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1,3-DIPOLAR CYCLOADDITIONS OF DIAZOALKANES TO HETEROAROMATIC SYSTEMS. THE SYNTHESIS OF TRIAZOLO[4,3-b][1,2]DIAZEPINE AND CYCLOPROPA[e]PYRAZOLO[4,3-c]AZOLO[1,5-a]PYRIDINE DERIVATIVES

Branko Stanovnik, Gorazd Habjan, Miha Tišler, Ljubo Golič, and Ivan Leban

Department of Chemistry, Edvard Kardelj University,
61000 Ljubljana, Yugoslavia

Abstract - 1,3-Dipolar cycloaddition of 2-diazopropane to 6-methyl-8-phenylsulphonyl-s-triazolo[4,3-b]pyridazine (4), 6-nitro-s-triazolo[4,3-a]pyridine (9) and 6-nitrotetrazolo[1,5-a]pyridine (10) produced the corresponding cycloadducts, which were transformed into derivatives of s-triazolo[4,3-b][1,2]diazepine (5), cyclopropa[e]pyrazolo[4,3-c]-s-triazolo[1,5-a]pyridine (13) and cyclopropa[e]pyrazolo[4,5-c]tetrazolo[1,5-a]pyridine (14), respectively.

Recently, we have described the highly regiospecific cycloadditions of diazoalkanes bo bicyclic azolo- and azinopyridazines in which the corresponding azolopyrazolo- and azinopyrazolopyridazines are formed in high yields.[1-8] It has been observed that the cycloaddition in monocyclic pyridazines is dependent on the substituents at the position 4 and/or 5. However, only halogenated derivatives have been studied.[9]

In s-triazolo[4,3-b]pyridazine series the cycloaddition of 2-diazopropane is taking place regiospecifically to give pyrazolo[4,3-d]-s-triazolo[4,3-b]pyridazines as the only products.[2,6] The derivatives of the isomeric system, i.e. pyrazolo-[3,4-d]-s-triazolo[4,3-b]pyridazine, have been prepared only by an independent procedure starting from tetrazolo[1,5-b]pyridazines followed by azido-tetrazolo isomerization.[4]

In our attempts to prepare the derivatives of the isomeric system pyrazolo[3,4-d]-s-triazolo[4,3-b]pyridazine by direct cycloaddition of diazoalkanes we prepared some 8-substituted s-triazolo[4,3-b]pyridazines, such as 8-chloro- (1), 8-phenylthio- (2), 8-phenylsulphinyl- (3) and 8-phenylsulphonyl-6-methyl-s-triazolo[4,3-b] pyridazine (4). When the compounds 1-3 were treated with 2-diazopropane no re-

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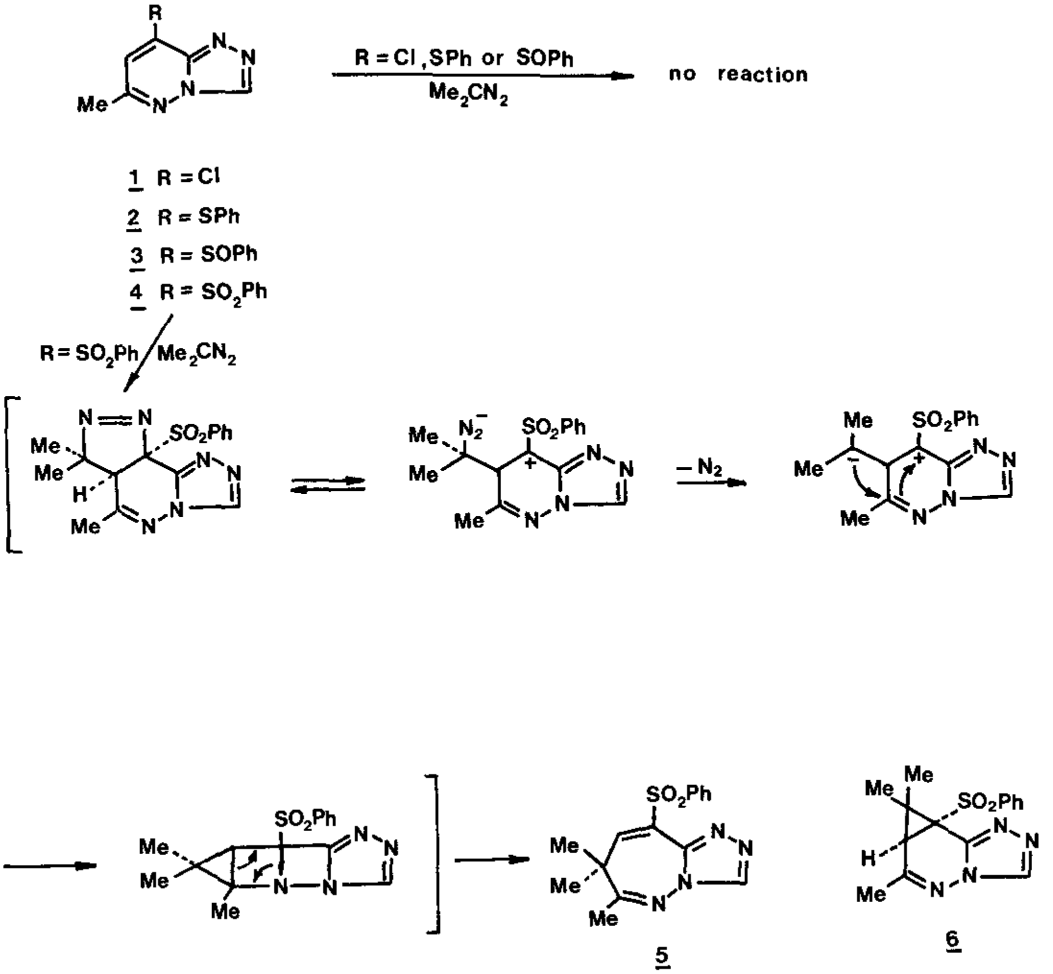
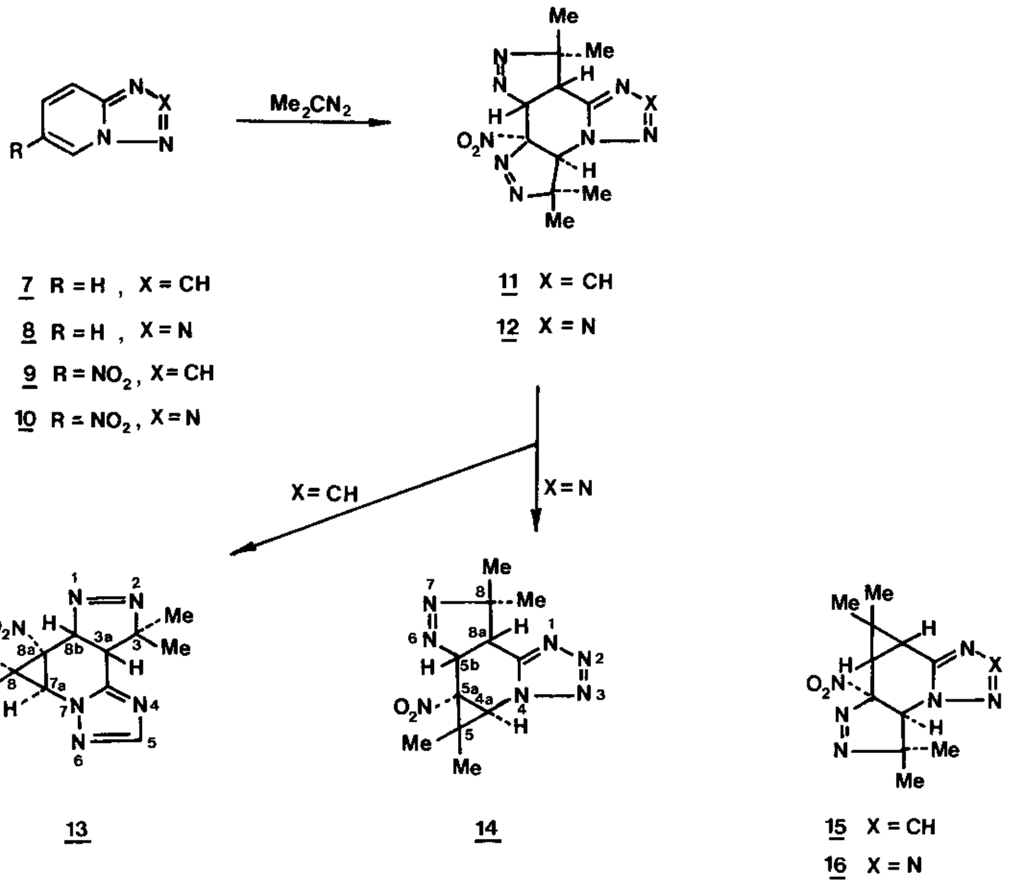
Dedicated to Sir Derek Barton, Professor of Texas A&M University, on the occasion of his 70th birthday.



Scheme 1

action was observed, while the phenylsulphonyl derivative 4 reacted vigorously at room temperature to produce the compound with molecular formula $C_{15}H_{16}N_4O_2S$, indicating that the primary cycloadduct is unstable under these conditions, and that a molecule of nitrogen is eliminated. This type of reaction has been observed previously to take place in pyrazolo[4,3-d]-s-triazolo[4,3-b]pyridazine series only under photochemical conditions producing 1,3-diradicals reacting further depending on the reaction conditions.[10-12] The ^1H nmr spectrum of this new compound shows a singlet at δ=1.31 ppm integrating for two equivalent methyl groups, a sin-



Scheme 2

glet at δ=2.27 ppm for one methyl group attached to a double bond, two singlets at δ=7.16 ppm and δ=8.46 ppm, each integrating for one proton, and two multiplets at δ=7.44-7.58 ppm and δ=8.09-8.20 ppm integrating for three and two protons, respectively, characteristic for the phenylsulphonyl group. The equivalence of the two methyl groups and the absence of a high-field proton excludes the structure with a fused cyclopropane ring 6. Furthermore, it also indicates that the rearrangements of the pyridazine ring occured to give s-triazolo[4,3-b][1,2]diazepine derivative 5, as suggested on the Scheme 1. The structure of this compound was confirmed by X-ray analysis (Fig.1, Table 1).

In search for other bicyclic systems, with a bridgehead nitrogen atom, reactive as 1,3-dipolarophiles, we selected s-triazolo[1,5-a]pyridine and tetrazolo-[1,5-a]pyridine derivatives. The parent s-triazolo[1,5-a]pyridine (7)[13] and tetrazolo[1,5-a]pyridine (8)[14] turned out to be unreactive. On the other hand, their 6-nitro derivatives 9[13] and 10[14] react with an excess of 2-diazopropane to give products, for which molecular formulas $C_{12}H_{16}N_6O_2$ and $C_{11}H_{15}N_7O_2$ were established, respectively. This indicates that the addition of two moles of 2-diazopropane to one mole of the substrate was taking place followed by elimination of one mole of nitrogen. The ^1H nmr spectrum of the cycloadduct $C_{12}H_{16}N_6O_2$ in $CDCl_3$ shows a singlet at δ=0.86 ppm integrating for one methyl group, a singlet at δ=1.33 ppm integrating for two methyl groups, a singlet at δ=1.69 ppm integrating for one methyl group, two doublets at δ=3.20 ppm and δ=5.60 ppm, each integrating for one proton, with a coupling constant, J=9.0 Hz, and a singlet at δ=7.97 ppm integrating for one proton, while the cycloadduct $C_{11}H_{15}N_7O_2$ in DMSO-d_6 at 140°C shows four singlets δ=0.78 ppm, δ=1.23 ppm, δ=1.30 ppm, and δ=1.50 ppm corresponding to four methyl groups, two doublets at δ=3.68 ppm and δ=5.58 ppm, each integrating for one proton, with a coupling constant, J=9.0 Hz, and a singlet at δ=5.08 ppm integrating for one proton. These data indicate that the nitro group at position 6 activates both the C_5-C_6 and C_7-C_8 double bonds of the pyridine part of the bicyclic systems for cycloaddition producing bis-cycloadducts 11 and 12 as intermediates. The subsequent elimination of one molecule of nitrogen afforded fused cyclopropane systems to which either structures 13 and 14 or 15 and 16 could be assigned. In order to differentiate between both pairs of isomeric structures, the X-ray analysis of the cycloadduct $C_{11}H_{15}N_7O_2$ was carried out, showing that the product 14 was formed in this reaction. (Fig. 2, Table 2). Since the ^1H nmr spectrum of the cycloadduct $C_{12}H_{16}N_6O_2$ is analogous, we assigned to it the structure 13. (Scheme 2).

EXPERIMENTAL

Melting points were taken on a Kofler micro hot stage. ^1H Nmr spectra were obtained on a JEOL 90 Q FT spectrometer with TMS as internal standard and elemental analyses for C, H, and N on a PERKIN-ELMER CHN Analyser 240 C.

6-Methyl-8-phenylthio-s-triazolo[4,3-b]pyridazine (2). - To a solution of 1[15] (1.686 g, 0.01 mole) in chloroform (25 ml) thiophenol (1.115 g, 0.011 mole) and triethylamine (1.015 g, 0.01 mole) were added and the mixture was heated under reflux (30 min). The precipitate formed after cooling the reaction mixture to room temperature was collected by filtration to give 2.005 g (83 %) of 2, mp 246-249°C (from ethanol), nmr ($CDCl_3$) δ: 2.37 (s, 6-Me), 6.07 (s, H_7), 7.31-7.67 (m, Ph), 8.96 (s, H_3). Anal.Calcd for $C_{12}H_{10}N_4S$: C, 59.48; H, 4.16; N, 23.12. Found: C, 59.31; H, 4.22; N, 23.29.

6-Methyl-8-phenylsulphinyl-s-triazolo[4,3-b]pyridazine (3). - To a solution of 2 (485 mg, 0.002 mole) in a mixture of chloroform and methanol (1:1, 10 ml) cooled in a mixture of CO_2/acetone t-butyl hypochlorite (230 mg, 0.002 mole) was added dropwise and the reaction mixture was left to warm to room temperature. The solvents were evaporated in vacuo and the solid residue was recrystallized from ethanol to give 3 (455 mg, 88%), mp 195-199°C, nmr ($CDCl_3$) δ: 2.68 (s, 6-Me), 7.45-7.52 (m, Ph), 7.65 (s, H_7), 8.01-8.12 (m, Ph), 9.04 (s, H_3). Anal.Calcd for $C_{12}H_{10}N_4OS$: C, 55.80; H, 3.90; N, 21.69. Found: C, 55.45; H, 3.68; N, 21.56.

6-Methyl-8-phenylsulphonyl-s-triazolo[4,3-b]pyridazine (4). - To a suspension of 3 (970 mg, 0.004 mole) in water (100 ml) sodium periodate (2.80 g, 0.013 mole) was added and the mixture was heated under reflux until all the starting material was consumed (approx. 80 h). The reaction was followed by tlc (DC Fertigplatten Kieselgel 60 F 254, E. Merck, and acetonitrile as solvent). Water was evaporated in vacuo, ethanol (70 ml) was added to the solid residue, the mixture was heated to boiling and filtered. The precipitate was, after cooling, collected by filtration to give 4 (786 mg, 72 %), mp 209-210°C (from ethanol), nmr ($CDCl_3$) δ: 2.71 (s, 6-Me), 7.51-7.63 (m) and 8.31-8.42 (m) (Ph), 7.72 (s, H_7), 9.06 (s, H_3). Anal.Calcd for $C_{12}H_{10}N_4O_2S$: C, 52.55; H, 3.67; N, 20.43. Found: 52.71; H, 3.59; N, 20.53.

9-Phenylsulphonyl-6,7,7-trimethyl-7H-s-triazolo[4,3-b][1,2]diazepine (5). - To a solution of 4 (275 mg, 0.001 mole) in chloroform (15 ml) a solution of 2-diazopropane, prepared from acetone hydrazone (0.6 g) in ether (30 ml),[16] was added at room temperature. The solvents were evaporated after 30 min and ethanol (5 ml) was added to the oily residue. The crystals were collected by filtration to give 205 mg (65 %) of 5, mp 247-250°C (from ethanol), nmr ($CDCl_3$) δ: 1.31 (s, 7,7-diMe), 2.27 (s, 6-Me), 7.16 (s, H_8), 7.44-7.58 (m, Ph), 8.09-8.20 (m, Ph), 8.46 (s, H_3). Anal. Calcd for $C_{15}H_{16}N_4O_2S$: C, 56.95; H, 5.10; N, 17.71. Found: C, 57.06; H, 5.29; N, 17.35.

3,3a,7a,8,8a,8b-Hexahydro-3,3,8,8-tetramethyl-8a-nitrocyclopropa[e]pyrazolo[4,3-c]-s-triazolo[1,5-a]pyridine (13)[17]. - To a solution of 9[13] (164 mg, 0.001 mole) in nitromethane (20 ml) a solution of 2-diazopropane, prepared from acetone hydrazone (1.5 g) in ether,[16] was added and the solution was left at room temperature (3 h).

The solvents were evaporated in vacuo and methanol (5 ml) was added to the oily residue. The crystals formed after standing in refrigerator for several hours were collected by filtration to give 70 mg (25 %) of 13, mp 169-171^{o}C (from methanol), nmr ($CDCl_3$) δ: 0.86 (s, Me), 1.33 (s, two Me), 1.69 (s, Me), 3.20 (d, H_{3a}), 4.50 (s, H_{7a}), 5.60 (d, H_{8b}), 7.97 (s, H_2), $J_{H_{3a},H_{8b}}$ = 9.0 Hz. Anal.Calcd for $C_{12}H_{16}N_6O_2$: C, 52.17; H, 5.84; N, 30.42. Found: C, 51.83; H, 5.92; N, 30.11.

4a,5,5a,8,8a-Hexahydro-5,5,8,8-tetramethyl-5a-nitrocyclopropa[e]pyrazolo[4,3-c]tetrazolo[1,5-a]pyridine (14).[17] - To a solution of 10[14] (826 mg, 0.005 mole) in acetone (80 ml) a solution of 2-diazopropane, prepared from 3.0 g of acetone hydrazone in ether,[16] was added at room temperature. The reaction was finished in 5 min. The solvents were evaporated in vacuo, ether (10 ml) was added to the dry residue and the solid separated by filtration to give 982 mg (71%) of 14, mp 189-192^{o}C (from ethanol), nmr (DMSO-d_6, 140^{o}C) δ: 0.78 (s, Me), 1.23 (s, Me), 1,30 (s, Me), 1.50 (s, Me), 3.68 (d, $J_{H_{5b},H_{8a}}$ = 9.0 Hz, H_{8a}), 5.08 (s, H_{4a}), 5.58 (d, $J_{H_{5b},H_{8a}}$ = 9.0 Hz, H_{5b}). Anal.Calcd for $C_{11}H_{15}N_7O_2$: C, 47.65; H, 5.45; N, 35.36. Found: C, 47.37; H, 5.46; N, 35.30.

X-Ray Crystal Structures. - Crystal suitable for diffraction studies were grown from ethanol solution. Crystal of size 0.20x0.43x0.76 mm (5) and 0.33x0.49x0.51 mm (14) were used for data collection. Crystal data: (5) $C_{15}H_{16}N_4O_2S$, M = 316.38, orthorhombic, space group $P2_12_12_1$, a = 0.9545(2), b = 1.2477(3), c = 1.2973(4) nm, U = 1.545(1) nm^3, D_m = 1.36(2), D_c = 1.360 Mg/m^3, Z = 4, μ_{MoK_α} = 0.211 mm^{-1}, F(000)= 664, T = 293(1)K; (14) $C_{11}H_{15}N_7O_2$, M = 277.29, monoclinic, space group $P2_1/n$, a = 0.8305(1), b = 1.4375(1), c = 1.1731(1) nm, β = 107.04(1)^{o}, U = 1.3390(1) nm^3, D_m = 1.37(4), D_c = 1.376 Mg/m^3, Z = 4, μ_{MoK_α} = 0.0945 mm^{-1}, F(000) = 584, T = 293(1) K. Data were collected with a CAD-4 diffractometer using graphite-monochromated MoK_α radiation (λ = 0.07107 nm). Lattice parameters were determined from settings and least-squares refinement of 75 (5) and 100 (14) reflections with $9<\theta<15^{o}$. Hemispheres were measured. A total of 8840 with $0\leq l$ (5) and 6841 with $0\leq k$ (14) and with $\theta\leq 28^{o}$ reflections were collected using ω-2θ scan, scan width $(0.8 + 0.3tg\theta)^{o}$, 25% on each side used for background measurement, horizontal aperture (2.4 + 0,9tgθ) mm, vertical aperture 4 mm, maximum scan time 60 s. Three standard reflections were measured after each 8000 s of measuring time, no decay, no absorption correction. Merging of data gave 2148 (5) and 3204 (14) unique reflections with R_{int} 0.07 and 0.02, 870 (5) and 1204 (14) reflections were unobserved ($I<3\sigma(I)$). Structures were solved by direct methods using MULTAN80[17]. Full matrix least-squares refinement with anisotropic thermal parameters for all nonhydrogen atoms and isotropic thermal parameters for hydrogen atoms gave conventional R values of 0.041 and 0.039 An empirical weighting function was applied in order to keep $\Sigma w(\Delta F)^2$ uniform over the ranges of $\sin\Theta/\lambda$ and $|F_o|$. In the final refinement cycle there were 1480 and 2528 contributing reflections with 263 and 242 variables. Average shift to error ratio was 0.16 and 0.01. Atomic scattering and dispersion factors for neutral S, O, N, C[18,19] and H[20] atoms were used. A DEC-10 computer at the University Computer Centre Ljubljana and the XRAY-76[21] system of crystallographic programs were used for calculations.

Structures consist of packing of molecules with no intermolecular contact of nonhydrogen atoms of less then 0.315 nm. Molecular structures and numbering of atoms are shown in Figs. 1. and 2., bond lenghts and angles are given in Tables 1. and 2., they are within expected regions.

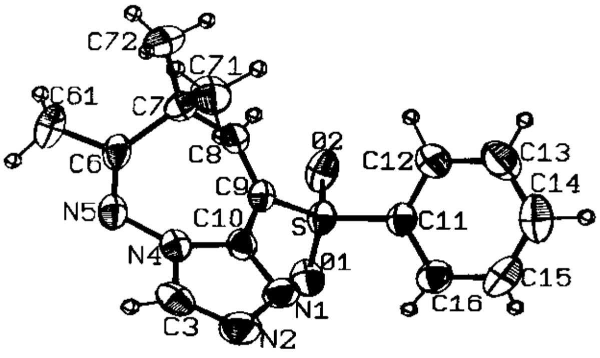


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Fig. 1

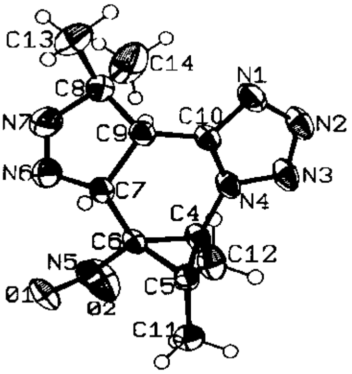

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Fig. 2

Table 1. - Bond lengths (nm) and bond angles (^{o}) of 5.

S - O(1)	0.1437(3)	C(15) - C(16)	0.1384(7)	C(6) - N(5)	0.1274(5)
S - O(2)	0.1420(3)	C(16) - C(11)	0.1374(5)	N(5) - N(4)	0.1402(4)
S - C(9)	0.1781(3)	C(9) - C(8)	0.1319(5)	N(4) - C(10)	0.1376(4)
S - C(11)	0.1764(4)	C(8) - C(7)	0.1501(5)	N(4) - C(3)	0.1339(5)
C(11) - C(12)	0.1386(5)	C(7) - C(71)	0.1548(6)	C(3) - N(2)	0.1303(5)
C(12) - C(13)	0.1369(7)	C(7) - C(72)	0.1523(7)	N(2) - N(1)	0.1376(5)

C(13) - C(14)	0.1370(7)	C(7) - C(6)	0.1544(5)	N(1) - C(10)	0.1309(5)
C(14) - C(15)	0.1370(8)	C(6) - C(61)	0.1497(5)	C(10) - C(9)	0.1445(5)

O(1) - S - O(2)	119.3(2)	C(8) - C(7) - C(71)	110.2(3)
O(1) - S - C(9)	108.1(2)	C(8) - C(7) - C(72)	108.8(3)
O(1) - S - C(11)	108.2(2)	C(71) - C(7) - C(72)	109.2(3)
O(2) - S - C(9)	106.6(2)	C(71) - C(7) - C(6)	107.9(3)
O(2) - S - C(11)	108.3(2)	C(72) - C(7) - C(6)	111.4(3)
C(9) - S - C(11)	105.5(2)	C(7) - C(6) - C(61)	119.8(3)
S - C(11) - C(12)	118.3(3)	C(7) - C(6) - N(5)	127.5(3)
S - C(11) - C(16)	120.3(3)	C(61) - C(6) - N(5)	112.7(3)
C(12) - C(11) - C(16)	121.3(4)	C(6) - N(5) - N(4)	119.0(3)
C(11) - C(12) - C(13)	118.6(4)	N(5) - N(4) - C(10)	131.4(3)
C(12) - C(13) - C(14)	120.8(5)	N(5) - N(4) - C(3)	122.0(3)
C(13) - C(14) - C(15)	120.4(5)	C(10) - N(4) - C(3)	104.9(3)
C(14) - C(15) - C(16)	120.1(5)	N(4) - C(3) - N(2)	111.1(4)
C(15) - C(16) - C(11)	118.9(4)	C(3) - N(2) - N(1)	107.2(3)
S - C(9) - C(8)	118.7(3)	N(2) - N(1) - C(10)	107.5(3)
S - C(9) - C(10)	117.5(2)	N(1) - C(10) - N(4)	109.4(3)
C(8) - C(9) - C(10)	123.8(3)	N(1) - C(10) - C(9)	127.5(3)
C(9) - C(8) - C(7)	126.9(3)	N(4) - C(10) - C(9)	123.1(3)
C(8) - C(7) - C(6)	109.3(3)		

Table 2. - Bond lengths (nm) and bond angles (°) of 14.

N(1) - N(2)	0.1364(2)	C(5) - C(11)	0.1514(3)	C(7) - N(6)	0.1502(3)
N(2) - N(3)	0.1293(2)	C(5) - C(12)	0.1507(2)	N(6) - N(7)	0.1223(4)
N(3) - N(4)	0.1357(2)	C(5) - C(6)	0.1523(2)	N(7) - C(8)	0.1486(3)
N(4) - C(10)	0.1331(2)	C(6) - N(5)	0.1496(2)	C(8) - C(13)	0.1524(3)
C(10) - N(1)	0.1324(2)	N(5) - O(1)	0.1208(2)	C(8) - C(14)	0.1516(3)
N(4) - C(4)	0.1432(2)	N(5) - O(2)	0.1211(2)	C(8) - C(9)	0.1558(3)
C(4) - C(5)	0.1518(2)	C(6) - C(7)	0.1520(2)	C(9) - C(10)	0.1494(2)
C(4) - C(6)	0.1499(2)	C(7) - C(9)	0.1547(2)		

C(10) - N(1) - N(2)	105.2(1)	C(4) - C(6) - C(7)	122.2(1)
N(1) - N(2) - N(3)	111.7(1)	C(5) - C(6) - N(5)	114.4(1)
N(2) - N(3) - N(4)	105.3(1)	C(5) - C(6) - C(7)	123.5(1)
N(3) - N(4) - C(10)	109.1(1)	N(5) - C(6) - C(7)	111.9(1)
N(3) - N(4) - C(4)	122.9(1)	C(6) - N(5) - O(1)	116.6(1)
C(4) - N(4) - C(10)	127.8(1)	C(6) - N(5) - O(2)	119.5(1)
N(4) - C(10) - N(1)	108.6(1)	O(1) - N(5) - O(2)	123.8(1)
N(4) - C(10) - C(9)	123.6(1)	C(6) - C(7) - N(6)	109.1(1)
N(1) - C(10) - C(9)	127.7(1)	C(6) - C(7) - C(9)	117.6(1)
N(4) - C(4) - C(5)	119.2(1)	N(6) - C(7) - C(9)	104.8(1)
N(4) - C(4) - C(6)	114.0(1)	C(7) - N(6) - N(7)	113.0(2)

C(5)	C(4)	C(6)	60.6(1)	N(6)	N(7)	C(8)	114.6(2)
C(4)	C(5)	C(6)	59.1(1)	N(7)	C(8)	C(9)	104.4(2)
C(4)	C(5)	C(11)	116.1(1)	N(7)	C(8)	C(13)	107.4(2)
C(4)	C(5)	C(12)	120.8(1)	N(7)	C(8)	C(14)	106.2(2)
C(11)	C(5)	C(12)	113.9(2)	C(13)	C(8)	C(14)	110.0(2)
C(11)	C(5)	C(6)	118.6(1)	C(13)	C(8)	C(9)	111.8(2)
C(12)	C(5)	C(6)	117.8(1)	C(14)	C(8)	C(9)	116.3(2)
C(4)	C(6)	C(5)	60.3(1)	C(8)	C(9)	C(10)	114.2(1)
C(4)	C(6)	N(5)	115.6(1)	C(8)	C(9)	C(7)	103.0(1)
				C(7)	C(9)	C(10)	114.7(1)

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