STRUCTURAL ANALYSIS OF *N*-(ω-PHENYLALKYL)SUBSTITUTED QUINOXALIN-2(1*H*)-ONES AND -THIONES[†]

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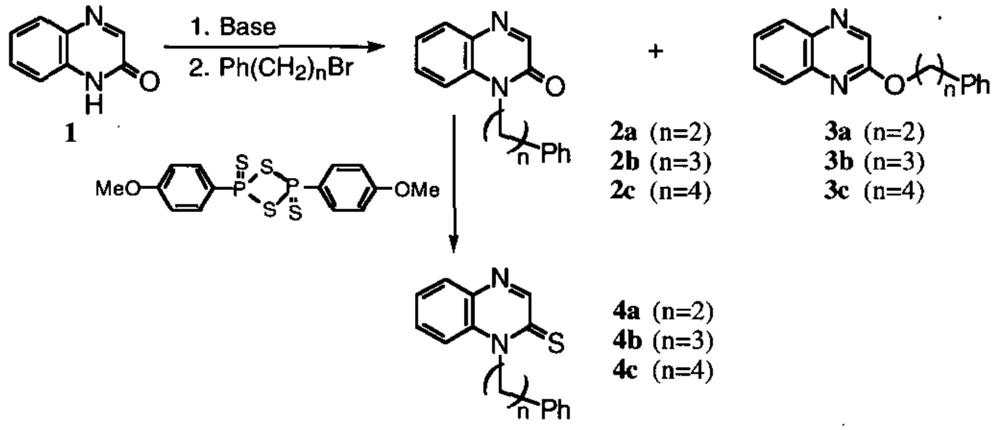
Abstract – Reaction of quinoxalin-2(1*H*)-one (**1**) with ω-phenylalkyl halides in the presence of bases gave a mixture of *N*- and *O*-alkylated products, which were separated by column chromatography. *N*-Alkylquinoxalin-2(1*H*)-ones (**2a-c**) were easily converted into the corresponding thiones (**4a-c**) by treatment with Lawesson's reagent. From X-ray crystallographic analysis, it was revealed that the molecular arrangement of *N*-phenethylquinoxalin-2(1*H*)-one (**2a**) was quite different from that of the corresponding thione (**4a**). Compound (**4a**) existed in a pair of conformational isomers in the crystalline state, and this was also supported by the solid-state ^{13}C nmr spectral data.

Pyrazine and quinoxaline derivatives have received much attention because of their pharmaceutical and bioluminescent interests.[1-3] We have intensively investigated chemical reactivities,[4,5] photochemical behaviors,[6] and the application to the fluorescence derivatization reagent[7] of quinoxaline and related compounds. On the other hand, no paper concerning quinoxalinone derivatives bearing the ω-phenylalkyl substituents at N–1 position has been reported, to the best of our knowledge. As a part of our studies, we describe here synthesis and the solid state structure of *N*-(ω-phenylalkyl)substituted quinoxalin-2(1*H*)-ones and -thiones.

[†] Dedicated to Dr. Shigeru Oae, Professor Emeritus, University of Tsukuba, on the occasion of his 77th birthday.

Synthesis of *N*-(ω-Phenylalkyl)substituted Quinoxalin-2(1*H*)-ones and -thiones

Reaction of quinoxalin-2(1*H*)-one (**1**) with phenylalkyl bromides was carried out in the presence of bases to give a mixture of *N*- and *O*-alkylated products (**2** and **3**) (Scheme 1). The ratio of *N*- and *O*-alkylated products changed by the employed bases such as NaH, NaOMe, and K_2CO_3 as summarized in Table 1.



Scheme 1

Table 1 Alkylation of **1** with phenethyl bromide

Run	Base	Yield (%)			
		2a	**3a**	**2a** : **3a**	
1	NaH	29	40	42 : 58	(19 %)a)
2	NaOMe	12	0	100 : 0	(69 %)a)
3	K_2CO_3	51	48	52 : 48	

a) Recovery of the starting material

N-Phenylalkylquinoxalin-2(1*H*)-ones (**2a-c**) were easily converted into the corresponding thiones (**4a-c**) by treatment with 2,4-bis(*p*-methoxyphenyl)-1,3-dithia-2,4-diphosphetane-2,4-disulfide (Lawesson's reagent) (Scheme 1).

Structural Characteristics of Quinoxalin-2(1*H*)-ones and -thiones

On ^1H nmr spectra, the methylene protons adjacent to nitrogen atom of **2a** were observed as a broad singlet at δ 4.44 ppm, while those of 1-phenethylpyrazin-2(1*H*)-one appeared as a triplet at δ 4.11 ppm. This lower magnetic field shift of $-N-CH_2-$ should be attributable to the anisotropic effect of the benzene ring of quinoxalin-2(1*H*)-one and -thiones. Furthermore, the broad singlet changed into a triplet-like signal at above 100 °C, suggesting that the rotation around a N–C single bond was restricted by steric repulsion between carbonyl or thiocarbonyl group and a hydrogen at the peri-position. ^{13}C Nmr spectra of **4a** were measured both in solution and in the crystalline state (Figure 1). The signals at δ 30.6, 137.2, 156.8, and 176.7 ppm in solution were observed as sets of two signals in the CPMAS spectrum, indicating that **4a** existed in two conformational isomers in the crystalline state.

Compounds (**2a** and **4a**) were crystallized from THF to give single crystals suitable for X-ray crystallographic analysis. ORTEP drawings, packing diagrams, and views of aromatic interactions are shown in Figures 2, 3, and 4, respectively. The dihedral angle between least-square planes of quinoxalinone (qo) and the benzene ring (ph) of **2a** was calculated to be 18.0°.[8] As shown in Figure 4, the distance between two quinoxalinone rings of **2a** was estimated to be 3.56 Å, indicating a significant face-to-face interaction.[9-11] Further, this distance is comparable with early reported values.[12,13] On the other hand, **4a** existed in a pair of isomers (**4a-1** and **-2**) in the crystalline state as shown in Figure 2. This was consistent with the solid-state ^{13}C nmr spectral data. The dihedral angles of the quinoxalinthione (qs) and benzene rings were 7.7° [qs(1)···ph(1)] for the isomer (**4a-1**) and 2.4° [qs(2)···ph(2)] for the isomer (**4a-2**), respectively, indicating that each benzene ring is almost parallel to the quinoxalinthione ring. Compound (**4a**) had two types of edge-to-face interactions (T-shaped interactions) of ph···ph and qs···qs, as shown Figure 4. Distances between the least-square planes of the ph (*p*-position H)···ph and qs (5-position H)···qs were calculated to be 2.87 Å and 2.70 Å, respectively, indicating significant edge-to-face interactions between the planes.[9-11] The interplane angles of two types of T-shaped interactions were within degrees of being nearly perpendicular to the planes.

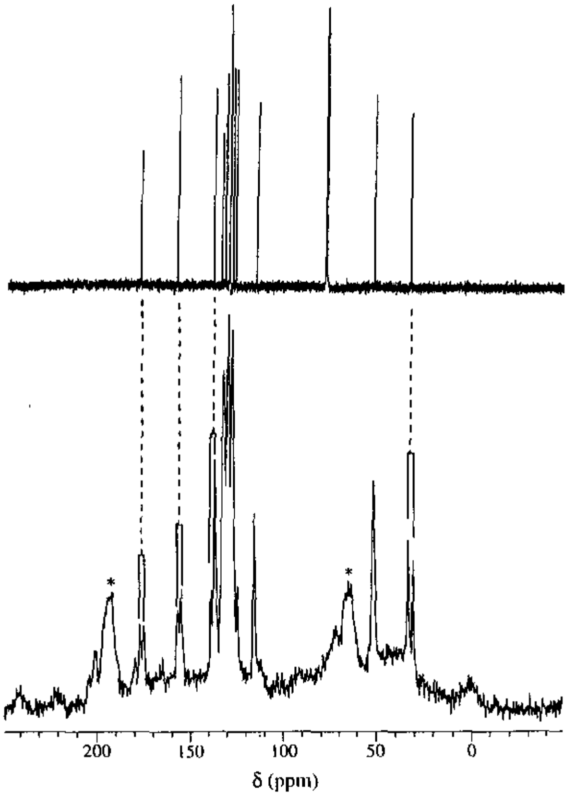


Figure 1 ^{13}C Nmr spectra of **4a** ; (top) in $CDCl_3$ solution, (bottom) in the crystalline state by CPMAS mode ; spinning side band (*)

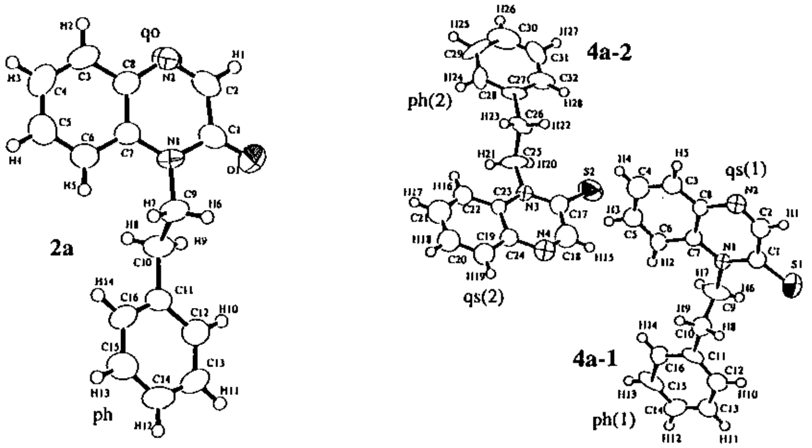


Figure 2 ORTEP drawings of **2a** (left) and **4a** (right) showing 50 and 40% probability displacement ellipsoids

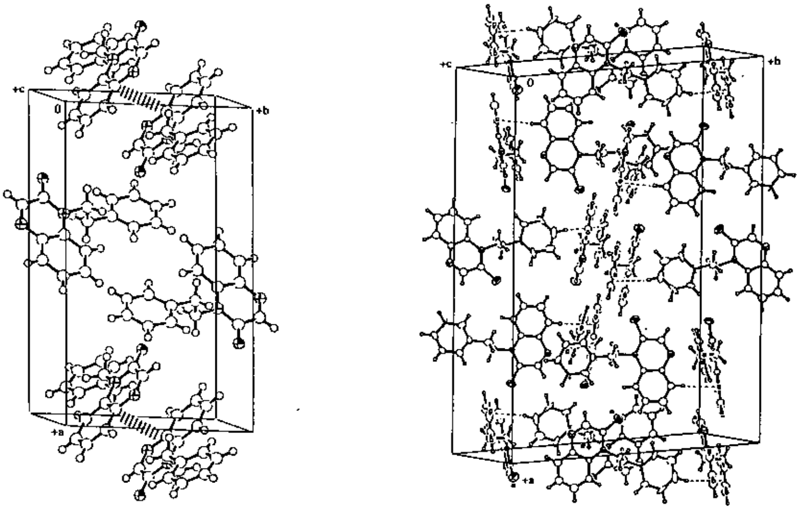


Figure 3 Packing diagrams of molecules in the unit cells of **2a** (left) and **4a** (right)

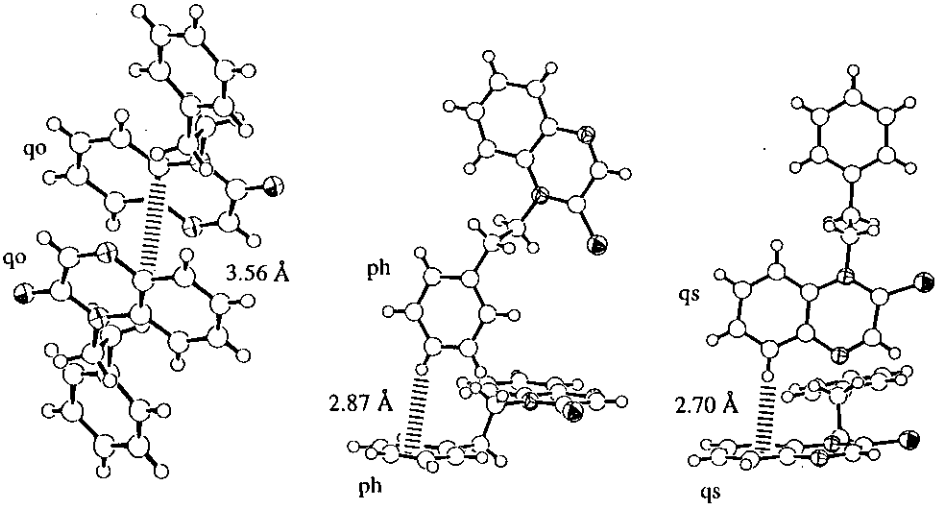


Figure 4 Views of aromatic interactions for **2a** (left) and **4a** (center and right)

EXPERIMENTAL

Melting points were measured with a Mel–Temp apparatus and are uncorrected. Ir spectra were recorded on a JASCO FT/IR-230 infrared spectrophotometer. ^{1}H and ^{13}C nmr spectra were recorded on a JEOL GX-270 spectrometer using Me_4Si as an internal standard. Solid-state high-resolution ^{13}C nmr spectrum was recorded on a JEOL EX-270 spectrometer by using the CPMAS mode, and the chemical shifts are referred to the CH_2 peak of external adamantane at 29.4 ppm from TMS.[14] Combustion analyses were performed on a Yanako MT-3 CHN CORDER.

Alkylation of quinoxalin-2(1*H*)-one (1) with phenethyl bromide : *Method 1 :* NaH (60% in an oil, 242 mg, 6.05 mmol) was washed with hexane, and then suspended in dry DMF (5 ml). To the suspension was added a solution of quinoxalin-2(1*H*)-one (**1**) (585 mg, 4.00 mmol) in dry DMF (12 ml). After stirring for several min, a solution of phenethyl bromide (891 mg, 4.81 mmol) in dry DMF (5 ml) was added dropwise to the emulsion. The reaction mixture was stirred for 30 min, and then heated for another 5 h at 120 °C. After quenching with a small amount of water, AcOEt (300 ml) was added to the reaction mixture. The organic layer was successively washed with H_2O (100 ml × 5), 5% $NaHCO_3$ (100 ml × 2) and sat. NaCl (100 ml), and then dried over anhydrous Na_2SO_4. After evaporation of the solvent, the residue was chromatographed on silica gel with $CHCl_3$. The first fraction was found to be *O*-alkylated product, 2-(2-phenethyloxy)quinoxaline (**3a**) as colorless plates ; yield 40% (400 mg), mp 64 °C (from AcOEt–petroleum ether), ir ν (KBr) cm^{-1} : 765 (δC–H), 702 (δC–H), ^{1}H nmr ($CDCl_3$, δ, ppm) : 3.17 (2H, t, J=6 Hz), 4.70 (2H, t, J=6 Hz), 7.21-7.33 (5H, m), 7.54 (1H, t, J=4 Hz), 7.65 (1H, t, J=4 Hz), 7.81 (1H, d, J=4 Hz), 8.00 (1H, d, J=4 Hz), 8.44 (1H, s). *Anal.* Calcd for $C_{16}H_{14}N_2O$: C, 76.78; H, 5.63; N, 11.19. Found : C, 76.97; H, 5.71; N, 11.13. The second fraction was *N*-alkylated product, 1-phenethylquinoxalin-2(1*H*)-one (**2a**) as pale yellow plates ; yield 29% (290 mg), mp 108-109 °C (from AcOEt–petroleum ether), ir ν (KBr) cm^{-1} : 1664 (νC=O), 754 (δC–H), 710 (δC–H), ^{1}H nmr ($CDCl_3$, δ, ppm) : 3.02 (2H, t, J=8 Hz), 4.44 (2H, t, J=8 Hz), 7.20-7.36 (7H, m), 7.58 (1H, t, J=8 Hz), 7.88 (1H, d, J=8 Hz), 8.30 (1H, s), ^{13}C nmr ($CDCl_3$, δ, ppm) : 33.1, 43.1, 123.4, 126.7, 128.6, 130.6, 130.8, 132.1, 133.4, 137.3, 150.0, 154.4. *Anal.* Calcd for $C_{16}H_{14}N_2O$: C, 76.78; H, 5.63; N, 11.19. Found : C, 76.88; H, 5.71; N, 11.14.

Method 2 : To a solution of NaOMe (639 mg, 11.83 mmol) in abs MeOH (5 ml) was added a suspension of **1** (585 mg, 4.00 mmol) in abs MeOH (5 ml). After stirring for several min, a solution of phenethyl bromide (1.63 g, 8.80 mmol) in abs MeOH (5 ml) was added dropwise to the solution. The reaction mixture was stirred for 30 min, and then refluxed for another 20 h. *N*-Alkylated product (**2a**) was only obtained in a 12% yield, and 69% of the starting material was recovered.

Method 3 : To a suspension of **1** (585 mg, 4.00 mmol) and K_2CO_3 (555 mg, 4.02 mmol) in dry DMF (11 ml) was added a solution of phenethyl bromide (890 mg, 4.81 mmol) in dry DMF (5 ml), and the reaction mixture was stirred for 24 h at 50 °C. *N*- and *O*-alkylated products (**2a** and **3a**) were obtained in 48 and 51% yields, respectively.

Similarly, other N- And O-alkylated products were prepared according to Method 1.

1-(3-Phenylpropyl)quinoxalin-2(1*H*)-one (2b) : yield 29%, mp 88 °C (from AcOEt–petroleum ether), ir ν (KBr) cm^{-1} : 1655 (νC=O), 757 (δC–H), 703 (δC–H), ^1H nmr ($CDCl_3$, δ, ppm) : 2.09 (2H, quint, J=8 Hz), 2.79 (2H, t, J=8 Hz), 4.24 (2H, t, J=8 Hz), 7.10 (1H, d, J=8 Hz), 7.21-7.34 (6H, m), 7.50 (1H, t, J=8 Hz), 7.86 (1H, d, J=8 Hz), 8.28 (1H, s). *Anal.* Calcd for $C_{17}H_{16}N_2O$: C, 77.25; H, 6.10; N, 10.60. Found : C, 77.65; H, 6.30; N, 10.43.

2-(3-Phenylpropyloxy)quinoxaline (3b) : yield 20%, mp 78 °C (from AcOEt–petroleum ether), ir ν (KBr) cm^{-1} : 767 (δC–H), 702 (δC–H), ^1H nmr ($CDCl_3$, δ, ppm) : 2.18 (2H, quint, J=8Hz), 2.84 (2H, t, J=8 Hz), 4.50 (2H, t, J=8 Hz), 7.16-7.32 (5H, m), 7.54 (1H, t, J=4 Hz), 7.65 (1H, t, J=4 Hz), 7.81 (1H, d, J=4 Hz), 8.01 (1H, d, J=4 Hz), 8.46 (1H, s). *Anal.* Calcd for $C_{17}H_{16}N_2O$: C, 77.25; H, 6.10; N, 10.60. Found : C, 77.03; H, 6.40; N, 10.49.

1-(4-Phenylbutyl)quinoxalin-2(1*H*)-one (2c) : yield 30%, mp 78-79 °C (from AcOEt–petroleum ether), ir ν (KBr) cm^{-1} : 1657 (νC=O), 754 (δC–H), 717 (δC–H), ^1H nmr ($CDCl_3$, δ, ppm) : 1.79 (4H, quint, J=5 Hz), 2.69 (2H, m), 4.23 (2H, m), 7.16-7.26 (6H, m), 7.33 (1H, t, J=8 Hz), 7.54 (1H, t, J=8 Hz), 7.87 (1H, d, J=8 Hz), 8.28 (1H, s). *Anal.* Calcd for $C_{18}H_{18}N_2O$: C, 77.67; H, 6.52; N, 10.06. Found : C, 77.64; H, 6.73; N, 9.72.

2-(4-Phenylbutyloxy)quinoxaline (3c) : yield 38%, mp 64 °C (from AcOEt–petroleum ether), ir ν (KBr) cm^{-1} : 764 (δC–H), 710 (δC–H), ^1H nmr ($CDCl_3$, δ, ppm) : 1.78-1.95 (4H, m), 2.72 (2H, t, J=7 Hz), 4.49 (2H, t, J=7 Hz), 7.18-7.31 (5H, m), 7.54 (1H, t, J=8 Hz), 7.65 (1H, t, J=8 Hz), 7.81 (1H, d, J=8 Hz), 8.01 (1H, d, J=8 Hz), 8.44 (1H, s). *Anal.* Calcd for $C_{18}H_{18}N_2O$: C, 77.67; H, 6.52; N, 10.06. Found : C, 77.93; H, 6.64; N, 10.27.

1-Phenethylquinoxalin-2(1*H*)-thione (4a) : A solution of 1-phenethylquinoxalin-2(1*H*)-one (**2a**) (399 mg, 1.59 mmol) and Lawesson's reagent (320 mg, 0.79 mmol) in toluene (30 ml) was refluxed for 2

h. After evaporation of the solvent, the residue was purified by column chromatography on silica gel with $CHCl_3$ and then with hexane–AcOEt mixture, and subsequent recrystallization from AcOEt–petroleum ether mixture to give the product (**4a**) as yellow needles ; yield 85% (361 mg), mp 140 °C (from AcOEt–petroleum ether), ir ν (KBr) cm^{-1} : 1133 (νC=S), 753 (δC–H), 705 (δC–H), ^1H nmr ($CDCl_3$, δ, ppm) : 3.10 (2H, t, J=8 Hz), 4.92 (2H, br), 7.23-7.45 (6H, m), 7.52 (1H, d, J=7 Hz), 7.64 (1H, t, J=7 Hz), 7.92 (1H, d, J=7 Hz), 8.82 (1H, s). *Anal.* Calcd for $C_{16}H_{14}N_2S$: C, 72.15; H, 5.30; N, 10.52. Found : C, 72.11; H, 5.37; N, 10.45.

1-(3-Phenylpropyl)quinoxalin-2(1*H*)-thione (4b) : yield 68%, mp 67-68 °C (from AcOEt–petroleum ether), ir ν (KBr) cm^{-1} : 1130 (νC=S), 760 (δC–H), 698 (δC–H), ^1H nmr ($CDCl_3$ δ, ppm) : 2.18 (2H, quint, J=7 Hz), 2.86 (2H, t, J=7 Hz), 4.75 (2H, br), 7.17 (1H, d, J=8 Hz), 7.26-7.42 (6H, m), 7.53 (1H, t, J=8 Hz), 7.90 (1H, d, J=8 Hz), 8.79 (1H, s). *Anal.* Calcd for $C_{17}H_{16}N_2O$: C, 72.82; H, 5.75; N, 9.99. Found : C, 72.58; H, 5.93; N, 9.86.

1-(4-Phenylbutyl)quinoxalin-2(1*H*)-thione (4b) : yield 56%, ir ν (neat) cm^{-1} : 1134 (νC=S), 752 (δC–H), 700 (δC–H), ^1H nmr ($CDCl_3$ δ, ppm) : 1.80 (4H, m), 2.67 (2H, m), 4.65 (2H, br), 7.12-7.36 (7H, m), 7.53 (1H, t, J=8 Hz), 7.81 (1H, d, J=8 Hz), 8.71 (1H, s). *Anal.* Calcd for $C_{18}H_{18}N_2S \cdot 0.4 H_2O$: C, 71.68; H, 6.28; N, 9.29. Found : C, 71.78; H, 6.07; N, 9.02.

X-Ray Analyses of 2a and 4a

X-Ray structure analyses of **2a** and **4a** were carried out in a Rigaku AFC5S diffractometer, and the cell parameters and the intensity data were measured with graphite monochromated Mo-Kα (λ=0.71069Å) radiation at 293 K. The crystal data are summarized in Table 2. The structures were solved by direct methods[15] and expanded using Fourier techniques.[16] The parameters of non-hydrogen atoms were refined by the full matrix least-square method with anisotropic temperature factors (or with isotopic factors, partly in the case of **4a**). The hydrogen atoms were located from a difference Fourier synthesis, and refined only the temperature factors isotropically. All calculations were performed using teXsan[8] crystallographic software package of Molecular Structure Corporation. The atomic coordinates for **2a** and **4a** are listed in Tables 3 and 4. The bond lengths and bond angles are listed in Tables 5 and 6. In the case of **4a**, a pair of conformational isomers were solved as a unit.

Table 2 Crystallographic data for **2a** and **4a**

	2a	**4a**
Formula	$C_{16}H_{14}N_2O$	$C_{32}H_{28}N_4S_2$
Fw	250.30	532.72
Color	colorless	yellow
Habit	prismatic	plate
Crystal size / mm	0.40×0.40×0.90	0.60×0.60×0.20
Crystal system	monoclinic	orthorhombic
Space group	$P2_1/n$	Pbca
a/Å	17.045(2)	30.02(2)
b/Å	10.197(2)	24.69(2)
c/Å	7.462(1)	7.36(2)
α/ °	90.000	90.000
β/ °	102.26(1)	90.000
γ/ °	90.000	90.000
V/Å^3	1267.5(3)	5457(19)
Z	4	8
Dc/g cm^{-3}	1.312	1.297
μ/cm^{-1}	0.83	2.24
$2\theta_{max}$/ °	60.0	50.0
No. of observations	1262	1059
No. of variables	173	244
R [a], R' [b]	0.046, 0.025	0.079, 0.054

[a] $R = \Sigma(||F_0| - |F_C||)/\Sigma|F_0|$. [b] $R' = [\Sigma w(|F_0| - |F_C|)^2/\Sigma w|F_0|^2]^{1/2}$.

Table 3 Atomic coordinates for **2a** with estimated standard deviations (e.s.d.s) in parentheses and B_{iso}/B_{eq}

Atom	x	y	z	B_{eq}
O(1)	0.2668(1)	0.0347(2)	0.7940(3)	6.32(7)
N(1)	0.3757(1)	0.1658(2)	0.8920(3)	3.55(7)
N(2)	0.4227(2)	-0.0030(3)	1.1916(3)	4.58(8)
C(1)	0.3288(2)	0.0587(3)	0.9052(4)	4.35(9)
C(2)	0.3589(2)	-0.0227(3)	1.0678(4)	4.89(10)
C(3)	0.5375(2)	0.1314(3)	1.3034(4)	4.74(9)
C(4)	0.5839(2)	0.2385(3)	1.2888(4)	5.5(1)
C(5)	0.5629(2)	0.3221(4)	1.1407(5)	5.4(1)
C(6)	0.4948(2)	0.3002(3)	1.0087(4)	4.38(9)
C(7)	0.4463(2)	0.1924(3)	1.0212(4)	3.39(8)
C(8)	0.4680(2)	0.1056(3)	1.1704(4)	3.64(8)
C(9)	0.3478(2)	0.2557(3)	0.7362(4)	4.13(8)
C(10)	0.3865(2)	0.2243(3)	0.5727(4)	4.41(8)
C(11)	0.3624(2)	0.3240(3)	0.4212(4)	3.63(8)
C(12)	0.3062(2)	0.2942(3)	0.2637(4)	4.31(9)
C(13)	0.2850(2)	0.3886(4)	0.1280(4)	4.92(10)
C(14)	0.3179(2)	0.5098(4)	0.1475(4)	5.1(1)
C(15)	0.3739(2)	0.5406(3)	0.3038(4)	5.9(1)
C(16)	0.3951(2)	0.4472(4)	0.4393(4)	4.83(9)

Table 4 Atomic coordinates for two isomers of **4a** with estimated standard deviations (e.s.d.s) in parentheses and B_{iso}/B_{eq}

Atom	x	y	z	B_{eq}	Atom	x	y	z	B_{eq}
S(1)	0.8192(2)	0.1617(2)	0.6915(7)	6.3(2)	C(14)	0.7046(8)	0.0161(8)	1.377(3)	4.7(7)
S(2)	0.5573(2)	0.3495(2)	0.4085(7)	7.2(2)	C(15)	0.6701(8)	0.0295(9)	1.268(3)	5.4(7)
N(1)	0.7306(4)	0.1501(5)	0.632(2)	2.6(3)	C(16)	0.6743(7)	0.0679(9)	1.137(3)	4.4(7)
N(2)	0.7352(5)	0.2249(5)	0.347(2)	3.9(4)	C(17)	0.5224(6)	0.3885(7)	0.508(2)	3.8(4)
N(3)	0.4779(5)	0.3946(5)	0.477(2)	2.8(3)	C(18)	0.5381(6)	0.4229(8)	0.657(3)	5.8(5)
N(4)	0.5145(5)	0.4584(5)	0.746(2)	4.8(4)	C(19)	0.4421(6)	0.4967(7)	0.815(2)	4.8(5)
C(1)	0.7713(6)	0.1717(6)	0.594(2)	3.4(4)	C(20)	0.3966(6)	0.4996(7)	0.780(3)	5.2(5)
C(2)	0.7692(6)	0.2103(6)	0.442(2)	4.0(5)	C(21)	0.3793(6)	0.4708(8)	0.646(3)	5.8(5)
C(3)	0.6545(6)	0.2155(6)	0.303(2)	4.1(5)	C(22)	0.4037(6)	0.4363(7)	0.542(2)	4.1(5)
C(4)	0.6140(6)	0.1953(7)	0.345(3)	5.6(5)	C(23)	0.4501(5)	0.4302(6)	0.568(2)	2.4(4)
C(5)	0.6138(5)	0.1607(7)	0.492(2)	4.1(4)	C(24)	0.4689(5)	0.4618(7)	0.712(2)	3.4(4)
C(6)	0.6497(5)	0.1441(6)	0.589(2)	3.2(4)	C(25)	0.4595(6)	0.3611(7)	0.330(2)	4.6(6)
C(7)	0.6911(5)	0.1632(7)	0.542(2)	3.0(4)	C(26)	0.4591(6)	0.3892(7)	0.149(2)	4.2(6)
C(8)	0.6931(5)	0.2013(6)	0.392(2)	2.6(4)	C(27)	0.4448(8)	0.3542(8)	-0.008(2)	3.9(7)
C(9)	0.7294(6)	0.1096(6)	0.781(2)	4.6(6)	C(28)	0.4004(7)	0.3512(9)	-0.054(3)	4.8(7)
C(10)	0.7188(6)	0.1350(7)	0.965(2)	4.3(6)	C(29)	0.3891(8)	0.3162(10)	-0.197(3)	6.2(8)
C(11)	0.7141(8)	0.0929(8)	1.114(3)	3.5(6)	C(30)	0.421(1)	0.2845(9)	-0.275(3)	6.5(9)
C(12)	0.7495(7)	0.0799(8)	1.222(3)	3.8(6)	C(31)	0.4628(8)	0.289(1)	-0.232(4)	5.8(8)
C(13)	0.7438(7)	0.0408(9)	1.354(3)	4.4(7)	C(32)	0.4750(8)	0.3223(9)	-0.093(3)	5.6(8)

Table 5 Bond distances (Å) and angles (°) for **2a**

O(1)–C(1)	1.221(3)	N(1)–C(1)	1.370(3)	N(1)–C(7)	1.399(3)
N(1)–C(9)	1.477(3)	N(2)–C(2)	1.284(3)	N(2)–C(8)	1.379(3)
C(1)–C(2)	1.470(4)	C(3)–C(4)	1.366(4)	C(3)–C(8)	1.399(3)
C(4)–C(5)	1.382(4)	C(5)–C(6)	1.372(4)	C(6)–C(7)	1.391(3)
C(7)–C(8)	1.409(3)	C(9)–C(10)	1.539(3)	C(10)–C(11)	1.511(3)
C(11)–C(12)	1.382(3)	C(11)–C(16)	1.370(4)	C(12)–C(13)	1.388(4)
C(13)–C(14)	1.353(4)	C(14)–C(15)	1.375(4)	C(15)–C(16)	1.380(4)
C(1)–N(1)–C(7)	122.3(3)	C(1)–N(1)–C(9)	117.1(2)	C(7)–N(1)–C(9)	120.5(3)
C(2)–N(2)–C(8)	116.9(3)	O(1)–C(1)–N(1)	123.0(3)	O(1)–C(1)–C(2)	123.2(3)
N(1)–C(1)–C(2)	113.7(3)	N(2)–C(2)–C(1)	126.8(3)	C(4)–C(3)–C(8)	120.7(3)
C(3)–C(4)–C(5)	120.1(3)	C(4)–C(5)–C(6)	120.7(3)	C(5)–C(6)–C(7)	120.3(3)
N(1)–C(7)–C(6)	122.9(3)	N(1)–C(7)–C(8)	117.9(3)	C(6)–C(7)–C(8)	119.2(3)
N(2)–C(8)–C(3)	118.7(3)	N(2)–C(8)–C(7)	122.3(3)	C(3)–C(8)–C(7)	119.0(3)
N(1)–C(9)–C(10)	112.0(2)	C(9)–C(10)–C(11)	111.0(2)	C(10)–C(11)–C(12)	121.2(3)
C(10)–C(11)–C(16)	120.2(3)	C(12)–C(11)–C(16)	118.7(3)	C(11)–C(12)–C(13)	119.6(3)
C(12)–C(13)–C(14)	121.1(3)	C(13)–C(14)–C(15)	119.7(3)	C(14)–C(15)–C(16)	119.5(3)
C(11)–C(16)–C(15)	121.4(3)				

Table 6 Bond distances (Å) and angles (°) for two isomers of **4a**

S(1)–C(1)	1.62(2)	S(2)–C(17)	1.60(2)	C(1)–N(1)–C(7)	125(1)	C(1)–N(1)–C(9)	115(1)
N(1)–C(1)	1.36(2)	N(1)–C(7)	1.40(2)	C(7)–N(1)–C(9)	119(1)	C(2)–N(2)–C(8)	117(1)
N(1)–C(9)	1.49(2)	N(2)–C(2)	1.29(2)	C(17)–N(3)–C(23)	125(1)	C(17)–N(3)–C(25)	115(1)
N(2)–C(8)	1.43(2)	N(3)–C(17)	1.36(2)	C(23)–N(3)–C(25)	119(1)	C(18)–N(4)–C(24)	118(1)
N(3)–C(23)	1.38(2)	N(3)–C(25)	1.47(2)	S(1)–C(1)–N(1)	130(1)	S(1)–C(1)–C(2)	118(1)
N(4)–C(18)	1.30(2)	N(4)–C(24)	1.39(2)	N(1)–C(1)–C(2)	111(1)	N(2)–C(2)–C(1)	128(1)
C(1)–C(2)	1.47(2)	C(3)–C(4)	1.35(2)	C(4)–C(3)–C(8)	123(1)	C(3)–C(4)–C(5)	114(1)
C(3)–C(8)	1.37(2)	C(4)–C(5)	1.38(2)	C(4)–C(5)–C(6)	126(1)	C(5)–C(6)–C(7)	118(1)
C(5)–C(6)	1.36(2)	C(6)–C(7)	1.37(2)	N(1)–C(7)–C(6)	124(1)	N(1)–C(7)–C(8)	118(1)
C(7)–C(8)	1.45(2)	C(9)–C(10)	1.53(2)	C(6)–C(7)–C(8)	116(1)	N(2)–C(8)–C(3)	122(1)
C(10)–C(11)	1.52(2)	C(11)–C(12)	1.37(2)	N(2)–C(8)–C(7)	118(1)	C(3)–C(8)–C(7)	119(1)
C(11)–C(16)	1.36(2)	C(12)–C(13)	1.38(2)	N(1)–C(9)–C(10)	112(1)	C(9)–C(10)–C(11)	112(1)
C(13)–C(14)	1.34(2)	C(14)–C(15)	1.35(2)	C(10)–C(11)–C(12)	120(2)	C(10)–C(11)–C(16)	119(2)
C(15)–C(16)	1.36(2)	C(17)–C(18)	1.47(2)	C(12)–C(11)–C(16)	120(1)	C(11)–C(12)–C(13)	118(1)
C(19)–C(20)	1.39(2)	C(19)–C(24)	1.40(2)	C(12)–C(13)–C(14)	121(1)	C(13)–C(14)–C(15)	119(1)
C(20)–C(21)	1.32(2)	C(21)–C(22)	1.36(2)	C(14)–C(15)–C(16)	121(2)	C(11)–C(16)–C(15)	119(1)
C(22)–C(23)	1.41(2)	C(23)–C(24)	1.44(2)	S(2)–C(17)–N(3)	129(1)	S(2)–C(17)–C(18)	118(1)
C(25)–C(26)	1.50(2)	C(26)–C(27)	1.51(2)	N(3)–C(17)–C(18)	112(1)	N(4)–C(18)–C(17)	126(1)
C(27)–C(28)	1.38(2)	C(27)–C(32)	1.36(2)	C(20)–C(19)–C(24)	119(1)	C(19)–C(20)–C(21)	119(1)
C(28)–C(29)	1.40(2)	C(29)–C(30)	1.36(3)	C(20)–C(21)–C(22)	122(1)	C(21)–C(22)–C(23)	121(1)
C(30)–C(31)	1.31(3)	C(31)–C(32)	1.36(3)	N(3)–C(23)–C(22)	126(1)	N(3)–C(23)–C(24)	117(1)
				C(22)–C(23)–C(24)	115(1)	N(4)–C(24)–C(19)	120(1)
				N(4)–C(24)–C(23)	119(1)	C(19)–C(24)–C(23)	120(1)
				N(3)–C(25)–C(26)	113(1)	C(25)–C(26)–C(27)	114(1)
				C(26)–C(27)–C(28)	119(2)	C(26)–C(27)–C(32)	119(2)
				C(28)–C(27)–C(32)	120(1)	C(27)–C(28)–C(29)	116(2)
				C(28)–C(29)–C(30)	120(2)	C(29)–C(30)–C(31)	121(2)
				C(30)–C(31)–C(32)	119(2)	C(27)–C(32)–C(31)	121(2)

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