRENZ, B. A. (1979). *Enraf–Nonius Structure Determination Package*. Enraf–Nonius, Delft.

HEMPEL, A. & GUPTA, M. P. (1978). *Acta Cryst.* B**34**, 3815–3817.

JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.

KARLE, I. L. (1961). *Acta Cryst.* **14**, 497–500.

KRAJEWSKI, J. W., URBAŃCZYK-LIPKOWSKA, Z. & GLUZIŃSKI, P. (1977). *Acta Cryst.* B**33**, 2967–2969.

LENSTRA, A. T. H., PETIT, G. H., DOMMISSE, R. A. & ALDERWEIRELDT, F. C. (1979). *Bull. Soc. Chim. Belg.* **88**, 133–141.

MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1980). *MULTAN80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.

MARKS, G. S. (1978). *The Effect of Chemicals on Hepatic Heme Biosynthesis* in *Handbook of Experimental Pharmacology*, Vol. 44, edited by F. DE MATTEIS & W. N. ALDRIDGE, pp. 201–237. Berlin: Springer.

Acta Cryst. (1985). C**41**, 413–415

Structure of 2-(*o*-Ammoniobenzyl)-3-(3-indolyl)-1*H*-quinolinium Bis(ethanesulfonate), $C_{24}H_{21}N_3^{2+}.2C_2H_5SO_3^-$

BY VIVIAN CODY

Medical Foundation of Buffalo, Inc., 73 High Street, Buffalo, New York 14203, *USA*

(*Received* 10 *July* 1984; *accepted* 18 *October* 1984)

Abstract. $M_r = 569{\cdot}7$, triclinic, $P\bar{1}$, $a = 13{\cdot}492$ (1), $b = 14{\cdot}789$ (1), $c = 8{\cdot}109$ (1) Å, $\alpha = 90{\cdot}17$ (1), $\beta = 113{\cdot}38$ (1), $\gamma = 108{\cdot}85$ (1)°, $V = 1389{\cdot}23$ (1) Å^3, $Z = 2$, $D_x = 1{\cdot}36$ g cm^{-3}, λ(Cu $K\alpha$) = 1·54178 Å, $\mu = 20{\cdot}7$ cm^{-1}, $F(000) = 600$, $T = 295$ K, $R = 0{\cdot}052$ for 3665 unique significant reflections. This is the first reported occurrence of this compound which is the product of an indole condensation reaction. The aminobenzyl ring is twist-skewed with respect to the quinoline ring and the indolyl ring is twisted −42·6 (4)° from the plane of the quinoline ring. As a 1:2 salt of ethanesulfonic acid, the parent molecule is protonated at the quinoline and amino nitrogen atoms. There is an extensive network of hydrogen bonds formed with the ethanesulfonate oxygen atoms.

Introduction. Protonation and electrophilic substitution are the most important processes in indole chemistry (Remers, 1972). In the presence of strong acids, indoles become protonated and, depending upon acid concentration, can form a mixture of dimer or trimer salts (Bocchi & Palla, 1983). Electrophilic substitution with

0108-2701/85/030413-03$01.50

© 1985 International Union of Crystallography