

$-6^\circ/\varphi' = 87^\circ$). The outer-ring orientation of both 3-T₁ and *r*-T₃ is different from that of the intramolecular charge-transfer complex model (Lehmann, 1972), in which the outer-ring plane interacts with the I atom on the inner ring. The φ and φ' values of the thyroinactive 3-T₁ and *r*-T₃ as well as L-thyronine (T₀) ($\varphi = -37^\circ/\varphi' = -67^\circ$) (Camerman & Camerman, 1974) are clearly different from those of the thyroactive compounds of the skewed or the twist-skewed conformation (near $\varphi = 108^\circ/\varphi' = -28^\circ$ or $\varphi = -108^\circ/\varphi' = 28^\circ$) (Cody, 1980). This result may reinforce the existence of a permissible region of φ and φ' angles for protein-binding ability to produce effective thymimetic activity. The alanine side-chain conformation is described by torsion angles $\chi^1[\text{C}(1)-\text{C}(7)-\text{C}(8)-\text{N}(8)]$, $\chi^2[\text{C}(2)-\text{C}(1)-\text{C}(7)-\text{C}(8)]$ and $\psi[\text{N}(8)-\text{C}(8)-\text{C}(9)-\text{O}(10)]$. χ^1 , χ^2 and ψ values of the 3-T₁ conformers are -59 , -55 and -21° for conformer (I) and -51 , 94 and 161° for conformer (II). There are no characteristics in the alanine side-chain conformations indicative of thyroactive or inactive compounds. The intermolecular interactions are indicated in the crystal packing shown in Fig. 3, in which the molecular arrangement is projected along the *b* axis. The 3-T₁

molecule is joined to neighboring molecules by the hydrogen-bond network involving carboxyl, amino and phenolic groups of 3-T₁, water molecules and Cl⁻ ions.

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Structure of the 2,4-Dinitrophenylhydrazine Adduct of Pyrroloquinolinequinone (PQQ) Dimethyl Ethyl Triester,* C₂₄H₁₈N₆O₁₁

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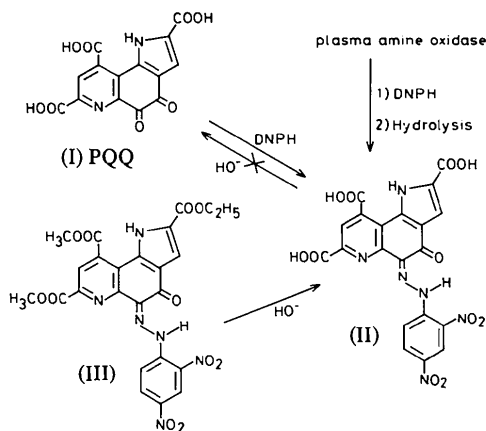
Abstract. *M_r* = 566.44, triclinic, *P* $\bar{1}$, *a* = 11.018 (3), *b* = 15.451 (3), *c* = 7.507 (2), α = 92.68 (3), β = 104.69 (3), γ = 86.83 (3)°, *V* = 1233.6 (10) Å³, *Z* = 2, *D_x* = 1.530 Mg m⁻³, Mo *K*α, λ = 0.71069 Å, μ = 0.15 mm⁻¹, *F*(000) = 584, *T* = 293 K, final *R* = 0.053 for 2238 observed data. The keto atom at C(5) in PQQ triester is substituted by dinitrophenylhydrazine *via* a

hydrazone bond. The fused-ring system of PQQ is coplanar with the phenylhydrazine moiety of the molecule because of an intramolecular bifurcated hydrogen bond. The structure analysis proves that the enzyme plasma amine oxidase contains a prosthetic group in which the basic structure of PQQ is retained.

Introduction. Compound (I), 4,5-dioxo-1*H*-pyrrolo[2,3-*f*]quinoline-2,7,9-tricarboxylic acid is known in the biochemical literature as pyrroloquinolinequinone (abbreviated to PQQ) (Duine, Frank & Verwiel, 1980) and

* IUPAC name: 2-ethyl 7,9-dimethyl 4,5-dihydro-5-(2,4-dinitrophenylhydrazono)-4-oxo-1*H*-pyrrolo[2,3-*f*]quinoline-2,7,9-tricarboxylate.

methoxatin (Salisbury, Forrest, Cruse & Kennard, 1979). It is the coenzyme of a novel class of oxidoreductases (Duine & Frank, 1981).



The presence of a PQQ-derived prosthetic group in the mammalian enzyme plasma amine oxidase was suspected. In order to release the tightly bound prosthetic group, the enzyme had to be extensively hydrolyzed, yielding a complex mixture of compounds. However, a well defined product could be obtained when the prosthetic group was derivatized with 2,4-dinitrophenylhydrazine (DNPH) prior to hydrolysis by proteases of the enzyme (Lobenstein-Verbeek, Jongejan, Frank & Duine, 1984).

This product showed the same chromatographic and spectral data as the adduct (II) obtained from PQQ and DNPH. Although ¹H NMR spectroscopy indicated (II) to be a monohydrazone of PQQ, attempts to liberate PQQ from this adduct failed and hence the presence of PQQ in (I) could not be conclusively established. X-ray analysis of (II) might give the solution. However, crystals of (II) could not be grown. Fortunately, compound (III), prepared from PQQ dimethyl ethyl triester and DNPH, gave suitable crystals. As (III) could be unequivocally converted to (II) upon mild hydrolysis, an X-ray analysis of (III) was undertaken. The analysis also gives an answer to the question, interesting from a mechanistic point of view, which carbonyl group in PQQ reacts with DNPH.

Experimental. Compound (III) obtained by reacting PQQ dimethyl ethyl triester (Corey & Tramontano, 1981) with DNPH under standard conditions. Crude product crystallized from acetone and ethyl acetate. Orange needle-shaped crystals by recrystallization from dichloromethane; recrystallization difficult, small crystal 0.10 × 0.05 × 0.30 mm produced. Cell constants refined from diffractometer angular settings of 25 centered reflections (8.0 < θ < 13.4°). Enraf-Nonius CAD-4F diffractometer, graphite-monochromated Mo Kα radiation, ω/2θ scan mode up to θ = 25°

(−13 ≤ h ≤ 12, −18 ≤ k ≤ 18, 0 ≤ l ≤ 18); three standard reflections monitored at intervals of 3600 s, no decay; 4320 reflections recorded, 2242 with I ≥ 1.0σ(I) used in refinement. Extinction and absorption neglected. Structure solved by direct methods (*MULTAN80*; Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980); H atoms (except for 5 ethyl H atoms) located from difference map. Anisotropic least-squares refinement (H atoms with fixed U's) on F, R_w = 0.053, w = 1, for 2238 observed reflections (4 low-order reflections rejected), S = 0.35. (Δ/σ)_{max} = 0.82 [z value C(21)]. Final difference map showed two peaks, 0.50 and 0.35 e Å⁻³, which might be connected with ethyl H atoms, and some rest density (≈ 0.25 e Å⁻³) in neighborhood of C(21) and C(22). Atomic scattering factors from *XRAY72* (Stewart, Kruger, Ammon, Dickinson & Hall, 1972). Calculations performed on the Delft University Amdahl 470/V7B (*XRAY72*; Stewart *et al.*, 1972) and the Utrecht University CDC-Cyber175 [*MULTAN80* (Main *et al.*, 1980) and *EUCLID* (Spek, 1982)] computers.

Discussion. The final atomic coordinates together with their e.s.d.'s and equivalent isotropic thermal parameters are given in Table 1.* Table 2 lists bond lengths and bond angles. The single C(21)–C(22) bond length is very small (1.36 Å). This might be caused by neglecting disorder of the ethyl group or by using the wrong space group. Disorder (whether of dynamic or static origin) is indicated by the high temperature factors of C(21) and C(22) and by inspection of the final difference map. The possibility of generating a second harmonic signal is in favor of space group *P1* instead of *P1̄*. The structure has not been refined in *P1* because of the very limited data set.

Fig. 1 is a labeled perspective view of the molecule (Spek, 1982). The skeleton of the molecule is practically planar with no C or N atom lying further than 0.15 Å from the least-squares plane through 24 atoms: all ring atoms, all N atoms and O(4). Atom H(N3) is in this mean plane within experimental error. The planar conformation is stabilized by an intramolecular bifurcated H bond between H(N3) and O(4) and O(41). The NO₂ group concerned is inclined 13.2 (9)° to the phenyl ring. The corresponding angle for the second NO₂ group is 4.0 (9)°. The three carboxylate substituents in order of increasing atom number are inclined 5.7, 11.0 and 33.8 (9)°, respectively, to the plane of the associated aromatic ring. There is another intramolecular H bond between H(N1) and O(91).

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters (including distances and angles) have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39759 (20 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The geometry of the fused-ring system is analogous to that found for the acetone adduct of PQQ (Cruse, Kennard & Salisbury, 1980) except for the geometry around C(5). In the acetone adduct the fused-ring system is slightly twisted about C(1a)–C(9a) and C(4)–C(5) to accommodate the fully substituted sp^3

Table 1. Final coordinates and equivalent isotropic thermal parameters

$$U_{eq} = \frac{1}{3}(U_{11} + U_{22} + U_{33}).$$

	x	y	z	$U_{eq}(\text{\AA}^2)$
C(2)	1.2058 (5)	0.2291 (3)	0.2322 (7)	0.049
C(3)	1.2194 (5)	0.1495 (3)	0.3081 (7)	0.048
C(3a)	1.1034 (4)	0.1114 (3)	0.2507 (6)	0.042
C(4)	1.0669 (4)	0.0271 (3)	0.2874 (6)	0.040
C(5)	0.9401 (4)	0.0042 (3)	0.1924 (6)	0.039
C(5a)	0.8536 (4)	0.0657 (3)	0.0663 (6)	0.039
C(7)	0.6591 (4)	0.0881 (3)	-0.1259 (6)	0.047
C(8)	0.6824 (5)	0.1734 (3)	-0.1459 (7)	0.054
C(9)	0.7968 (4)	0.2059 (3)	-0.0636 (6)	0.045
C(9a)	0.8915 (4)	0.1504 (3)	0.0444 (6)	0.041
C(9b)	1.0190 (4)	0.1687 (3)	0.1357 (6)	0.042
C(20)	1.2905 (5)	0.2984 (3)	0.2392 (8)	0.064
C(21)	1.5055 (8)	0.3438 (5)	0.3727 (12)	0.124
C(22)	1.5437 (9)	0.3380 (6)	0.2140 (17)	0.156
C(70)	0.5357 (4)	0.0534 (4)	-0.2259 (6)	0.052
C(71)	0.4118 (6)	-0.0677 (5)	-0.3106 (10)	0.077
C(90)	0.8157 (5)	0.2993 (3)	-0.0951 (7)	0.055
C(91)	0.7151 (8)	0.4385 (4)	-0.1337 (14)	0.103
C(1')	0.9065 (4)	-0.2048 (3)	0.3294 (6)	0.042
C(2')	0.9712 (4)	-0.2726 (3)	0.4401 (6)	0.046
C(3')	0.9140 (6)	-0.3484 (3)	0.4495 (8)	0.061
C(4')	0.7931 (6)	-0.3577 (3)	0.3561 (8)	0.063
C(5')	0.7250 (5)	-0.2921 (4)	0.2525 (8)	0.060
C(6')	0.7819 (5)	-0.2167 (3)	0.2383 (7)	0.051
N(1)	1.0840 (4)	0.2392 (2)	0.1280 (6)	0.049
N(2)	0.8914 (3)	-0.0690 (2)	0.2064 (5)	0.040
N(3)	0.9615 (4)	-0.1287 (2)	0.3150 (5)	0.041
N(4)	1.1000 (4)	-0.2652 (3)	0.5472 (6)	0.055
N(5)	0.7333 (7)	-0.4382 (4)	0.3691 (9)	0.091
N(6)	0.7422 (3)	0.0352 (2)	-0.0185 (5)	0.043
O(4)	1.1406 (3)	-0.0235 (2)	0.3914 (4)	0.049
O(21)	1.4062 (4)	0.2766 (3)	0.3342 (6)	0.089
O(22)	1.2591 (4)	0.3674 (2)	0.1709 (6)	0.084
O(41)	1.1616 (3)	-0.2062 (3)	0.5224 (6)	0.075
O(42)	1.1416 (4)	-0.3185 (3)	0.6666 (6)	0.082
O(51)	0.7979 (6)	-0.4968 (3)	0.4541 (8)	0.128
O(52)	0.6226 (6)	-0.4432 (3)	0.2904 (9)	0.125
O(71)	0.4532 (3)	0.0995 (3)	-0.3150 (5)	0.078
O(72)	0.5277 (3)	-0.0299 (2)	-0.2101 (5)	0.059
O(91)	0.9100 (4)	0.3295 (2)	-0.1082 (5)	0.075
O(92)	0.7091 (4)	0.3451 (29)	-0.1100 (6)	0.078
H(N1)	1.059 (4)	0.283 (3)	0.077 (6)	0.048*
H(N3)	1.046 (4)	-0.114 (3)	0.371 (6)	0.048*

* Kept fixed during refinement.

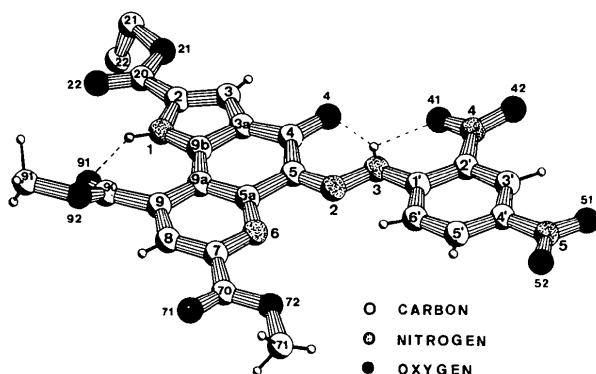


Fig. 1. Perspective view of the title compound with atom numbering.

Table 2. Bond distances (\AA), some intramolecular $O\cdots H$ distances (\AA) and bond angles ($^\circ$) involving non-H atoms

C(9b)–N(1)	1.347 (6)	C(70)–O(72)	1.308 (7)
C(9b)–C(3a)	1.402 (6)	C(71)–O(72)	1.447 (7)
C(9b)–C(9a)	1.436 (6)	C(90)–O(91)	1.190 (8)
C(2)–N(1)	1.375 (6)	C(90)–O(92)	1.320 (7)
C(2)–C(3)	1.365 (7)	C(91)–O(92)	1.468 (8)
C(2)–C(20)	1.449 (8)	C(1')–N(3)	1.374 (6)
C(3)–C(3a)	1.395 (7)	C(1')–C(2')	1.412 (6)
C(3a)–C(4)	1.442 (6)	C(2')–N(4)	1.374 (8)
C(4)–O(4)	1.244 (5)	C(2')–N(4)	1.450 (6)
C(4)–C(5)	1.453 (6)	C(3)–C(4')	1.351 (8)
C(5)–N(2)	1.299 (6)	C(4')–N(5)	1.457 (9)
C(5)–C(5a)	1.495 (6)	C(4')–C(5')	1.375 (8)
C(5a)–C(9a)	1.424 (6)	C(5')–C(6')	1.373 (8)
C(5a)–N(6)	1.332 (6)	C(1')–C(6')	1.388 (7)
C(7)–N(6)	1.328 (6)	N(2)–N(3)	1.336 (5)
C(7)–C(70)	1.492 (6)	N(4)–O(41)	1.215 (6)
C(7)–C(8)	1.379 (7)	N(4)–O(42)	1.229 (6)
C(8)–C(9)	1.367 (7)	N(5)–O(51)	1.220 (7)
C(9)–C(9a)	1.421 (6)	N(5)–O(52)	1.217 (9)
C(9)–C(90)	1.507 (7)	N(1)–H(N1)	0.79 (4)
C(20)–O(21)	1.327 (7)	N(3)–H(N3)	0.95 (4)
C(20)–O(22)	1.200 (7)		
C(21)–O(21)	1.515 (9)	H(N1)–O(91)	1.99 (4)
C(21)–C(22)	1.358 (17)	H(N3)–O(4)	1.77 (4)
C(70)–O(71)	1.203 (6)	H(N3)–O(41)	2.04 (4)
N(1)–C(9b)–C(3a)	105.9 (3)	O(21)–C(21)–C(22)	101.2 (7)
N(1)–C(9b)–C(9a)	129.6 (4)	C(7)–C(70)–O(71)	121.4 (5)
C(3a)–C(9b)–C(9a)	124.5 (4)	C(7)–C(70)–O(72)	114.3 (4)
N(1)–C(2)–C(3)	107.7 (4)	O(71)–C(70)–O(72)	124.3 (4)
N(1)–C(2)–C(20)	118.7 (4)	C(9)–C(90)–O(91)	127.0 (5)
C(3)–C(2)–C(20)	133.6 (4)	C(9)–C(90)–O(92)	109.7 (5)
C(2)–C(3)–C(3a)	107.2 (4)	O(91)–C(90)–O(92)	123.3 (5)
C(9b)–C(3a)–C(3)	108.4 (4)	N(3)–C(1')–C(2')	122.3 (4)
C(9b)–C(3a)–C(4)	121.5 (4)	N(3)–C(1')–C(6')	120.4 (4)
C(3)–C(3a)–C(4)	130.0 (4)	C(2')–C(1')–C(6')	117.2 (4)
C(3a)–C(4)–O(4)	121.9 (4)	C(1')–C(2')–C(3')	120.8 (4)
C(3a)–C(4)–C(5)	116.1 (3)	C(1')–C(2')–N(4)	121.6 (4)
O(4)–C(4)–C(5)	122.0 (4)	C(3')–C(2')–N(4)	117.5 (4)
C(4)–C(5)–N(2)	124.9 (4)	C(2')–C(3')–C(4')	119.9 (5)
C(4)–C(5)–C(5a)	121.1 (4)	C(3')–C(4')–C(5')	121.2 (5)
N(2)–C(5)–C(5a)	114.0 (4)	C(3')–C(4')–N(5)	119.2 (5)
C(5)–C(5a)–N(6)	115.0 (4)	C(5')–C(4')–N(5)	119.6 (5)
C(5)–C(5a)–C(9a)	120.5 (4)	C(4')–C(5')–C(6')	119.5 (5)
N(6)–C(5a)–C(9a)	124.5 (4)	C(1)–C(6')–C(5')	121.3 (5)
N(6)–C(7)–C(8)	122.5 (4)	C(9b)–N(1)–C(2)	110.8 (4)
N(6)–C(7)–C(70)	118.1 (4)	C(5)–N(2)–N(3)	118.6 (3)
C(8)–C(7)–C(70)	119.4 (4)	N(2)–N(3)–C(1')	117.2 (4)
C(7)–C(8)–C(9)	120.8 (4)	C(2')–N(4)–O(41)	120.3 (4)
C(8)–C(9)–C(9a)	118.9 (4)	C(2')–N(4)–O(42)	117.6 (4)
C(8)–C(9)–C(90)	117.6 (4)	O(41)–N(4)–O(42)	122.0 (49)
C(9a)–C(9)–C(90)	123.5 (4)	C(4')–N(5)–O(51)	117.9 (6)
C(9b)–C(9a)–C(5a)	116.1 (4)	C(4')–N(5)–O(52)	117.8 (5)
C(9b)–C(9a)–C(9)	128.7 (4)	O(51)–N(5)–O(52)	124.3 (7)
C(5a)–C(9a)–C(9)	115.2 (4)	C(5a)–N(6)–C(7)	117.9 (4)
C(2)–C(20)–O(21)	111.5 (4)	C(20)–O(21)–C(21)	119.3 (5)
C(2)–C(20)–O(22)	124.1 (4)	C(70)–O(72)–C(71)	116.7 (4)
O(21)–C(20)–O(22)	124.4 (4)	C(90)–O(92)–C(91)	115.5 (5)

C(5) atom, where, in the title compound, with an sp^2 C(5) atom, the ring system is planar. Both structures show that the keto group at C(5) is the more reactive site. The reaction of DNPH with free PQQ and with the enzyme-bound prosthetic group, respectively, yields the same C(5) adduct (II). Apparently, the C(5)=O function in the enzyme is free to react with DNPH. The structure analysis gives the final proof that the enzyme contains bound PQQ, in which the basic structure of PQQ is retained.

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Conformational Similarities and Structures of Two Isomeric Ten-Membered Ring Lactams, C₁₃H₂₅NO: (I) 4,4,7,7-Tetramethylazacyclodecan-2-one and (II) 6,6,9,9-Tetramethylazacyclodecan-2-one*

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Abstract. (I) $M_r = 211.4$, monoclinic, $C2/c$, $a = 19.002$ (10), $b = 16.224$ (3), $c = 9.8983$ (13) Å, $\beta = 121.14$ (2)°, $V = 2612$ (2) Å³ at 138 K, $a = 19.18$ (2), $b = 16.458$ (9), $c = 9.941$ (4) Å, $\beta = 121.33$ (4)°, $V = 2680$ (3) Å³ at 298 K; $Z = 8$, $D_m = 1.06$, $D_x = 1.047$ g cm⁻³, $\text{Cu } K\alpha$, $\lambda = 1.5418$ Å, $\mu = 4.4$ cm⁻¹, $F(000) = 944$, $R = 0.035$ for 2217 observed reflections, $R = 0.049$ for 2686 unique reflections. (II) $M_r = 211.4$, monoclinic, $P2_1/c$, $a = 8.6282$ (15), $b = 17.790$ (10), $c = 9.768$ (3) Å, $\beta = 120.855$ (12)°, $V = 1287.1$ (9) Å³ at 138 K, $a = 8.728$ (8), $b = 17.938$ (12), $c = 9.825$ (8) Å, $\beta = 121.15$ (7)°, $V = 1316$ (2) Å³ at 298 K; $Z = 4$, $D_m = 1.07$, $D_x = 1.067$ g cm⁻³, $\text{Cu } K\alpha$, $\lambda = 1.5418$ Å, $\mu = 4.5$ cm⁻¹, $F(000) = 472$, $R = 0.052$ for 2019 observed reflections, $R = 0.077$ for 2641 unique reflections. After a reversal of the relative positions of the amide nitrogen and carbonyl positions, a close similarity is observed in the conformations of compounds (I), (II) and the unsubstituted parent compound pelargolactam. Both (I) and (II) have a *trans* amide group with the amide bond distorted from planarity. The molecules are linked by N–H...O hydrogen bonds to form chains along **c** in (I) and parallel to **a** in (II).

Introduction. Smolíková, Havel, Vašíčková, Vitek, Svoboda & Bláha (1974) have studied the effect of

geminal methyl substitution on the solution conformations of nine- and ten-membered lactams. The predicted effect of such substitution is a decreased number of conformers, with *cis* or *trans* amide conformers being favored to varying degrees dependent on the location of the substitutions. Another characteristic of medium-ring lactams is the non-planarity of the amide bond (Dunitz & Winkler, 1975; Ealick & van der Helm, 1977; Ealick, Washecheck & van der Helm, 1976; Hossain, Baker & van der Helm, 1981). We report here the structures of the 4,4,7,7- and 6,6,9,9-tetramethyl derivatives of azacyclodecan-2-one.

Experimental. Both compounds obtained from Dr K. Bláha; crystals grown in thermal gradient with aqueous ethanol as solvent; D_m measured by flotation in KI solutions; (I) colorless plate, 0.12 × 0.19 × 0.31 mm; (II) colorless needle, 0.1 × 0.1 × 0.42 mm; Enraf-Nonius CAD-4 diffractometer with liquid N₂ low-temp. device; 48 reflections with $12 < \theta < 35^\circ$, $\text{Cu } K\alpha_1$ ($\lambda = 1.54051$ Å) at 138 K, 24 reflections with $5 < \theta < 15^\circ$, $\text{Mo } K\alpha_1$ ($\lambda = 0.70926$ Å) at 298 K used to refine cell constants; systematic absences: (I) hkl , $h + k = 2n + 1$, $h0l$, $l = 2n + 1$; (II) $h0l$, $l = 2n + 1$, $0k0$, $k = 2n + 1$; no absorption correction applied; $2\theta_{\text{max}} = 150^\circ$; (I) $-23 \leq h \leq 23$, $0 \leq k \leq 20$, $0 \leq l \leq 12$, (II) $-10 \leq h \leq 10$, $0 \leq k \leq 22$, $0 \leq l \leq 12$; three standard reflections measured after every 7200 s of X-ray exposure showed no deterioration; (I) 2686 unique reflections, 2217 observed, (II) 2641 unique reflections, 2019 observed [$I \geq 2\sigma(I)$]; structures solved by direct methods with *SHELX* (Sheldrick, 1976);

* Alternative names: 4,4,7,7-tetramethylazocan-2-one and 6,6,9,9-tetramethylazocan-2-one.

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