

University of Missouri-St. Louis

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2-Phenyl-3-(5,6,7,7a-tetrahydro-1H,3H-pyrrolo[1,2-c]oxazol-3-ylidene)-1-propene-1,1-dicarbonitril
and
4-(4-Methoxyphenyl)-2,6-bis(methylthio)pyridine-3-carbo

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Comment

It has been shown recently (Peseke *et al.*, 1994) that the reaction of certain secondary amines with 3-aryl-2-cyano-5,5-bis(methylthio)penta-2,4-dienitriles, (1), could lead to the 5-monoamino- or 5,5-diamino-substitution product or a pyridine derivative, depending upon the reaction conditions. As part of an ongoing research programme on the design and synthesis of donor-acceptor push-pull polyenes capable of second harmonic generation, we have synthesized compounds (3a) and (3b) from the reaction of (1) and L-(–)-2-hydroxymethylpyrrolidine, (2) (George *et al.*, 1997). It was observed that (1a) and (1b) undergo an intramolecular rearrangement to give the pyridine derivatives (4a) and (4b), respectively, when refluxed in dry methanol in the presence of any base, such as pyridine or secondary amines, or even potassium carbonate, as catalyst.

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2-Phenyl-3-(5,6,7,7a-tetrahydro-1H,3H-pyrrolo[1,2-c]oxazol-3-ylidene)-1-propene-1,1-dicarbonitrile and 4-(4-Methoxyphenyl)-2,6-bis(methylthio)pyridine-3-carbonitrile

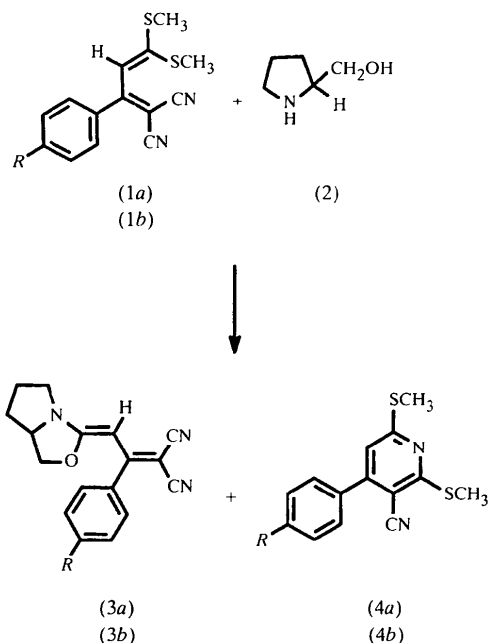
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Abstract

The reaction of 3-aryl-2-cyano-5,5-bis(methylthio)penta-2,4-dienitrile, (1), with L-(–)-2-hydroxymethylpyrrolidine, (2), gave two types of product, the normal substitution product, (3), and a pyridine derivative, (4). The structures of two representative examples, 2-phenyl-3-(5,6,7,7a-tetrahydro-1H,3H-pyrrolo[1,2-c]oxazol-3-ylidene)-1-propene-1,1-dicarbonitrile, (3a), as its hemibenzene solvate, C₁₇H₁₅N₃O.0.5C₆H₆, and 4-(4-methoxyphenyl)-2,6-bis(methylthio)pyridine-3-carbonitrile, (4b), C₁₅H₁₄N₂OS₂, have been unambiguously established by X-ray crystallographic analysis. The molecular packing of (4b) involves loosely held dimers, with S1···S1' distances of 3.424(1) Å.



For (a) R=H,
 and (b) R=OCH₃

We report herein the X-ray structures of compounds (3a) and (4b) (Figs. 1 and 2). Molecule (3a) crystallizes with half a molecule of benzene located on a twofold rotation axis. The absolute configuration of this compound could not be determined reliably [Flack (1983) parameter = –0.4(20)]. The molecular structure of (3a) incorporates a diene-dicarbonitrile skeleton attached to a pyrrolo-oxazole unit at one end and a phenyl substituent at the C2 position. The mean planes containing the phenyl ring (C6–C11, mean deviation 0.005 Å) and the diene-dicarbonitrile moiety (C1, C2, C4, N1, C5 and N2, mean deviation 0.005 Å) make an angle of 84.5(2)° with each other.

Compound (4b) is a pyridine derivative with methylthio substituents at C2 and C6, a cyano substituent at C3 and a *p*-methoxyphenyl group at C4. The two six-membered rings are planar within experimental error (phenyl ring C8–C13, mean deviation 0.005 Å; pyridine ring N1, C2–C6, mean deviation 0.005 Å) and form an angle of 40.89 (9)° with each other. The nitrile group is fully conjugated with the C3=C4 double bond [torsion angle N2–C7–C3–C4 = -179 (1)°; $\cos^2(\text{angle}) = 1$ (Jones *et al.*, 1997)].

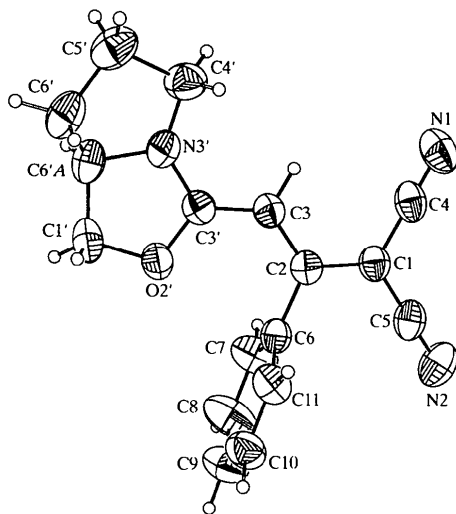


Fig. 1. View of the molecule of (3a) with 50% probability ellipsoids.

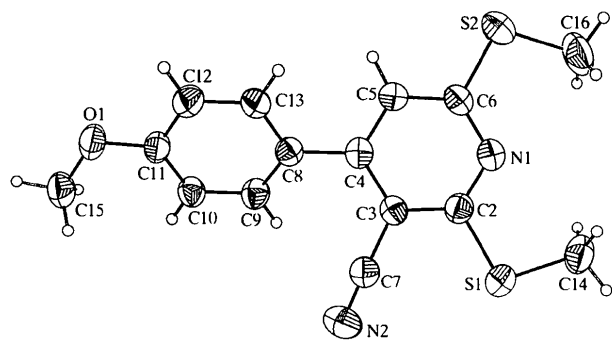


Fig. 2. View of the molecule of (4b) with 50% probability ellipsoids.

Crystal-packing diagrams for (3a) and (4b) are presented in Figs. 3 and 4, respectively. Compound (4b) crystallizes with discrete molecules in the lattice, and the molecular packing consists of loosely held dimers with S1...S1(-x, -y, 1-z) distances of 3.424 (1) Å. The molecules pack in a 'head-to-tail' fashion down the *a* axis. In (3a), the solvent benzene molecules are located perpendicular to the molecular-packing plane. For a material to exhibit non-linear optical properties, it must lack a centre of symmetry. Furthermore, the mol-

ecules must be arranged in such a way in the lattice so that the net dipole of the bulk will be large (the effects of the individual dipoles should add, not cancel one another; Singer *et al.*, 1987). Compound (3a) crystallizes in a chiral space group, which satisfies the first condition. Even though individual molecules of (3a) have a net dipole, the bulk packing arrangement (head-to-tail) would probably result in the cancellation of the net dipole. More sophisticated calculations or experimental measurements would be required to establish this property, which is beyond the scope of this work.

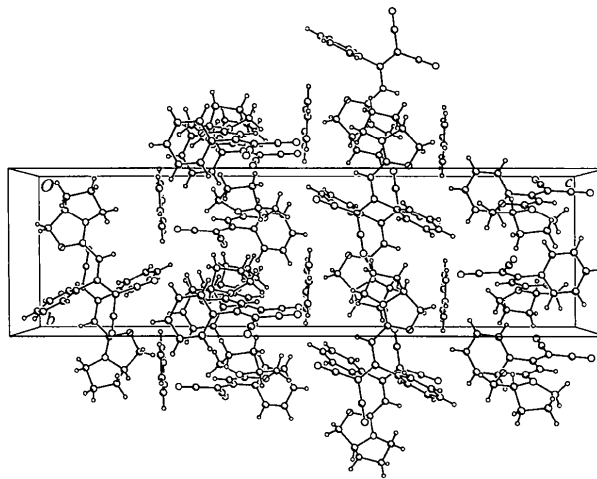


Fig. 3. The packing of (3a) viewed down the *a* axis.

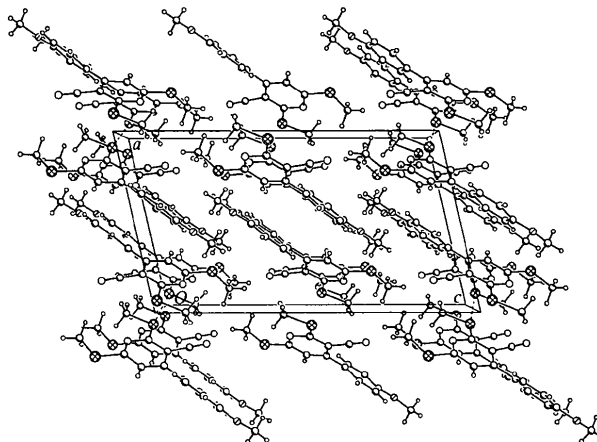


Fig. 4. The packing of (4b) viewed down the *b* axis.

Experimental

The substitution products (3a) and (3b) were obtained as major products on refluxing (1a) and (1b) in base-free tetrahydrofuran. Compounds (3a) (m.p. 406 K) and (4b) (m.p. 431 K) were obtained as good quality crystals by recrystallization from a mixture of chloroform and hexane (2:1), and a mixture of ethyl acetate and hexane (1:4), respectively.

Compound (3a)

Crystal data

C₁₇H₁₅N₃O.0.5C₆H₆

M_r = 316.37

Tetragonal

P4₃2₁2

a = 9.8769 (1) Å

c = 35.3642 (2) Å

V = 3449.89 (5) Å³

Z = 8

D_x = 1.218 Mg m⁻³

D_m not measured

Data collection

Siemens CCD diffractometer

ω scans

Absorption correction: none

73 530 measured reflections

3773 independent reflections

2701 reflections with

I > 2 σ (*I*)

Refinement

Refinement on *F*²

R[*F*² > 2 σ (*F*²)] = 0.050

wR(*F*²) = 0.118

S = 1.043

3767 reflections

219 parameters

H atoms riding

w = 1/[$\sigma^2(F_o^2) + (0.0528P)^2 + 0.4285P$]

where *P* = (*F_o*² + 2*F_c*²)/3

(Δ/σ)_{max} < 0.001

$\Delta\rho$ _{max} = 0.133 e Å⁻³

$\Delta\rho$ _{min} = -0.127 e Å⁻³

Mo *K* α radiation

λ = 0.71073 Å

Cell parameters from 8192

reflections

θ = 2.0–25.0°

μ = 0.077 mm⁻¹

T = 223 (2) K

Irregular

0.40 × 0.30 × 0.20 mm

Yellow

*R*_{int} = 0.10

θ _{max} = 27°

h = -8 → 9

k = 0 → 13

l = 0 → 47

Extinction correction:

SHELXTL-Plus (Sheldrick, 1995)

Extinction coefficient:

0.0036 (6)

Scattering factors from

International Tables for Crystallography (Vol. C)

Absolute structure: Flack (1983)

Flack parameter = -0.4 (20)

Compound (4b)

Crystal data

C₁₅H₁₄N₂OS₂

M_r = 302.40

Monoclinic

*P*2₁/*c*

a = 10.598 (2) Å

b = 7.5746 (10) Å

c = 19.053 (4) Å

β = 103.026 (11)°

V = 1490.1 (4) Å³

Z = 4

D_x = 1.348 Mg m⁻³

D_m not measured

Mo *K* α radiation

λ = 0.71073 Å

Cell parameters from 45

reflections

θ = 4.22–12.52°

μ = 0.354 mm⁻¹

T = 295 (2) K

Irregular

0.5 × 0.4 × 0.2 mm

Colourless

Data collection

Siemens *P4* diffractometer

ω scans

Absorption correction: none

4727 measured reflections

3579 independent reflections

2197 reflections with

I > 2 σ (*I*)

*R*_{int} = 0.023

θ _{max} = 28°

h = -1 → 13

k = -1 → 10

l = -25 → 24

3 standard reflections

every 97 reflections

intensity decay: 5.92%

Refinement

Refinement on *F*²

R[*F*² > 2 σ (*F*²)] = 0.050

wR(*F*²) = 0.114

S = 1.015

3542 reflections

181 parameters

H atoms riding

w = 1/[$\sigma^2(F_o^2) + (0.0376P)^2 + 0.5282P$]

where *P* = (*F_o*² + 2*F_c*²)/3

(Δ/σ)_{max} = 0.001

$\Delta\rho$ _{max} = 0.236 e Å⁻³

$\Delta\rho$ _{min} = -0.197 e Å⁻³

Extinction correction: none

Scattering factors from

International Tables for Crystallography (Vol. C)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²) for (3a)

$$U_{eq} = (1/3)\sum_i\sum_jU^{ij}a^i a^j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
O2'	0.70980 (15)	0.47391 (14)	0.07500 (4)	0.0521 (4)
N1	0.6390 (2)	0.6815 (2)	0.23384 (6)	0.0701 (6)
N2	0.5432 (2)	1.0106 (2)	0.15521 (7)	0.0739 (6)
N3'A	0.7479 (2)	0.3203 (2)	0.11890 (5)	0.0491 (4)
C1'	0.7676 (2)	0.3567 (2)	0.05503 (6)	0.0601 (6)
C1	0.6237 (2)	0.7653 (2)	0.16503 (5)	0.0456 (5)
C2	0.6550 (2)	0.6798 (2)	0.13463 (5)	0.0408 (4)
C3'	0.7193 (2)	0.4497 (2)	0.11213 (5)	0.0439 (5)
C3	0.6940 (2)	0.5457 (2)	0.14001 (5)	0.0441 (5)
C4'	0.8160 (2)	0.2602 (2)	0.15152 (6)	0.0610 (6)
C4	0.6317 (2)	0.7197 (2)	0.20332 (6)	0.0525 (5)
C5'	0.8793 (2)	0.1326 (2)	0.13461 (7)	0.0667 (6)
C5	0.5796 (2)	0.9009 (2)	0.15940 (6)	0.0533 (6)
C6'A	0.7696 (2)	0.2438 (2)	0.08382 (6)	0.0542 (5)
C6'	0.8983 (2)	0.1658 (2)	0.09276 (7)	0.0617 (6)
C6	0.6419 (2)	0.7416 (2)	0.09625 (5)	0.0422 (4)
C7	0.5179 (2)	0.7467 (3)	0.07829 (6)	0.0673 (7)
C8	0.5041 (3)	0.8085 (3)	0.04344 (7)	0.0863 (10)
C9	0.6146 (3)	0.8673 (3)	0.02660 (7)	0.0723 (7)
C10	0.7379 (2)	0.8635 (2)	0.04387 (6)	0.0626 (6)
C11	0.7516 (2)	0.8007 (2)	0.07856 (6)	0.0540 (5)
C1S	0.3822 (4)	0.3822 (4)	0	0.1008 (14)
C2S	0.2486 (4)	0.4173 (3)	0.00247 (9)	0.0991 (10)
C3S	0.1516 (3)	0.3180 (4)	0.00219 (8)	0.0930 (10)
C4S	0.1859 (3)	0.1859 (3)	0	0.0860 (12)

Table 2. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²) for (4b)

$$U_{eq} = (1/3)\sum_i\sum_jU^{ij}a^i a^j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
S1	0.07935 (8)	0.19310 (10)	0.52814 (4)	0.0637 (2)
S2	0.22234 (8)	0.74596 (11)	0.69884 (4)	0.0651 (2)
O1	0.5527 (2)	0.9367 (2)	0.31134 (9)	0.0556 (5)
N1	0.1570 (2)	0.4805 (3)	0.60621 (9)	0.0425 (5)
N2	0.1837 (2)	0.3014 (3)	0.37062 (12)	0.0675 (7)
C2	0.1557 (2)	0.3997 (3)	0.54379 (12)	0.0404 (5)
C3	0.2143 (2)	0.4703 (3)	0.49085 (11)	0.0376 (5)
C4	0.2818 (2)	0.6309 (3)	0.50435 (11)	0.0374 (5)
C5	0.2815 (2)	0.7150 (3)	0.56901 (11)	0.0418 (5)
C6	0.2175 (2)	0.6366 (3)	0.61748 (11)	0.0411 (5)
C7	0.1982 (2)	0.3778 (3)	0.42339 (13)	0.0452 (6)
C8	0.3527 (2)	0.7078 (3)	0.45269 (11)	0.0370 (5)
C9	0.4268 (2)	0.6029 (3)	0.41748 (11)	0.0416 (5)
C10	0.4953 (2)	0.6738 (3)	0.37057 (12)	0.0419 (6)
C11	0.4905 (2)	0.8536 (3)	0.35756 (12)	0.0414 (5)
C12	0.4182 (2)	0.9613 (3)	0.39281 (12)	0.0479 (6)
C13	0.3512 (2)	0.8895 (3)	0.44013 (12)	0.0426 (6)
C14	0.0178 (3)	0.1626 (4)	0.60727 (14)	0.0628 (8)
C15	0.6161 (3)	0.8286 (4)	0.26859 (14)	0.0580 (7)
C16	0.1309 (3)	0.6037 (5)	0.74337 (14)	0.0739 (9)

Preliminary examination and data collection were performed employing Siemens CCD and P4 automated single-crystal X-ray diffractometers using graphite-monochromated Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$). In the case of the CCD data set [for (3a)], ω -scan and double-pass methods were used for data collection. The first 50 frames were recollected at the end of the data collection to monitor crystal decay. SADABS correction (Blessing, 1995) was applied to the raw data. The structures were solved by direct methods. The non-H atoms were refined (least squares) anisotropically to convergence. H atoms were treated using an appropriate riding model [C—H = 0.94 \AA and $U(\text{H}) = 1.2U_{\text{eq}}(\text{carrier})$, or, for methyl H atoms, C—H = 0.98 \AA and $U(\text{H}) = 1.5U_{\text{eq}}(\text{carrier})$].

Data collection: SMART (Siemens, 1996b) for (3a); XSCANS (Siemens, 1996c) for (4b). Cell refinement: SAINT (Siemens, 1996a) for (3a); XSCANS for (4b). Data reduction: SAINT for (3a); SHELXTL-Plus (Sheldrick, 1995) for (4b). For both compounds, program(s) used to solve structures: SHELXTL-Plus; program(s) used to refine structures: SHELXTL-Plus; molecular graphics: SHELXTL-Plus; software used to prepare material for publication: SHELXTL-Plus.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1077). Services for accessing these data are described at the back of the journal.

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N,N'-Methylenebis[(*S*)-5-phenyloxazolidine]

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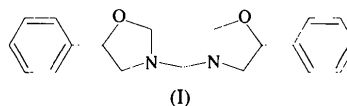
(Received 14 July 1997; accepted 6 November 1997)

Abstract

The 2:3 condensation product, C₁₉H₂₂N₂O₂, formed by reaction of (*S*)-(+)-2-amino-1-phenylethanol with formaldehyde has an *N,N'*-methylenebis(oxazolidine) heterocyclic skeleton. The two oxazolidine rings have envelope-type conformations, with their N atoms displaced by 0.604 (5) and 0.537 (6) \AA from the mean planes formed by the remaining four atoms of each ring. The dihedral angle between the two planes is 110.2 (2) $^\circ$.

Comment

The condensation product of (\pm)-2-amino-1-phenylethanol with formaldehyde in a respective molar ratio of 2:3 was first described as a synthetic reagent in 1994 and was assumed to have an *N,N'*-methylenebis(oxazolidine) heterocyclic skeleton (Pevarello *et al.*, 1994). While it has been shown that a similar aminoalcohol, (–)-norephedrine, with formaldehyde gives a 2:3 adduct which has this type of structure (Engel *et al.*, 1982), another related aminoalcohol, (–)-2-amino-2-phenylethanol, gives a quite different isomeric 2:3 adduct, having a 1,6-diaza-3,8-dioxabicyclo[4.4.1]undecane skeleton (Aitken *et al.*, 1991). This latter observation casts some doubt on the assumption of the structure of the title compound, (I), and since firm knowledge of its molecular structure is necessary in order to understand its chemical reactivity, confirmation was sought by an X-ray diffraction study.



The title compound consists of two 5-phenyloxazolidine rings with an –NCH₂N– bridge. Corresponding bond angles and distances in each of the