

C1	0.8796 (5)	0.5466 (5)	-0.2532 (5)	5.3 (1)
C2	0.8067 (4)	0.5017 (4)	-0.1422 (4)	3.80 (9)
C3	0.7181 (5)	0.3680 (4)	-0.1477 (4)	4.4 (1)
C4	0.6481 (5)	0.3268 (4)	-0.0476 (4)	3.91 (9)
C5	0.6664 (4)	0.4216 (4)	0.0633 (4)	3.10 (8)
C6	0.7526 (5)	0.5554 (4)	0.0680 (4)	4.2 (1)
C7	0.8216 (5)	0.5955 (4)	-0.0329 (4)	4.4 (1)
C8	0.5959 (4)	0.3776 (4)	0.1714 (4)	2.99 (8)
C9	0.5056 (4)	0.3678 (4)	0.3719 (4)	3.23 (8)
C10	0.3871 (4)	0.1478 (4)	0.3451 (4)	3.20 (8)
C11	0.3266 (4)	-0.0018 (4)	0.2906 (4)	3.80 (9)
C12	0.1928 (4)	-0.0738 (4)	0.3377 (4)	3.34 (8)
C13	0.2165 (5)	-0.1661 (4)	0.4398 (4)	4.0 (1)
C14	0.0961 (5)	-0.2314 (4)	0.4901 (4)	4.4 (1)
C15	-0.0449 (5)	-0.2056 (4)	0.4413 (4)	3.95 (9)
C16	-0.0742 (4)	-0.1137 (4)	0.3344 (4)	3.38 (8)
C17	-0.2225 (5)	-0.0866 (5)	0.2802 (5)	4.5 (1)
C18	-0.2501 (5)	0.0037 (5)	0.1770 (5)	5.2 (1)
C19	-0.1317 (6)	0.0698 (5)	0.1273 (5)	4.9 (1)
C20	0.0130 (5)	0.0461 (4)	0.1770 (4)	4.1 (1)
C21	0.0459 (4)	-0.0471 (4)	0.2836 (4)	3.10 (8)

Table 2. Geometric parameters (\AA , $^\circ$)

S—C8	1.769 (4)	C5—C8	1.463 (6)
S—C9	1.720 (4)	C6—C7	1.382 (7)
N1—N2	1.377 (5)	C10—C11	1.495 (5)
N1—C8	1.292 (4)	C11—C12	1.510 (6)
N2—C9	1.365 (5)	C12—C13	1.383 (6)
N2—C10	1.361 (5)	C12—C21	1.406 (5)
N3—N4	1.406 (4)	C13—C14	1.408 (7)
N3—C10	1.318 (6)	C14—C15	1.349 (7)
N4—C9	1.302 (6)	C15—C16	1.419 (6)
C1—C2	1.506 (7)	C16—C17	1.419 (6)
C2—C3	1.384 (6)	C16—C21	1.413 (6)
C2—C7	1.387 (6)	C17—C18	1.380 (7)
C3—C4	1.384 (7)	C18—C19	1.391 (7)
C4—C5	1.397 (6)	C19—C20	1.372 (7)
C5—C6	1.379 (5)	C20—C21	1.430 (6)
C8—S—C9	87.7 (2)	N2—C9—N4	110.0 (3)
N2—N1—C8	107.6 (3)	N2—C10—N3	108.2 (4)
N1—N2—C9	118.5 (3)	N2—C10—C11	125.4 (4)
N1—N2—C10	135.2 (3)	N3—C10—C11	126.4 (4)
C9—N2—C10	106.5 (3)	C10—C11—C12	112.0 (4)
N4—N3—C10	108.9 (3)	C11—C12—C13	119.1 (4)
N3—N4—C9	105.6 (3)	C11—C12—C21	122.0 (3)
C1—C2—C3	121.7 (4)	C13—C12—C21	118.9 (4)
C1—C2—C7	120.6 (4)	C12—C13—C14	120.7 (4)
C3—C2—C7	117.6 (4)	C13—C14—C15	121.5 (5)
C2—C3—C4	122.1 (5)	C14—C15—C16	119.4 (4)
C3—C4—C5	119.9 (3)	C15—C16—C17	120.3 (4)
C4—C5—C6	118.3 (4)	C15—C16—C21	119.6 (4)
C4—C5—C8	120.0 (3)	C17—C16—C21	120.1 (4)
C6—C5—C8	121.7 (4)	C16—C17—C18	120.1 (4)
C5—C6—C7	121.3 (4)	C17—C18—C19	119.9 (4)
C2—C7—C6	120.9 (4)	C18—C19—C20	121.6 (4)
S—C8—N1	116.9 (4)	C19—C20—C21	120.1 (4)
S—C8—C5	119.9 (2)	C12—C21—C16	119.9 (3)
N1—C8—C5	123.2 (3)	C12—C21—C20	121.9 (4)
S—C9—N2	109.3 (3)	C16—C21—C20	118.2 (4)
S—C9—N4	139.8 (3)		

The structure was determined by direct methods and refined by least-squares techniques. The melting point was determined on an X-4 microscopic melting apparatus and is uncorrected. Elemental analysis was performed on an Italian 1106 analyser, IR spectra on a Nicolet FT-5DX (KBr), ^1H NMR spectra on a Varian FT-80A using tetramethylsilane as the internal standard and deuterated dimethyl sulfoxide as the solvent.

Data collection: *CAD-4 Software* (Enraf-Nonius, 1985). Cell refinement: *CAD-4 Software*. Data reduction: *SDP/PDP* (Enraf-Nonius, 1985). Program(s) used to solve structure: *SDP/PDP*. Program(s) used to refine structure: *SDP/PDP*. Molecular graphics: *ORTEPII* (Johnson, 1976).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: TA1008). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

- Enraf-Nonius (1977). *CAD-4 Software*. Enraf-Nonius, Delft, The Netherlands.
- Enraf-Nonius (1985). *Structure Determination Package. SDP/PDP User's Guide*. Version 3.0. Enraf-Nonius, Delft, The Netherlands.
- Fornies-Marquina, J. M., Courseille, C. & Elguero, J. (1974). *Cryst. Struct. Commun.* **3**, 7–9.
- Gogoi, P. C. & Katakya, C. S. (1990). *Indian J. Chem. B*, **29**, 176–177.
- Holla, B. S., D'Souza, A. & Kalluraya, B. (1991). *J. Indian Chem. Soc.* **68**, 250–251.
- Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- Molina, P., Arques, A., Alias, M. A., Llamas Saiz, A. L. & Foces-Foces, M. C. (1989). *Liebigs Ann. Chem.* pp. 1055–1059.
- Patel, H. V., Fernandes, P. S. & Vyas, K. A. (1990). *Indian J. Chem. B* **29**, 135–141.

Acta Cryst. (1996). **C52**, 2789–2791

(2,4-Dinitrophenyl)(10-methyl-3-phenothiazinyl)diazene Hemimethanol Solvate

YING ZHU,^a BO LIU,^b QING-XIANG GUO^{b,c} AND YOU-CHENG LIU^{b,c}

^aAnalytical Centre, Lanzhou University, Lanzhou 730000, People's Republic of China, ^bNational Laboratory of Applied Organic Chemistry, Lanzhou University, Lanzhou 730000, People's Republic of China, and ^cDepartment of Modern Chemistry, University of Science and Technology of China, Hefei 230026, People's Republic of China

(Received 31 January 1995; accepted 6 June 1996)

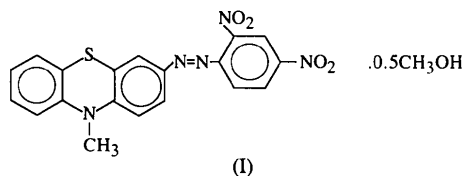
Abstract

In the title compound, $\text{C}_{19}\text{H}_{13}\text{N}_5\text{O}_4\text{S}\cdot 0.5\text{CH}_3\text{OH}$, the phenylazo group and the substituted benzene ring of the phenothiazine system are almost in the same plane, resulting in the formation of a conjugated system.

Comment

Phenothiazine and its substituted derivatives are highly reactive compounds. Because of this, they have aroused the curiosity of chemists and an increasing number of new derivatives have been synthesized. We have prepared recently a series of new phenothiazineazo derivatives by the reaction of 10-alkyl phenothiazine radical cations with 2,4-dinitrophenylhydrazine (Liu, Liu & Guo, 1994). In order to confirm their structures,

the structure of the title compound, 10-methylphenothiazine-3-azo(2',4'-dinitrobenzene), (I), was studied by single-crystal X-ray diffraction.



The molecule of (I) is not overall planar and a butterfly angle of 144.7 (1)° is formed between the rings of the 10-methylphenothiazine system (Fig. 1). The thiazine ring of this molecule has a boat conformation, as is the case in unsubstituted phenothiazine (McDowell, 1976). The S5 and N10 atoms are displaced from the plane of the thiazine ring by $-0.308(1)$ and $-0.296(1)$ Å, respectively. The N1'—N3 bond length of 1.258 (4) Å is typical of a double bond. The N3 and N1' atoms are only displaced from the benzene ring of the 2',4'-dinitrophenyl substituent by 0.032 (4) and $-0.050(4)$ Å, respectively. The phenylazo group and the substituted benzene ring of the 10-methylphenothiazine system are almost in the same plane, the dihedral angle between them being 4.4 (8)°. This results in the formation of an extended conjugated system, which is evidenced by the compound having a characteristic UV-visible absorption at $\lambda_{\max} = 524$ nm. In addition, the length of the N10—C14 bond is longer than that of N10—C11, but the S5—C13 and S5—C12 bond lengths are not noticeably different.

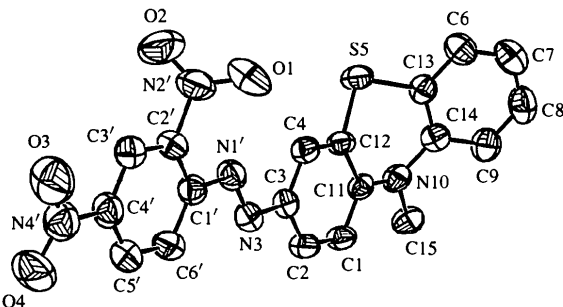


Fig. 1. The molecular structure of (I) showing 50% probability displacement ellipsoids. H atoms have been omitted for clarity.

Experimental

The synthesis of (I) was carried out by reaction of the hexachloroantimonate salt of the 10-methylphenothiazine radical cation and 2,4-dinitrophenylhydrazine (molar ratio 2:1) in acetonitrile under argon for 12 h at room temperature. The product was recrystallized from an acetone–methanol mixture to yield intense-violet needles.

Crystal data

C₁₉H₁₃N₅O₄S·0.5CH₃O
M_r = 423.43

Cu *K*α radiation
 $\lambda = 1.54184$ Å

Monoclinic

*P*2₁/*n*

a = 14.5086 (15) Å

b = 34.527 (3) Å

c = 3.8910 (8) Å

$\beta = 91.61(1)^\circ$

V = 1948.4 Å³

Z = 4

D_x = 1.443 Mg m⁻³

D_m = 1.422 Mg m⁻³

D_m measured by flotation

Cell parameters from 25 reflections

$\theta = 17.56\text{--}24.58^\circ$

$\mu = 1.79$ mm⁻¹

T = 294 (2) K

Needle

0.25 × 0.15 × 0.05 mm

Violet

Data collection

Enraf–Nonius CAD-4 diffractometer

$\omega/2\theta$ scans

Absorption correction:

ψ scans of high χ reflections (North, Phillips & Mathews, 1968)

T_{min} = 0.88, *T_{max}* = 0.91

2853 measured reflections

2631 independent reflections

2002 observed reflections [*I* > 3σ(*I*)]

R_{int} = 0.105

$\theta_{\max} = 58^\circ$

h = 0 → 15

k = 0 → 38

l = -4 → 4

3 standard reflections

frequency: 60 min

intensity decay: 2.0%

Refinement

Refinement on *F*

R = 0.075

wR = 0.075

S = 1.528

2002 reflections

280 parameters

Only coordinates of H atoms refined (except the H atom of the methanol molecule)

Unit weights applied

(Δ/σ)_{max} = 0.03

$\Delta\rho_{\max} = 0.38$ e Å⁻³

$\Delta\rho_{\min} = -0.37$ e Å⁻³

Extinction correction: none

Atomic scattering factors

from *International Tables for X-ray Crystallography* (1974, Vol. IV)

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

	$B_{\text{eq}} = (4/3)\sum_i \sum_j \beta_{ij} a_i \cdot a_j$			
	<i>x</i>	<i>y</i>	<i>z</i>	<i>B_{eq}</i>
S5	0.70794 (8)	0.22460 (4)	0.1984 (4)	4.25 (3)
O1	0.6600 (3)	0.3572 (1)	-0.701 (1)	8.4 (1)
O2	0.6062 (3)	0.4042 (2)	-0.421 (2)	10.9 (2)
O3	0.7675 (3)	0.5142 (1)	-1.070 (1)	7.6 (1)
O4	0.9067 (3)	0.5232 (1)	-0.883 (1)	8.0 (1)
N3	0.9019 (3)	0.3404 (1)	-0.222 (1)	3.94 (9)
N10	0.8963 (3)	0.1908 (1)	0.319 (1)	3.80 (8)
N1'	0.8260 (3)	0.3555 (1)	-0.312 (1)	4.00 (9)
N2'	0.6663 (3)	0.3893 (1)	-0.574 (1)	5.7 (1)
N4'	0.8364 (3)	0.5040 (1)	-0.916 (1)	5.6 (1)
C1	0.9788 (3)	0.2493 (2)	0.159 (1)	3.9 (1)
C2	0.9770 (3)	0.2861 (2)	0.028 (1)	4.1 (1)
C3	0.8951 (3)	0.3037 (1)	-0.076 (1)	3.6 (1)
C4	0.8117 (3)	0.2835 (1)	-0.037 (1)	3.6 (1)
C6	0.6723 (4)	0.1504 (2)	-0.007 (1)	4.9 (1)
C7	0.6945 (4)	0.1117 (2)	-0.053 (2)	5.9 (1)
C8	0.7834 (5)	0.0995 (2)	0.023 (2)	5.9 (1)
C9	0.8505 (4)	0.1247 (2)	0.145 (1)	4.9 (1)
C11	0.8969 (3)	0.2284 (1)	0.195 (1)	3.26 (9)
C12	0.8130 (3)	0.2470 (1)	0.102 (1)	3.29 (9)
C13	0.7386 (3)	0.1761 (1)	0.119 (1)	3.9 (1)
C14	0.8285 (3)	0.1639 (1)	0.197 (1)	3.8 (1)
C15	0.9815 (3)	0.1749 (2)	0.471 (1)	4.5 (1)
C1'	0.8348 (3)	0.3923 (1)	-0.465 (1)	3.6 (1)
C2'	0.7550 (3)	0.4098 (1)	-0.593 (1)	4.1 (1)
C3'	0.7527 (4)	0.4462 (2)	-0.738 (1)	4.4 (1)
C4'	0.8363 (4)	0.4653 (1)	-0.750 (1)	4.3 (1)

C5'	0.9173 (4)	0.4498 (2)	-0.628 (1)	4.7 (1)
C6'	0.9172 (3)	0.4131 (2)	-0.484 (1)	4.5 (1)
OM†	0	0	1/2	9.8 (8)
OM1†	0.476 (2)	0.4881 (9)	0.784 (7)	8.2 (7)
OM2†	0.518 (2)	0.5084 (8)	0.748 (7)	7.7 (7)
CM†	-0.021 (3)	0.024 (1)	0.53 (1)	9 (1)
CM1†	-0.024 (2)	0.0083 (9)	0.017 (9)	8.6 (7)

† Partially occupied (see below).

Table 2. Selected geometric parameters (\AA , $^\circ$)

S5—C12	1.758 (4)	N3—C3	1.394 (5)
S5—C13	1.762 (4)	N4'—C4'	1.482 (5)
O3—N4'	1.205 (5)	C1—C2	1.370 (6)
O4—N4'	1.221 (6)	C2—C3	1.384 (5)
N10—C11	1.385 (5)	C3—C4	1.410 (5)
N10—C14	1.426 (5)	C4—C12	1.369 (5)
N10—C15	1.465 (5)	C1—C11	1.400 (5)
N1'—N3	1.258 (4)		
C12—S5—C13	99.1 (2)	O1—N2'—C2'	118.2 (4)
C11—N10—C14	120.4 (4)	N10—C11—C1	122.1 (3)
N10—C11—C12	120.0 (3)	S5—C12—C4	119.1 (3)
S5—C12—C11	119.4 (3)	N1'—C1'—C6'	124.9 (4)
C11—N10—C15	118.8 (3)	N1'—C1'—C2'	117.4 (3)
N1'—N3—C3	114.8 (3)	N2'—C2'—C3'	116.6 (4)
O1—N2'—O2	123.4 (4)	N2'—C2'—C1'	119.7 (4)

The methanol molecule had a site-occupation factor of 0.5. The structure was solved by direct and Fourier methods and refined by full-matrix least-squares techniques. H atoms were located by difference Fourier synthesis. During refinement, a disordered region consisting of partially occupied methanol molecules was identified. This region contains molecules in orientations which would be mutually incompatible were they to be fully occupied. The disordered C and O atoms of methanol were labelled OM, OM1, OM2, CM and CM1, and their occupation factors refined to be 0.14, 0.18, 0.18, 0.20 and 0.30, respectively. The atoms were refined with isotropic displacement parameters. All calculations were performed with the *SDP-Plus* program system (Frenz, 1985) on a DEC PDP11/44 computer system.

Data collection: *CAD-4 Software* (Enraf-Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *SDP-Plus*. Program(s) used to solve structure: *SDP-Plus*. Program(s) used to refine structure: *SDP-Plus*. Molecular graphics: *ORTEPII* (Johnson, 1976).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BM0002). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

- Enraf-Nonius (1989). *CAD-4 Software*. Version 5.0. Enraf-Nonius, Delft, The Netherlands.
- Frenz, B. A. (1985). *Enraf-Nonius SDP-Plus Structure Determination Package*. Version 3.0. Enraf-Nonius, Delft, The Netherlands.
- Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- Liu, Y.-C., Liu, B. & Guo, Q.-X. (1994). *Chin. Chem. Lett.* **5**, 729–732.
- McDowell, J. J. H. (1976). *Acta Cryst.* **B32**, 5–10.
- North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* **A24**, 351–359.

Acta Cryst. (1996). **C52**, 2791–2793

A Pyridine-2,6(1*H*,3*H*)-dione Alkaloid

YING ZHU,^{a*} ZHONG-JIAN JIA,^a JIAN-GONG SHI^b AND HAN-QING WANG^b

^aNational Laboratory of Applied Organic Chemistry, Lanzhou University, Lanzhou 730000, People's Republic of China, and ^bLanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, People's Republic of China

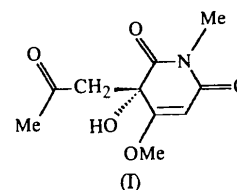
(Received 26 October 1995; accepted 29 January 1996)

Abstract

The crystal structure of the pyridine-2,6(1*H*,3*H*)-dione alkaloid 3-acetyl-3-hydroxy-4-methoxy-1-methylpyridine-2,6(1*H*,3*H*)-dione, C₁₀H₁₃NO₅, has been determined. The tetrahydropyridine ring possesses a distorted half-chair conformation. The unit-cell molecular packing appears to be stabilized by hydrogen bonding.

Comment

Speranskia tuberculata (Bge.) Baill (Chinese name: Tou Gu Cao) is a Chinese herb which is widely distributed in the Gansu, Jiling, Hebei, Shandong and Anhui Provinces of China. It has been used for the treatment of rheumatic arthritis, contracture, sores, swelling, pain and inflammatory diseases (Jiangsu Xingyi Xueyuan, 1977). No work has been published previously on this genus. We isolated a novel pyridine-2,6(1*H*,3*H*)-dione alkaloid, (I), from the dried whole plant of *S. tuberculata*, which grows in Beizai, Gansu Province of China, and report here its structure.



The C(4)—C(5) bond length exhibits double-bond character. The torsion angles of the tetrahydropyridine ring possess approximate local C_2 symmetry about an axis bisecting the C(2)—C(3) and C(5)—C(6) bonds. The asymmetry parameter ΔC_2 is 2.7 indicating that the ring preferably adopts a distorted half-chair conformation (Duax, Weeks & Rohrer, 1976) similar to most 1,2,3,6- and 1,2,5,6-tetrahydropyridine rings that exist in half-chair conformations (Bandoli, Dolmella, Moos, Nicolini & Ongaro, 1991).

The molecules are linked through intermolecular hydrogen bonds; O(2)—HO(2) 0.90 (5), HO(2)···O(1ⁱ) 1.90 (5), O(2)···O(1ⁱ) 2.764 (3) \AA and O(2)—HO(2)···O(1ⁱ) 161 (4) $^\circ$ [symmetry code: (i) $x, \frac{1}{2} - y, z - \frac{1}{2}$].