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Structure of 1,3,9-Trimethylalloxazine

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Abstract

The structure of 1,3,9-trimethylbenzo[*g*]pteridine-2,4(1*H*,3*H*)-dione (1,3,9-MALL) was solved by direct methods. The molecule is flat and the 14 atoms in the three rings are coplanar to within 0.052 (2) Å; the methyl C atoms deviate at most 0.11 (3) Å from the plane. The crystal packing of 1,3,9-MALL can be described as a 'herringbone' type.

Comment

The title compound was synthesized (Kozioł, Koziołowa, Konarski, Panek-Janc & Dawidowski, 1980) as part of a continuing study of a series of

9-methylalloxazines (9-MALL). Alloxazines are photolysis products of flavin (Ohkawa, Ohishi & Yagi, 1983) and can replace flavin in the bacterial bioluminescence reaction (Matheson, Lee & Müller, 1981). These compounds, when unsubstituted at N(1), show double fluorescence resulting from excited-state concerted double-proton transfer in the presence of compounds having proton donor and/or acceptor properties. Such substances are, for example, water, carboxylic and phosphoric acids, pyridine and other bases (Koziołowa, 1979; Szafran, Kozioł & Heelis, 1990). The aim of the crystal structure determination of 1,3,9-MALL was to provide more information on 9-methyl-substituted alloxazines and a comparison with earlier studies (Csöregi, Kierkegaard, Kozioł & Müller, 1987).

A perspective drawing of the molecule is shown in Fig. 1 (Motherwell & Clegg, 1978). Distances, bond angles, selected torsion angles (Klyne & Prelog, 1960; Stanford & Waser, 1972) and deviations from 120° for selected endocyclic angles are listed in Tables 2 and 3. The conformational features were computed using the program *PARST* (Nardelli, 1983). Fig. 2 is a stereoscopic packing illustration.

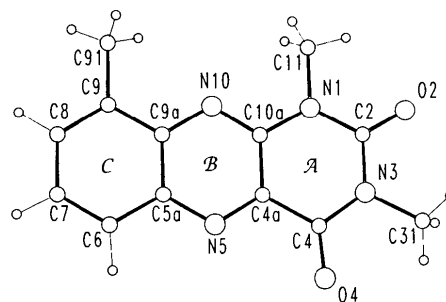


Fig. 1. A *PLUTO* (Motherwell & Clegg, 1978) illustration of 1,3,9-methylalloxazine showing the crystallographic atom numbering scheme. H atoms are unlabeled and the tricyclic rings are assigned labels *A*, *B* and *C*.

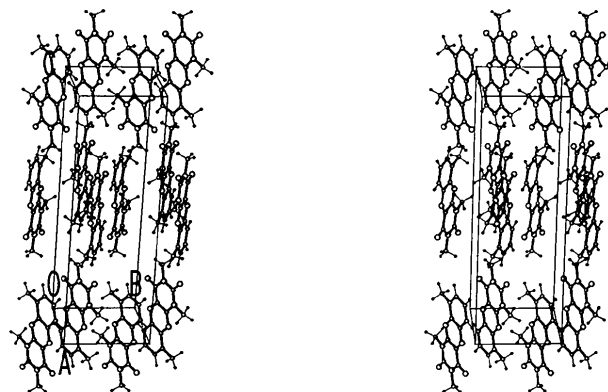


Fig. 2. A stereoscopic packing illustration viewed along the crystallographic *a* axis.

Comparison between the 9-methyl-, 1,3,9-trimethyl- and 1,3,8,9-tetramethylalloxazines shows that methyl substitution generally lengthens adjacent bond distances. This result follows a trend found earlier (Csöreg, Kierkegaard, Koziol & Müller, 1987). One exception is the C(7)—C(8) bond in tetra-MAll. It is noteworthy that the C(9)—C(9a) bond is significantly shorter in 1,3,9-MAll than in the methyl- and tetramethylalloxazines studied. All other values are in agreement within experimental error. The deviations from 120° of the endocyclic bond angles in the benzene, pyrimidine and pyrazine ring moieties of 1,3,9-MAll are given in Table 3. Substitution of one or more of the H atoms attached to a benzene ring is known to give distortions from the 6/*mmm* symmetry of the ring (Bent, 1961; Carter, McPhail & Sim, 1966). The substitution causes a redistribution of the electrons of the ring system and thus affects both the intramolecular bond angles and bond distances, but in most cases the benzene rings remain planar (Norrestam & Schepper, 1981). The methyl substitution on the benzene ring in the case of 1,3,9-MAll was found to affect bond distances and bond angles. The angles at C(7) and C(8), for example, deviate significantly when 1,3,9-MAll and 1,3,8,9-MAll are compared. The pyrimidine part of the molecule also shows significant deviation in bond angles around N(1), C(2) and N(3). The molecule of 1,3,9-MAll is flat. The 14 ring atoms of the tricyclic alloxazine moiety are coplanar to within 0.052 (2) Å.

The molecular conformation is very similar in all alloxazines studied, but the crystal packing is different. In the crystal of 9-MAll monohydrate the presence of hydrogen bonds strongly directs the packing formation. 1,3,9-MAll and 1,3,8,9-MAll have similar molecular packing which can be described as a 'herringbone' type of stacking. The angle between the planes of the symmetry-related molecules in 1,3,9-MAll is approximately 120°. The dihedral angle between ring *A* of one molecule and ring *C* of another at site $-x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$ is 124.2 (1)°. The crystal structure is stabilized by van der Waals forces.

Experimental

Crystal data

C₁₃H₁₂N₄O₂

M_r = 256.3

Monoclinic

*P*2₁/*n*

a = 7.052 (1) Å

b = 7.616 (1) Å

c = 22.429 (3) Å

β = 93.42 (1)°

V = 1202.5 (3) Å³

Z = 4

D_x = 1.4155 (3) Mg m⁻³

Cu *K*α radiation

λ = 1.54183 Å

Cell parameters from 38 reflections

θ = 10.7–27.6°

μ = 0.782 mm⁻¹

T = 295 K

Clean faces

0.73 × 0.52 × 0.21 mm

Yellow

Data collection

Siemens Stoe AED-2

diffractometer

ω–2θ scans

Absorption correction:

none

2600 measured reflections

1987 independent reflections

1451 observed reflections

[*I* > 3σ(*I*)]

Refinement

Refinement on *F*

R = 0.048

wR = 0.069

1451 reflections

183 parameters

Only H-atom *U*'s refined

riding on respective parent

atoms

*R*_{int} = 0.0623

θ_{max} = 69.53°

h = 0 → 8

k = 0 → 9

l = –27 → 27

5 standard reflections

frequency: 90 min

intensity variation: 2%

w = [σ²(*F*) + 0.00024|*F*|²]⁻¹

(Δ/σ)_{max} = 0.02

Δρ_{max} = 0.07 e Å⁻³

Δρ_{min} = –0.08 e Å⁻³

Atomic scattering factors

from *International Tables*

for *X-ray Crystallography*

(1974, Vol. IV)

Table 1. Fractional atomic coordinates and equivalent displacement parameters (Å²)

$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
N(1)	0.1751 (3)	0.1729 (2)	0.6112 (1)	0.042 (1)
C(11)	0.3587 (4)	0.0963 (4)	0.5978 (1)	0.054 (1)
C(2)	0.1348 (4)	0.1911 (3)	0.6701 (1)	0.049 (1)
O(2)	0.2417 (3)	0.1397 (3)	0.7107 (1)	0.074 (1)
N(3)	–0.0365 (3)	0.2725 (3)	0.6820 (1)	0.050 (1)
C(31)	–0.0762 (6)	0.2949 (5)	0.7453 (1)	0.077 (1)
C(4)	–0.1685 (3)	0.3387 (3)	0.6398 (1)	0.044 (1)
O(4)	–0.3120 (2)	0.4122 (3)	0.6540 (1)	0.058 (1)
C(4a)	–0.1212 (3)	0.3128 (3)	0.5773 (1)	0.037 (1)
N(5)	–0.2419 (2)	0.3692 (2)	0.5347 (1)	0.038 (1)
C(5a)	–0.1946 (3)	0.3455 (3)	0.4775 (1)	0.037 (1)
C(6)	–0.3181 (3)	0.4101 (3)	0.4304 (1)	0.043 (1)
C(7)	–0.2697 (4)	0.3888 (3)	0.3730 (1)	0.048 (1)
C(8)	–0.0994 (4)	0.3024 (3)	0.3604 (1)	0.048 (1)
C(9)	0.0265 (3)	0.2393 (3)	0.4046 (1)	0.042 (1)
C(91)	0.2108 (4)	0.1550 (4)	0.3911 (1)	0.056 (1)
C(9a)	–0.0212 (3)	0.2614 (3)	0.4647 (1)	0.036 (1)
N(10)	0.1018 (2)	0.2026 (2)	0.5097 (1)	0.039 (1)
C(10a)	0.0529 (3)	0.2290 (3)	0.5641 (1)	0.036 (1)

Table 2. Geometric parameters (Å, °)

N(1)—C(11)	1.468 (3)	N(5)—C(5a)	1.358 (3)
N(1)—C(2)	1.373 (3)	C(5a)—C(6)	1.417 (3)
N(1)—C(10a)	1.391 (3)	C(5a)—C(9a)	1.424 (3)
C(2)—O(2)	1.212 (3)	C(6)—C(7)	1.360 (3)
C(2)—N(3)	1.398 (3)	C(7)—C(8)	1.414 (4)
N(3)—C(31)	1.472 (3)	C(8)—C(9)	1.377 (3)
N(3)—C(4)	1.382 (3)	C(9)—C(91)	1.496 (4)
C(4)—O(4)	1.216 (3)	C(9)—C(9a)	1.419 (3)
C(4)—C(4a)	1.474 (3)	C(9a)—N(10)	1.367 (3)
C(4a)—N(5)	1.313 (3)	N(10)—C(10a)	1.304 (3)
C(4a)—C(10a)	1.430 (3)		
C(2)—N(1)—C(10a)	123.0 (2)	N(5)—C(5a)—C(9a)	120.8 (2)
C(11)—N(1)—C(10a)	118.7 (2)	N(5)—C(5a)—C(6)	118.9 (2)
C(11)—N(1)—C(2)	118.2 (2)	C(6)—C(5a)—C(9a)	120.2 (2)
N(1)—C(2)—N(3)	117.3 (2)	C(5a)—C(6)—C(7)	119.0 (2)
N(1)—C(2)—O(2)	122.4 (2)	C(6)—C(7)—C(8)	120.7 (2)
O(2)—C(2)—N(3)	120.3 (2)	C(7)—C(8)—C(9)	122.4 (2)
C(2)—N(3)—C(4)	125.8 (2)	C(8)—C(9)—C(9a)	117.6 (2)
C(2)—N(3)—C(31)	116.9 (2)	C(8)—C(9)—C(91)	122.3 (2)
C(31)—N(3)—C(4)	117.3 (2)	C(91)—C(9)—C(9a)	120.0 (2)
N(3)—C(4)—C(4a)	114.9 (2)	C(5a)—C(9a)—C(9)	120.0 (2)
N(3)—C(4)—O(4)	121.7 (2)	C(9)—C(9a)—N(10)	119.1 (2)

O(4)—C(4)—C(4a)	123.4 (2)	C(5a)—C(9a)—N(10)	120.9 (2)
C(4)—C(4a)—C(10a)	120.1 (2)	C(9a)—N(10)—C(10a)	116.7 (2)
C(4)—C(4a)—N(5)	118.3 (2)	C(4a)—C(10a)—N(10)	122.7 (2)
N(5)—C(4a)—C(10a)	121.6 (2)	N(1)—C(10a)—N(10)	118.5 (2)
C(4a)—N(5)—C(5a)	117.3 (2)	N(1)—C(10a)—C(4a)	118.7 (2)
C(11)—N(1)—C(2)—N(3)	176.8 (2)		
C(11)—N(1)—C(10a)—C(4a)	-176.4 (2)		
C(11)—N(1)—C(2)—O(2)	-3.1 (4)		
C(11)—N(1)—C(10a)—N(10)	3.7 (3)		
N(1)—C(2)—N(3)—C(31)	-178.6 (2)		
C(31)—N(3)—C(4)—C(4a)	179.9 (2)		
C(31)—N(3)—C(4)—O(4)	-0.2 (4)		
O(2)—C(2)—N(3)—C(31)	1.3 (4)		
C(91)—C(9)—C(9a)—C(5a)	178.5 (2)		
C(7)—C(8)—C(9)—C(91)	-177.2 (2)		
C(91)—C(9)—C(9a)—N(10)	-0.9 (3)		

Table 3. Deviations from 120° of selected endocyclic bond angles in 1,3,9-MAll, 9-MAll and 1,3,8,9-MAll

Benzene ring	C(5a)	C(6)	C(7)	C(8)	C(9)	C(9a)
1,3,9-MAll	+0.2 (2)	-1.0 (2)	+0.7 (2)	+2.4 (2)	-2.4 (2)	-0.0 (2)
9-MAll	+0.6 (2)	-1.4 (2)	+0.8 (2)	+3.0 (2)	-2.5 (2)	-0.5 (2)
1,3,8,9-MAll	+0.0 (4)	-1.9 (5)	+3.4 (5)	+0.2 (5)	-2.9 (4)	+1.1 (4)

Pyrimidine ring	N(1)	C(2)	N(3)	C(4)	C(4a)	C(10a)
1,3,9-MAll	+3.0 (2)	-2.7 (2)	+5.8 (2)	-5.1 (2)	+0.1 (2)	-1.3 (2)
9-MAll	+4.3 (2)	-4.3 (2)	+6.9 (2)	-5.2 (2)	-0.3 (2)	-1.5 (2)
1,3,8,9-MAll	+1.6 (4)	-1.2 (4)	+4.7 (4)	-4.7 (4)	+0.1 (4)	-0.6 (4)

Corrections for background, decay, Lorentz and polarization factors, but not for absorption effects, were included in the data reduction. The structure was solved by direct methods with the program *MITHRIL* (Gilmore, 1983), which resulted in reliable positions for all 19 non-H atoms. The initial model was refined with *SHELX76* (Sheldrick, 1976). Four low- θ reflections had F_{obs} systematically lower than F_{calc} indicating extinction and were excluded from the last refinement.

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Lists of structure factors, anisotropic thermal parameters, least-squares-planes data and H-atom coordinates and geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71382 (17 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AB1075]

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3-(4-*tert*-Butylphenyl)-3-hydroxy-1-(4-methoxyphenyl)-2-propen-1-one: an SHG Active β -Diketone

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Abstract

The molecular structure of 3-(4-*tert*-butylphenyl)-1-(4-methoxyphenyl)-1,3-propanedione in its crystal state was determined as an enol structure, 3-(4-*tert*-butylphenyl)-3-hydroxy-1-(4-methoxyphenyl)-2-propen-1-one (BPMP), $C_{20}H_{22}O_3$, with a disordered *tert*-butyl group attached to the benzene ring. BPMP has a powder second-order harmonic generation (SHG) efficiency ten times that of urea.

Comment

Organic materials are popular in second-order harmonic generation (SHG) devices such as laser diodes because they show large optical non-linearities and offer architectural flexibility (Chemla & Zyss, 1987) compared with inorganic materials. However, the majority of organic compounds have centrosymmetric crystal structures and are therefore SHG inactive. There are also other associated problems, such as thermal instabilities, growth of a large single crystal and processing for SHG devices. In addition, organic materials with large hyperpolarizabilities absorb light in longer-wavelength regions. In an attempt to develop new organic SHG materials, we