

Methylergometrine maleate from synchrotron powder diffraction data

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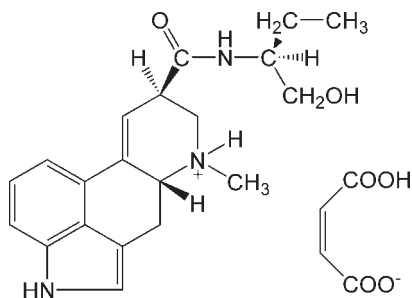
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Key indicators: powder synchrotron study; $T = 293$ K; mean $\sigma(C-C) = 0.004$ Å; R factor = 0.060; wR factor = 0.080; data-to-parameter ratio = 6.2.

The title compound {systematic name: 9,10-didehydro-*N*-[1-(hydroxymethyl)propyl]-*D*-lysergamide maleate}, $C_{20}H_{26}N_3 \cdot O_2^+ \cdot C_4H_3O_4^-$, contains a large rigid ergolene group. This group consists of an indole plane connected to a six-membered carbon ring adopting an envelope conformation and *N*-methyltetrahydropyridine where the methyl group is in an equatorial position. In the crystal, intermolecular $N-H \cdots O$, $O-H \cdots N$ and $O-H \cdots O$ hydrogen bonds form an extensive three-dimensional hydrogen-bonding network, which holds the cations and anions together.

Related literature

For background to ergometrine, see: Dudley & Moir (1935); Kharasch & Legault (1935). Formethylergometrine, see Stoll & Hofmann (1943). For crystal structure determinations of ergometrine, see: Čejka *et al.* (1996); Hušák *et al.* (1998).



Experimental

Crystal data

$C_{20}H_{26}N_3O_2^+ \cdot C_4H_3O_4^-$ $c = 33.1455$ (4) Å
 $M_r = 455.51$ $V = 2416.93$ (5) Å³
 Orthorhombic, $P2_12_12_1$ $Z = 4$
 $a = 5.71027$ (5) Å Synchrotron radiation
 $b = 12.76978$ (17) Å $\lambda = 0.6996$ Å

$T = 293$ K
 Specimen shape: cylinder
 $40 \times 1 \times 1$ mm

Specimen prepared at 101 kPa
 Specimen prepared at 293 K
 Particle morphology: needle, white

Data collection

BM01B, ESRF, Grenoble
 Specimen mounting: 1.0 mm borosilicate glass capillary
 Specimen mounted in transmission mode

Scan method: step
 Absorption correction: none
 $2\theta_{\min} = 0.5$, $2\theta_{\max} = 29.5^\circ$
 Increment in $2\theta = 0.003^\circ$

Refinement

$R_p = 0.060$
 $R_{wp} = 0.080$
 $R_{exp} = 0.021$
 $R_B = 0.088$
 $S = 3.76$
 Wavelength of incident radiation: 0.6996 Å
 Excluded region(s): none
 Profile function: pseudo-Voigt
 profile coefficients as parameterized in Thompson *et al.*

(1987), asymmetry correction according to Finger *et al.* (1994)
 617 reflections
 100 parameters
 96 restraints
 H-atom parameters not refined
 Preferred orientation correction: March–Dollase (Dollase, 1986); direction of preferred orientation - 011, MD = 1.26

Table 1

Hydrogen-bond geometry (Å, °).

| $D-H \cdots A$ | $D-H$ | $H \cdots A$ | $D \cdots A$ | $D-H \cdots A$ |
|----------------------------|-------|--------------|--------------|----------------|
| $O2s-H202 \cdots O4s$ | 1.20 | 1.28 | 2.479 (5) | 179 |
| $N13-H131 \cdots O3s$ | 0.86 | 1.77 | 2.634 (4) | 173 |
| $O23-H232 \cdots O19^i$ | 0.83 | 2.12 | 2.925 (8) | 160 |
| $N20-H201 \cdots O1s^{ii}$ | 0.87 | 2.04 | 2.912 (5) | 177 |
| $N1-H11 \cdots O19^{iii}$ | 0.88 | 2.03 | 2.852 (4) | 154 |

Symmetry codes: (i) $x - 1, y, z$; (ii) $x - \frac{1}{2}, -y + \frac{3}{2}, -z$; (iii) $-x, y - \frac{1}{2}, -z + \frac{1}{2}$.

Data collection: ESRF *SPEC* package (Certified Scientific Software, 2003); cell refinement: *GSAS* (Larson & Von Dreele, 1994); data reduction: *CRYSFIRE* (Shirley, 2000); program(s) used to solve structure: *FOX* (Favre-Nicolin & Černý, 2002); program(s) used to refine structure: *GSAS*; molecular graphics: *Mercury* (Macrae *et al.*, 2006) and *PLATON* (Spek, 2003); software used to prepare material for publication: *enCIFer* (Allen *et al.*, 2004).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: CV2630).

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Methylergometrine maleate from synchrotron powder diffraction data

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Comment

Methylergometrine is a semisynthetic ergot alkaloid derived from (+)-lysergic acid and (*S*)-(+)-2-amino-1-butanol (Stoll & Hofmann, 1943). It is nearly isostructural with natural ergot alkaloid ergometrine maleate (Čejka *et al.*, 1996). Previous attempts to solve this structure by molecular modeling using ergometrine maleate as the starting model were successful, but the result was not very precise (Čejka *et al.*, 1996). Hence the crystal structure was not published. In this paper we report crystal structure determination of the title compound (I) from synchrotron powder diffraction data.

The asymmetric unit of (I) contains a methylergometrinium cation and one molecule of maleate (Fig. 1). All bond lengths and angles in (I) are comparable with reported structure of ergometrine maleate (Čejka *et al.*, 1996). The molecule of maleate is situated in the same position and the hydrogen bonding system is practically the same. Intermolecular N—H \cdots O, O—H \cdots N and O—H \cdots O hydrogen bonds (Table 1) form an extensive three-dimensional hydrogen-bonding network which held cations and anions together.

Experimental

Crystallization of methylergometrine maleate from various solvents (alcohols, acetic acid esters, acetone, dioxane, dimethyl sulphoxide) provided hair-like long needle crystals in all cases. One crystalline form with distinct powder patterns was found.

Refinement

The powder diffraction data measurement was done on BM01B beamline (Swiss-Norwegian Beamlines) at the ESRF, Grenoble. Before the measurement the diffractometer was calibrated by using LaB₆ standard sample and the value of wavelength was checked (0.6996 Å). The powder sample was placed in a 1 mm capillary. The measurement was done at room temperature. The capillary was rotating during the data collection. The diffractogram was measured from 0.515° to 29.49° 2 θ with 0.0025° step scan and the sample was irradiated for 1 s per step. The data from all six detectors were finally binned.

The indexation confirmed unit-cell parameters and space group obtained from previous measurement (Čejka *et al.*, 1996): $a = 5.71$ Å, $b = 12.77$ Å, $c = 33.15$ Å, $Z = 4$, $V = 2417$ Å³, $P2_12_12_1$. Molecule of ergometrine (Čejka *et al.*, 1996) was used as a starting model for structure solution. This model was transferred to the z -matrix and the missing methyl group was added in the standard C—C distance (1.52 Å). This way changed z -matrix was loaded into the program FOX (Favre-Nicolin & Černý, 2002) and structure was solved by using parallel tempering algorithm. The structure solution result confirmed similarity with ergometrine maleate, see Fig.2. Refinement of this result was carried out in *GSAS* (Larson & Von Dreele, 1994). Hydrogen atoms were placed in their theoretical positions and structure was refined with bonds, angles and planar groups restraints (N1—C10, C9/C10/C12/C16, C17/C18/O19/N20, C6s/C5s/O1s/O2s, C7s/C8s/O3s/O4s and C5s/C6s/C7s/C8s). All atomic coordinates and U_{iso} parameters of non-hydrogen atoms were refined. Hydrogen atoms were not refined, it was necessary to relocate H atoms into the correct positions after few cycles. Hydrogen atom H202 was manually placed between oxygen

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atoms O2s and O4s. At the final stage of the refinement, only atomic coordinates of non-hydrogen atoms were refined to the final agreement factors $R_p = 0.0631$ and $R_{wp} = 0.0831$. The diffraction profiles and differences between the measured and calculated profiles are shown in Fig. 3.

Figures

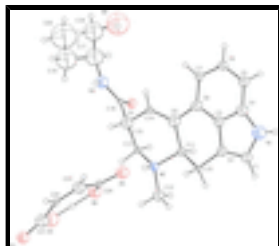


Fig. 1. The molecular structure of methylergometrine maleate showing the atomic numbering. Displacement spheres are drawn at the 30% probability level.

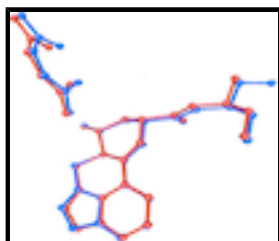


Fig. 2. Overlaid asymmetric parts of unit cells of methylergometrine maleate (blue) and ergometrine maleate (red)

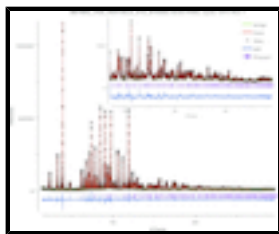
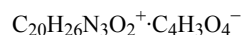


Fig. 3. The final Rietveld plot showing the measured data (black thin-plus), calculated data (red line) and difference curve (blue line). Calculated positions of the reflection are shown by vertical bars.

9,10-didehydro-N-[1-(hydroxymethyl)propyl]-D-lysergamide maleate

Crystal data



$M_r = 455.51$

Orthorhombic, $P2_12_12_1$

$a = 5.71027$ (5) Å

$b = 12.76978$ (17) Å

$c = 33.1455$ (4) Å

$V = 2416.93$ (5) Å³

$Z = 4$

$F(000) = 960.0$

$D_x = 1.246$ Mg m⁻³

Synchrotron radiation, $\lambda = 0.6996$ Å

$T = 293$ K

Particle morphology: needle

white

cylinder, 40×1 mm

Specimen preparation: Prepared at 293 K and 101 kPa

Data collection

ID31

diffractometer

Radiation source: X-Ray

Scan method: step

$2\theta_{\min} = 0.52^\circ$, $2\theta_{\max} = 29.49^\circ$, $2\theta_{\text{step}} = 0.0025^\circ$

Si(111) DUMMY
 Specimen mounting: 1.0 mm borosilicate glass capillary DUMMY
 Data collection mode: transmission

Refinement

Least-squares matrix: full Profile function: Pseudo-Voigt profile coefficients as parameterized in Thompson *et al.* (1987), asymmetry correction according to Finger *et al.* (1994)
 $R_p = 0.060$ 100 parameters
 $R_{wp} = 0.080$ 96 restraints
 $R_{exp} = 0.021$ 0 constraints
 $R_{Bragg} = 0.088$ H-atom parameters not refined
 $R(F^2) = 0.08232$ Weighting scheme based on measured s.u.'s $w = 1/\sigma(Y_{obs})^2$
 $\chi^2 = 14.138$ $(\Delta/\sigma)_{max} = 0.03$
 11591 data points Background function: Shifted Chebyshev
 Excluded region(s): no Preferred orientation correction: March–Dollase (Dollase, 1986); direction of preferred orientation - 011, MD = 1.26

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

| | x | y | z | U_{iso}^*/U_{eq} |
|-----|-------------|--------------|--------------|--------------------|
| N1 | -0.2972 (5) | 0.6888 (3) | 0.29856 (7) | 0.07305* |
| C2 | -0.1311 (5) | 0.6344 (2) | 0.27627 (8) | 0.04511* |
| C3 | -0.0706 (4) | 0.6910 (2) | 0.24331 (7) | 0.03699* |
| C4 | -0.2019 (3) | 0.7843 (2) | 0.24509 (6) | 0.03942* |
| C5 | -0.3442 (4) | 0.7819 (3) | 0.27994 (6) | 0.05116* |
| C6 | -0.4884 (4) | 0.8647 (3) | 0.28782 (7) | 0.04053* |
| C7 | -0.4901 (4) | 0.9470 (3) | 0.26187 (8) | 0.03292* |
| C8 | -0.3485 (4) | 0.9500 (2) | 0.22692 (7) | 0.02676* |
| C9 | -0.2007 (3) | 0.86750 (18) | 0.21789 (6) | 0.04409* |
| C10 | -0.0384 (3) | 0.85683 (16) | 0.18355 (6) | 0.05585* |
| C11 | 0.0703 (5) | 0.66917 (18) | 0.20642 (8) | 0.01406* |
| C12 | 0.1520 (3) | 0.77235 (18) | 0.18765 (6) | 0.02621* |
| N13 | 0.2572 (4) | 0.7525 (2) | 0.14658 (7) | 0.02834* |
| C14 | 0.4543 (6) | 0.6780 (3) | 0.14769 (10) | 0.04728* |
| C15 | 0.3333 (4) | 0.8518 (2) | 0.12743 (7) | 0.0149* |
| C16 | -0.0506 (3) | 0.9178 (3) | 0.15108 (8) | 0.01827* |
| C17 | 0.1276 (3) | 0.9217 (2) | 0.11776 (6) | 0.05457* |
| C18 | 0.2054 (3) | 1.0353 (2) | 0.11406 (5) | 0.01555* |
| O19 | 0.3842 (5) | 1.0675 (3) | 0.13078 (10) | 0.03564* |
| N20 | 0.0695 (5) | 1.0956 (2) | 0.09146 (10) | 0.0567* |
| C21 | 0.0846 (6) | 1.2096 (2) | 0.08735 (7) | 0.12048* |
| C22 | -0.1555 (8) | 1.2575 (4) | 0.09008 (13) | 0.13815* |
| O23 | -0.2828 (7) | 1.2409 (7) | 0.12481 (15) | 0.18992* |
| C24 | 0.1859 (9) | 1.2439 (4) | 0.04775 (12) | 0.16384* |

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| | | | | |
|------|-------------|--------------|---------------|----------|
| C25 | 0.254 (2) | 1.3598 (5) | 0.0502 (2) | 0.24862* |
| O1s | 0.1598 (8) | 0.5073 (3) | -0.05735 (10) | 0.05346* |
| O2s | 0.3200 (5) | 0.6095 (3) | -0.01229 (11) | 0.09409* |
| O3s | -0.0518 (7) | 0.6674 (3) | 0.09751 (9) | 0.05776* |
| O4s | 0.2452 (6) | 0.6788 (3) | 0.05636 (10) | 0.06078* |
| C5s | 0.1379 (6) | 0.56141 (17) | -0.02617 (8) | 0.06152* |
| C6s | -0.0894 (5) | 0.57248 (19) | -0.00445 (9) | 0.0169* |
| C7s | -0.1334 (5) | 0.61043 (19) | 0.03209 (9) | 0.05644* |
| C8s | 0.0294 (5) | 0.65414 (14) | 0.06283 (8) | 0.01622* |
| H21 | -0.0702 | 0.5649 | 0.2836 | 0.0541* |
| H61 | -0.5833 | 0.8631 | 0.3116 | 0.0486* |
| H71 | -0.5868 | 1.0027 | 0.268 | 0.0395* |
| H81 | -0.3514 | 1.0068 | 0.2101 | 0.0324* |
| H111 | 0.2034 | 0.6252 | 0.2141 | 0.0169* |
| H112 | -0.0222 | 0.629 | 0.1881 | 0.0169* |
| H121 | 0.273 | 0.7969 | 0.2049 | 0.0315* |
| H141 | 0.5132 | 0.6649 | 0.1216 | 0.0567* |
| H142 | 0.5746 | 0.7014 | 0.165 | 0.0567* |
| H143 | 0.4012 | 0.6094 | 0.1585 | 0.0567* |
| H151 | 0.4358 | 0.8844 | 0.1458 | 0.0179* |
| H152 | 0.4147 | 0.8326 | 0.1036 | 0.0179* |
| H161 | -0.1831 | 0.9588 | 0.1491 | 0.0219* |
| H171 | 0.0579 | 0.8964 | 0.0936 | 0.0655* |
| H211 | 0.1864 | 1.2337 | 0.1082 | 0.1804* |
| H221 | -0.1257 | 1.3314 | 0.0901 | 0.2258* |
| H222 | -0.2393 | 1.2362 | 0.0685 | 0.2258* |
| H241 | 0.0678 | 1.2255 | 0.0272 | 0.1966* |
| H242 | 0.3175 | 1.1955 | 0.0415 | 0.1966* |
| H251 | 0.3132 | 1.3721 | 0.0222 | 0.4183* |
| H252 | 0.118 | 1.3943 | 0.0536 | 0.4183* |
| H253 | 0.3677 | 1.3643 | 0.068 | 0.4183* |
| H601 | -0.223 | 0.549 | -0.019 | 0.0203* |
| H701 | -0.292 | 0.61 | 0.04 | 0.0677* |
| H11 | -0.3603 | 0.6651 | 0.3211 | 0.0877* |
| H201 | -0.0502 | 1.0631 | 0.0811 | 0.068* |
| H131 | 0.148 | 0.725 | 0.132 | 0.0411* |
| H202 | 0.285 | 0.643 | 0.021 | 0.1129* |
| H232 | -0.3996 | 1.2015 | 0.1235 | 0.27* |

Geometric parameters (Å, °)

| | | | |
|---------|-----------|----------|------|
| N13—C14 | 1.474 (4) | N13—H131 | 0.86 |
| N13—C15 | 1.483 (4) | N20—H201 | 0.87 |
| N20—C18 | 1.325 (4) | C2—H21 | 0.98 |
| N20—C21 | 1.465 (4) | C6—H61 | 0.96 |
| C2—C3 | 1.355 (4) | C7—H71 | 0.92 |
| C3—C4 | 1.409 (3) | C8—H81 | 0.91 |
| C3—C11 | 1.490 (4) | C11—H111 | 0.98 |
| C4—C5 | 1.413 (3) | C11—H112 | 0.95 |

| | | | |
|-------------|-------------|---------------|------|
| C4—C9 | 1.393 (3) | C12—H121 | 0.95 |
| C5—C6 | 1.365 (5) | C14—H141 | 0.94 |
| C6—C7 | 1.358 (5) | C14—H142 | 0.94 |
| C7—C8 | 1.413 (3) | C14—H143 | 0.99 |
| C8—C9 | 1.383 (3) | C15—H151 | 0.94 |
| C9—C10 | 1.474 (3) | C15—H152 | 0.95 |
| C10—C12 | 1.538 (3) | C16—H161 | 0.92 |
| C10—C16 | 1.330 (4) | C17—H171 | 0.95 |
| C11—C12 | 1.530 (3) | C21—H211 | 0.95 |
| C15—C17 | 1.510 (3) | C22—H221 | 0.96 |
| C16—C17 | 1.503 (3) | C22—H222 | 0.90 |
| C17—C18 | 1.522 (4) | C24—H241 | 0.99 |
| C21—C22 | 1.504 (6) | C24—H242 | 0.99 |
| C21—C24 | 1.500 (5) | C25—H251 | 1.00 |
| C24—C25 | 1.532 (9) | C25—H252 | 0.90 |
| O23—H232 | 0.84 | C25—H253 | 0.88 |
| N1—H11 | 0.88 | | |
| C2—N1—C5 | 109.2 (2) | C3—C2—H21 | 126 |
| C12—N13—C14 | 112.9 (2) | C5—C6—H61 | 119 |
| C12—N13—C15 | 111.0 (2) | C7—C6—H61 | 122 |
| C14—N13—C15 | 109.8 (2) | C6—C7—H71 | 117 |
| C18—N20—C21 | 126.6 (3) | C8—C7—H71 | 120 |
| N1—C2—C3 | 109.7 (2) | C7—C8—H81 | 121 |
| C2—C3—C4 | 106.4 (2) | C9—C8—H81 | 119 |
| C2—C3—C11 | 134.4 (2) | C3—C11—H111 | 108 |
| C4—C3—C11 | 118.7 (2) | C3—C11—H112 | 109 |
| C3—C4—C5 | 108.8 (2) | C12—C11—H111 | 111 |
| C3—C4—C9 | 127.96 (19) | C12—C11—H112 | 112 |
| C5—C4—C9 | 123.3 (2) | H111—C11—H112 | 107 |
| N1—C5—C4 | 106.0 (3) | N13—C12—H121 | 108 |
| N1—C5—C6 | 134.9 (2) | C10—C12—H121 | 110 |
| C4—C5—C6 | 119.1 (3) | C11—C12—H121 | 105 |
| C5—C6—C7 | 118.8 (2) | N13—C14—H141 | 111 |
| C6—C7—C8 | 122.4 (3) | N13—C14—H142 | 112 |
| C7—C8—C9 | 120.4 (2) | N13—C14—H143 | 110 |
| C4—C9—C8 | 115.97 (19) | H141—C14—H142 | 111 |
| C4—C9—C10 | 115.61 (18) | H141—C14—H143 | 106 |
| C8—C9—C10 | 128.4 (2) | H142—C14—H143 | 106 |
| C9—C10—C12 | 116.18 (17) | N13—C15—H151 | 106 |
| C9—C10—C16 | 122.53 (19) | N13—C15—H152 | 106 |
| C12—C10—C16 | 121.28 (18) | C17—C15—H151 | 111 |
| C3—C11—C12 | 109.71 (19) | C17—C15—H152 | 111 |
| N13—C12—C10 | 108.63 (17) | H151—C15—H152 | 110 |
| N13—C12—C11 | 110.09 (19) | C10—C16—H161 | 116 |
| C10—C12—C11 | 115.12 (17) | C17—C16—H161 | 119 |
| N13—C15—C17 | 111.62 (19) | C15—C17—H171 | 108 |
| C10—C16—C17 | 125.4 (2) | C16—C17—H171 | 109 |
| C15—C17—C16 | 110.6 (2) | C18—C17—H171 | 112 |
| C15—C17—C18 | 110.70 (16) | N20—C21—H211 | 107 |

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|--------------|-------------|---------------|-----|
| C16—C17—C18 | 106.8 (2) | C22—C21—H211 | 112 |
| O19—C18—N20 | 123.1 (3) | C24—C21—H211 | 108 |
| O19—C18—C17 | 121.6 (2) | O23—C22—H221 | 104 |
| N20—C18—C17 | 115.37 (19) | O23—C22—H222 | 110 |
| N20—C21—C22 | 110.2 (3) | C21—C22—H221 | 104 |
| N20—C21—C24 | 113.2 (3) | C21—C22—H222 | 108 |
| C22—C21—C24 | 106.6 (3) | H221—C22—H222 | 113 |
| O23—C22—C21 | 117.9 (4) | C21—C24—H241 | 106 |
| C21—C24—C25 | 109.5 (4) | C21—C24—H242 | 107 |
| C22—O23—H232 | 118 | C25—C24—H241 | 116 |
| C2—N1—H11 | 124 | C25—C24—H242 | 115 |
| C5—N1—H11 | 127 | H241—C24—H242 | 103 |
| C12—N13—H131 | 107 | C24—C25—H251 | 101 |
| C14—N13—H131 | 108 | C24—C25—H252 | 105 |
| C15—N13—H131 | 109 | C24—C25—H253 | 107 |
| C18—N20—H201 | 114 | H251—C25—H252 | 109 |
| C21—N20—H201 | 119 | H251—C25—H253 | 111 |
| N1—C2—H21 | 124 | H252—C25—H253 | 121 |

Hydrogen-bond geometry (\AA , $^\circ$)

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|-------------------------------------|-------|-------------|-------------|---------------|
| O2s—H202 \cdots O4s | 1.20 | 1.28 | 2.479 (5) | 179 |
| N13—H131 \cdots O3s | 0.86 | 1.77 | 2.634 (4) | 173 |
| O23—H232 \cdots O19 ⁱ | 0.83 | 2.12 | 2.925 (8) | 160 |
| N20—H201 \cdots O1s ⁱⁱ | 0.87 | 2.04 | 2.912 (5) | 177 |
| N1—H11 \cdots O19 ⁱⁱⁱ | 0.88 | 2.03 | 2.852 (4) | 154 |

Symmetry codes: (i) $x-1, y, z$; (ii) $x-1/2, -y+3/2, -z$; (iii) $-x, y-1/2, -z+1/2$.

Fig. 1

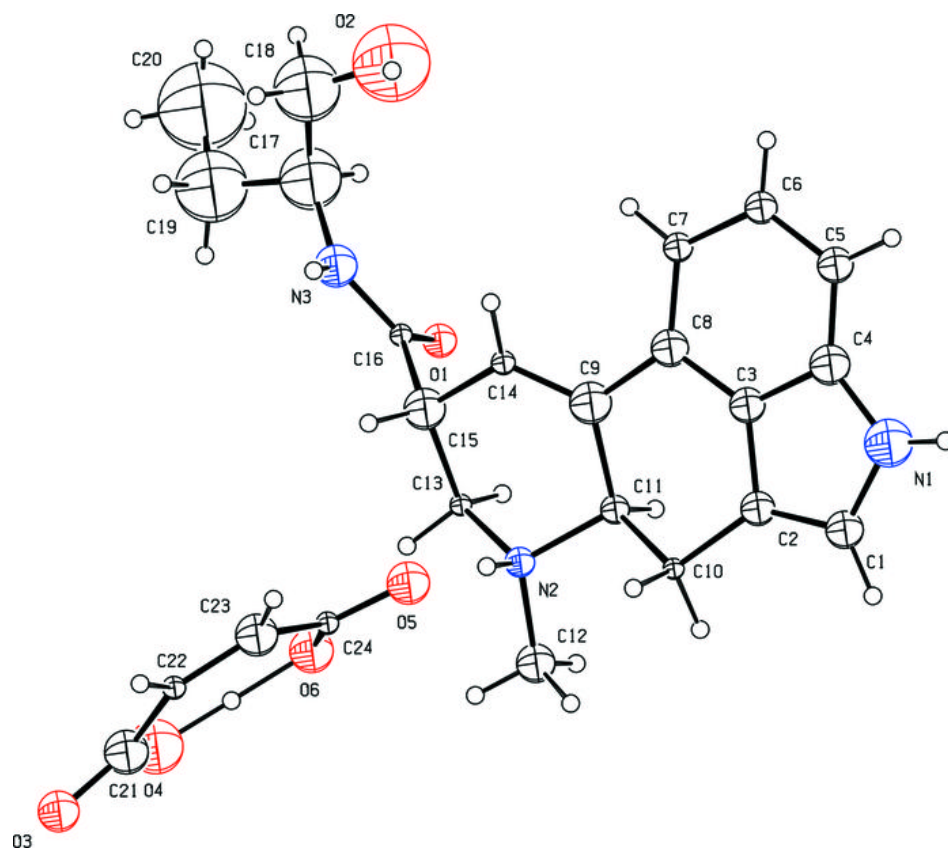


Fig. 2

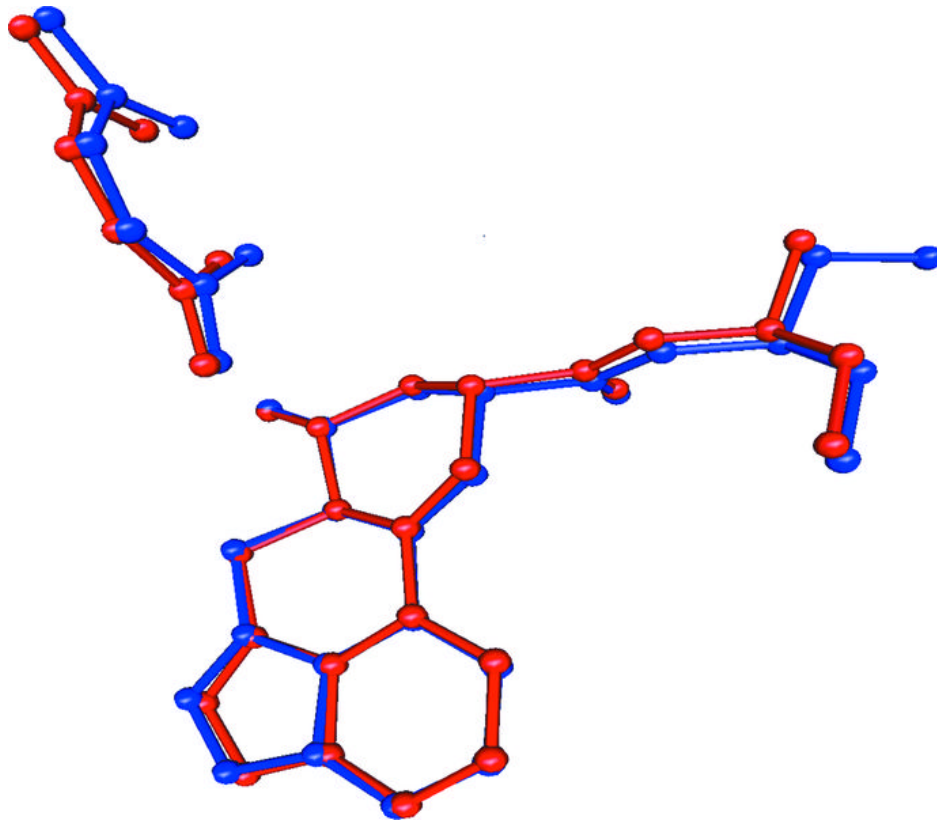


Fig. 3

