

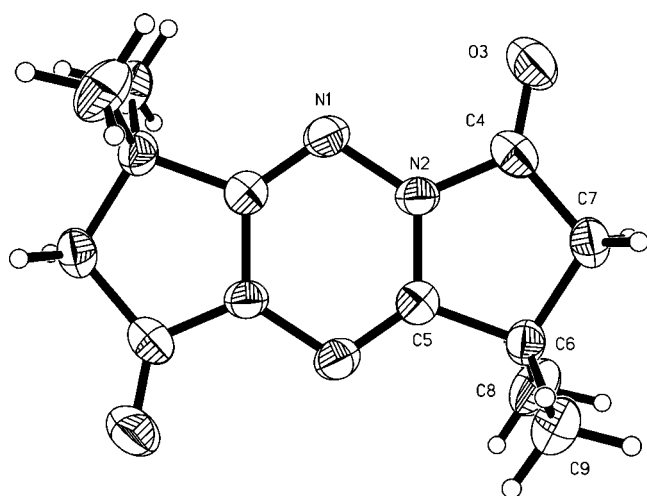
Crystal structure of 1,1,5,5-tetramethyl-1,2,5,6-tetrahydro-3a,4,7a,8-tetraza-*s*-indacene-3,7-dione, C₁₂H₁₆N₄O₂

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Abstract

C₁₂H₁₆N₄O₂, monoclinic, *P*12₁/*c*1 (No. 14), *a* = 9.306(2) Å, *b* = 5.755(1) Å, *c* = 11.499(2) Å, β = 98.15(3)°, *V* = 609.6 Å³, *Z* = 2, *R*_{gt}(*F*) = 0.045, *wR*_{ref}(*F*²) = 0.075, *T* = 294 K.

Source of material

Continued investigations on the formation of bicyclic [*b*]-annulated pyridazine derivatives from 4,4-dimethyl-tetrahydropyridazine-3,6-dione 3-hydrazone [1] required repeated and upscaled preparation of this compound in the reaction of a 3-cyano-3-methylbutyric ester with hydrazine hydrate [2]. A thorough reexamination of the latter reaction made it possible to isolate the title compound which was formed in minute amounts as a by-product [3].

Discussion

One half of the molecule forms the independent unit of the crystal. Therefore, the molecule in whole is centrosymmetric and consists of a tricyclic system with tetrazine and two saturated pyrrole rings. The tetrazine ring is planar with random deviations of fitted six atoms (with included symmetrical ones) amounting to only 0.02(1) Å. In such ring one bond, *d*(N1—C5^{*i*}) = 1.278(2) Å, (*i*: 2−*x*, −*y*, 1−*z*) is evidently double while the remaining two are lon-

ger (*d*(N1—N2) = 1.416(2) Å and *d*(N2—C5) = 1.386(2) Å). The bond lengths in the tetrazine ring are in agreement with the corresponding statistical values from Cambridge Structural Database [4]. The five-membered pyrrole ring consists of two carbon atoms in *sp*³ hybridization and is in a slightly screw position with the plane of asymmetry axis bisecting the N1—C4 bond and C6 atom. The respective asymmetry parameter [5] is as low as Δ*C*₅ = 0.77°. The C6 and C7 atoms are by only −0.031 Å and 0.096 Å, respectively, out of the ring plane determined by the three remaining ring atoms. Since the pyrrole rings are inclined to tetrazine at a very small angle of 2.9(2)°, the tricyclic skeleton may be considered as practically planar. Two weak intermolecular interactions, *d*(C8—H⋯O3^{*ii*}) = 3.489(2) Å and *d*(C9—H⋯O3^{*iii*}) = 3.362(2) Å, respectively, classified as weak H-bonds [6], were found in the crystal (*ii* = 2−*x*, 1−*y*, 1−*z*; *iii*: 2−*x*, 1/2+*y*, 3/2−*z*).

Table 1. Data collection and handling.

Crystal:	colourless cube, size 0.2 × 0.2 × 0.2 mm
Wavelength:	Mo <i>K</i> _α radiation (0.71073 Å)
μ:	0.96 cm ^{−1}
Diffractometer, scan mode:	Kuma KM4, θ/2ω
2θ _{max} :	50°
<i>N</i> (<i>hkl</i>) _{measured} , <i>N</i> (<i>hkl</i>) _{unique} :	2124, 1062
Criterion for <i>I</i> _{obs} , <i>N</i> (<i>hkl</i>) _{gt} :	<i>I</i> _{obs} > 2 σ(<i>I</i> _{obs}), 778
<i>N</i> (<i>param</i>) _{refined} :	83
Programs:	SHELXS-97 [7], SHELXL-97 [8]

Table 2. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso}
H(7A)	4e	1.2155	0.3491	0.7638	0.057
H(7B)	4e	1.2311	0.5241	0.6627	0.057
H(8A)	4e	1.3941	0.1674	0.4823	0.078
H(8B)	4e	1.4290	0.3827	0.5650	0.078
H(8C)	4e	1.2910	0.3841	0.4694	0.078
H(9A)	4e	1.3944	−0.1030	0.6488	0.069
H(9B)	4e	1.2955	−0.0587	0.7461	0.069
H(9C)	4e	1.4324	0.0973	0.7404	0.069

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Table 3. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₁₂	<i>U</i> ₁₃	<i>U</i> ₂₃
N(1)	4e	0.8655(2)	0.1154(2)	0.5154(1)	0.0284(8)	0.0459(8)	0.0330(8)	0.0026(6)	0.0040(6)	-0.0017(7)
N(2)	4e	1.0067(1)	0.1848(2)	0.5656(1)	0.0277(8)	0.0351(7)	0.0333(8)	0.0035(6)	0.0063(6)	-0.0014(6)
O(3)	4e	0.9407(2)	0.4949(2)	0.6680(1)	0.063(1)	0.0527(8)	0.0572(9)	0.0142(7)	0.0007(7)	-0.0209(6)
C(4)	4e	1.0326(2)	0.3669(3)	0.6419(2)	0.048(1)	0.0295(8)	0.038(1)	0.0007(8)	0.0125(8)	-0.0027(8)
C(5)	4e	1.1315(2)	0.0659(2)	0.5485(1)	0.0328(9)	0.0361(9)	0.0211(8)	-0.0011(7)	0.0060(7)	0.0039(7)
C(6)	4e	1.2626(2)	0.1837(3)	0.6129(1)	0.0318(9)	0.0378(8)	0.030(1)	-0.0037(7)	0.0023(7)	-0.0047(7)
C(7)	4e	1.1938(2)	0.3748(3)	0.6807(2)	0.043(1)	0.0328(8)	0.036(1)	-0.0033(8)	-0.0002(8)	-0.0054(7)
C(8)	4e	1.3527(2)	0.2890(3)	0.5241(2)	0.039(1)	0.072(1)	0.046(1)	-0.016(1)	0.0066(9)	0.011(1)

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