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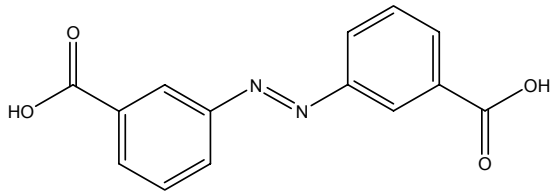
1. Syntheses of the azobenzene derivatives

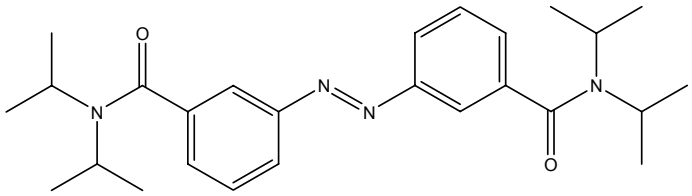
1.1 Synthesis of 4:



4

20.55 g (0.15 mol) 3-amino benzoic acid are solubilized under heating (60 deg.) in 200 ml glacial acetic acid. 15.7 g (0.1 mol) of sodium percarbonate are slowly added and the reaction mixture is stirred at 60 deg. for 4 h. After cooling down to room temperature the mixture is diluted with water and the brownish precipitate is filtered off to yield 14.12 g (0.051 mmol, 68 %) of **4**. **4** is used without further purification.

1.2 Synthesis of 2:

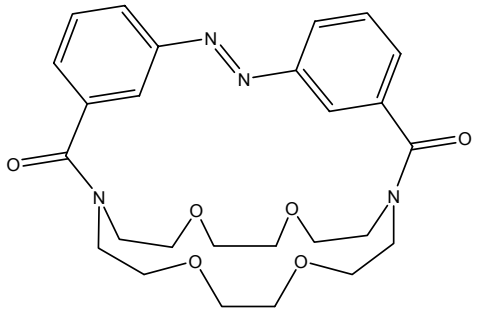


2

540 mg (2 mmol) of 3,3'-diazenediyl-bis-benzoic acid (**4**) and excess thionyl chloride are refluxed for 30 min. in an argon atmosphere after addition of 2 drops of dimethyl formamide. The remaining thionyl chloride is removed by bubbling argon through the solution. After drying the crude product *in vacuo* it is solubilized in toluene. The crude acid chloride is directly reacted with diisopropyl amine.

200 ml of dry toluene and 2 ml of triethyl amine are placed in a three-necked flask under argon atmosphere. The toluene solution of the acid chloride and 404 mg (4.0 mmol) of diisopropyl amine are simultaneously added dropwise to the stirred solution of triethylamine in toluene. After the formation of white fume has stopped the reaction mixture is stirred overnight at room temperature. The reaction mixture is washed with water, dried with $MgSO_4$ and the solvent is evaporated. The brownish crude product is purified by column chromatography (silica, cyclohexane:ethyl acetate 2:1, R_f 0.28) to yield **2** as a yellow solid (87 mg, 0.21 mmol, 21 %).

1.3 Synthesis of 1:



1

200 mg (0.72 mmol) of 3,3'-diazenediyl-bis-benzoic acid (**4**) are placed in a flask under argon. 3 ml thionyl chloride and 3 drops of dimethyl formamide are added and the mixture is refluxed for several minutes. The excess thionyl chloride is removed by bubbling argon through the reaction mixture and the residue is dried *in vacuo*. 50 ml of dry dichloromethane are added and the crude acid chloride is completely solubilized under sonication. This solution and a solution of 170 mg (0.65 mmol) 1,4,10,13-tetraoxa-7,16-diazacyclooctadecane in

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50 ml dry toluene are simultaneously added with a syringe pump over 6 h to a vigorously stirred solution of 3 ml triethyl amine in 500 ml dry toluene. To complete the reaction the mixture is stirred overnight. The solvent is removed, the residue dissolved in toluene, washed twice with sat. sodium carbonate solution and brine. After washing twice with water and drying over $MgSO_4$ the solution is concentrated and the product precipitates as a yellow solid, which is isolated by filtration and dried *in vacuo* (100 mg, 0.2 mmol, 31 %).

2. Crystal structure data of the bridged crown ether 1

Table 1. Crystal data and structure refinement for compound 1.

Identification code	comp1	
Empirical formula	$C_{26}H_{32}N_4O_6$	
Formula weight	496.56	
Temperature	220(2) K	
Wavelength	0.71073 Å	
Crystal system	monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 15.0689(12) Å	α= 90°.
	b = 7.8226(3) Å	β= 109.162(8)°.
	c = 22.3375(14) Å	γ = 90°.
Volume	2487.2(3) $Å^3$	
Z	4	
Density (calculated)	1.326 Mg/m^3	
Absorption coefficient	0.095 mm^{-1}	
F(000)	1056	
Crystal size	0.5 x 0.4 x 0.4 mm^3	
Theta range for data collection	2.78 to 28.00°.	
Index ranges	-14<=h<=19, -9<=k<=10, -29<=l<=29	
Reflections collected	12153	
Independent reflections	5753 [R(int) = 0.0309]	
Completeness to theta = 28.00°	95.7 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5753 / 0 / 325	
Goodness-of-fit on F^2	1.040	
Final R indices [I>2sigma(I)]	R1 = 0.0614, wR2 = 0.1696	
R indices (all data)	R1 = 0.0841, wR2 = 0.1852	
Largest diff. peak and hole	1.748 and -0.277 e.$Å^{-3}$	

Remarks:
All non-hydrogen atoms were refined using anisotropic displacement parameters. The hydrogen atoms were placed in calculated positions and were refined isotropically.
There is one residual electron density peak in the difference map which indicate the presence of some amounts of the corresponding azoxybenzene, which was not considered in the refinement.

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Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	6341(1)	8022(2)	7364(1)	33(1)
C(1)	6133(1)	6802(2)	6997(1)	24(1)
C(2)	5903(2)	7107(2)	6298(1)	24(1)
C(3)	6510(2)	8060(3)	6066(1)	31(1)
C(4)	6252(2)	8461(3)	5430(1)	36(1)
C(5)	5379(2)	7987(3)	5015(1)	34(1)
C(6)	4763(2)	7097(3)	5249(1)	29(1)
N(1)	3859(2)	6631(3)	4808(1)	35(1)
N(2)	3332(2)	6037(2)	5078(1)	32(1)
C(7)	5030(2)	6616(3)	5889(1)	28(1)
C(8)	2458(2)	5332(3)	4681(1)	28(1)
C(9)	1955(2)	5764(3)	4054(1)	34(1)
C(10)	1162(2)	4812(3)	3727(1)	37(1)
C(11)	888(2)	3386(3)	4003(1)	32(1)
C(12)	1391(2)	2975(3)	4634(1)	25(1)
C(13)	2148(2)	3992(3)	4974(1)	28(1)
C(14)	1240(2)	1292(3)	4914(1)	26(1)
O(2)	1214(1)	-36(2)	4609(1)	39(1)
N(3)	1220(1)	1259(2)	5520(1)	26(1)
C(15)	1190(2)	-451(3)	5795(1)	31(1)
C(16)	2107(2)	-1436(3)	5964(1)	35(1)
O(3)	2866(1)	-648(2)	6453(1)	36(1)
C(17)	3453(2)	416(3)	6224(1)	32(1)
C(18)	4371(2)	652(3)	6750(1)	31(1)
O(4)	4865(1)	2020(2)	6579(1)	30(1)
C(19)	5834(2)	2019(3)	6946(1)	32(1)
C(20)	6296(2)	3694(3)	6887(1)	28(1)
C(21)	865(2)	2707(3)	5797(1)	28(1)
C(22)	1439(2)	3101(3)	6481(1)	31(1)
O(5)	2306(1)	3904(2)	6523(1)	28(1)
C(23)	2905(2)	4012(3)	7166(1)	30(1)
C(24)	3798(2)	4945(3)	7190(1)	28(1)
O(6)	4451(1)	4638(2)	7811(1)	32(1)
C(25)	5248(2)	5746(3)	8009(1)	30(1)
C(26)	6104(2)	5054(3)	7868(1)	28(1)
N(4)	6017(1)	5187(2)	7195(1)	24(1)

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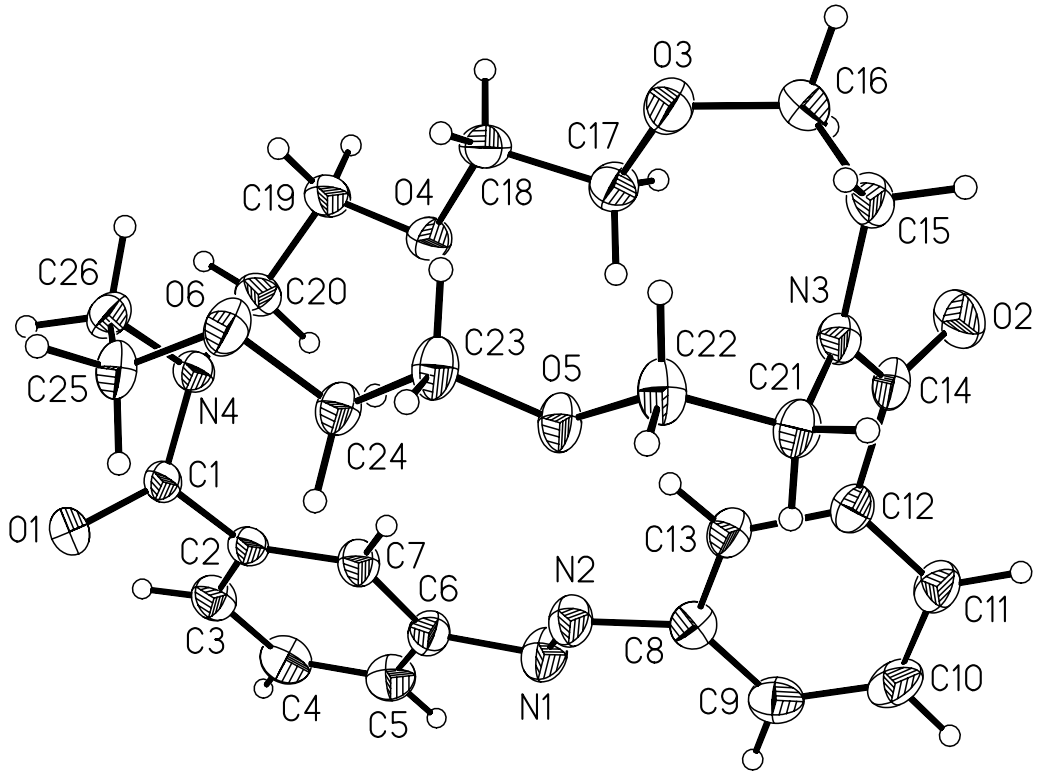

Figure 1. Crystal structure of compound **1** with labelling and displacement ellipsoids drawn at the 50% probability level.

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Table 3. Bond lengths [Å] and angles [°].

O(1)-C(1)	1.230(2)	C(14)-N(3)	1.364(2)
C(1)-N(4)	1.368(2)	N(3)-C(21)	1.473(3)
C(1)-C(2)	1.504(3)	N(3)-C(15)	1.478(3)
C(2)-C(7)	1.388(3)	C(15)-C(16)	1.517(3)
C(2)-C(3)	1.404(3)	C(16)-O(3)	1.436(3)
C(3)-C(4)	1.381(3)	O(3)-C(17)	1.425(3)
C(4)-C(5)	1.387(4)	C(17)-C(18)	1.503(3)
C(5)-C(6)	1.393(3)	C(18)-O(4)	1.426(3)
C(6)-C(7)	1.402(3)	O(4)-C(19)	1.421(3)
C(6)-N(1)	1.441(3)	C(19)-C(20)	1.510(3)
N(1)-N(2)	1.235(3)	C(20)-N(4)	1.484(2)
N(2)-C(8)	1.435(3)	C(21)-C(22)	1.518(3)
C(8)-C(13)	1.395(3)	C(22)-O(5)	1.425(3)
C(8)-C(9)	1.398(3)	O(5)-C(23)	1.426(2)
C(9)-C(10)	1.394(4)	C(23)-C(24)	1.516(3)
C(10)-C(11)	1.401(3)	C(24)-O(6)	1.432(2)
C(11)-C(12)	1.400(3)	O(6)-C(25)	1.428(3)
C(12)-C(13)	1.394(3)	C(25)-C(26)	1.524(3)
C(12)-C(14)	1.507(3)	C(26)-N(4)	1.471(2)
C(14)-O(2)	1.236(3)		
O(1)-C(1)-N(4)	122.25(18)	O(2)-C(14)-N(3)	121.65(19)
O(1)-C(1)-C(2)	119.36(18)	O(2)-C(14)-C(12)	119.10(17)
N(4)-C(1)-C(2)	118.11(16)	N(3)-C(14)-C(12)	118.99(17)
C(7)-C(2)-C(3)	119.70(19)	C(14)-N(3)-C(21)	122.14(17)
C(7)-C(2)-C(1)	119.09(18)	C(14)-N(3)-C(15)	116.24(17)
C(3)-C(2)-C(1)	120.75(19)	C(21)-N(3)-C(15)	117.22(16)
C(4)-C(3)-C(2)	120.1(2)	N(3)-C(15)-C(16)	114.51(18)
C(3)-C(4)-C(5)	120.8(2)	O(3)-C(16)-C(15)	113.91(19)
C(4)-C(5)-C(6)	119.1(2)	C(17)-O(3)-C(16)	114.32(17)
C(5)-C(6)-C(7)	120.8(2)	O(3)-C(17)-C(18)	108.17(17)
C(5)-C(6)-N(1)	117.86(19)	O(4)-C(18)-C(17)	108.09(17)
C(7)-C(6)-N(1)	121.3(2)	C(19)-O(4)-C(18)	111.89(16)
N(2)-N(1)-C(6)	112.13(18)	O(4)-C(19)-C(20)	111.43(18)
N(1)-N(2)-C(8)	116.71(18)	N(4)-C(20)-C(19)	115.67(18)
C(2)-C(7)-C(6)	119.4(2)	N(3)-C(21)-C(22)	114.44(19)
C(13)-C(8)-C(9)	119.8(2)	O(5)-C(22)-C(21)	111.30(16)
C(13)-C(8)-N(2)	112.27(18)	C(22)-O(5)-C(23)	110.92(15)
C(9)-C(8)-N(2)	127.8(2)	O(5)-C(23)-C(24)	109.03(16)
C(10)-C(9)-C(8)	119.0(2)	O(6)-C(24)-C(23)	105.87(16)
C(9)-C(10)-C(11)	121.4(2)	C(25)-O(6)-C(24)	116.02(16)
C(12)-C(11)-C(10)	119.1(2)	O(6)-C(25)-C(26)	113.78(18)
C(13)-C(12)-C(11)	119.6(2)	N(4)-C(26)-C(25)	112.91(17)
C(13)-C(12)-C(14)	118.68(18)	C(1)-N(4)-C(26)	114.64(16)
C(11)-C(12)-C(14)	120.87(19)	C(1)-N(4)-C(20)	119.45(16)
C(12)-C(13)-C(8)	120.84(19)	C(26)-N(4)-C(20)	118.37(16)

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Table 4. Anisotropic displacement parameters ($Å^2 x 10^3$). The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O(1)	37(1)	25(1)	30(1)	-5(1)	2(1)	-4(1)
C(1)	18(1)	22(1)	28(1)	-2(1)	4(1)	0(1)
C(2)	23(1)	21(1)	28(1)	-1(1)	8(1)	1(1)
C(3)	27(1)	29(1)	38(1)	-1(1)	12(1)	-3(1)
C(4)	38(1)	35(1)	42(1)	2(1)	22(1)	-4(1)
C(5)	38(1)	36(1)	32(1)	3(1)	15(1)	2(1)
C(6)	28(1)	32(1)	27(1)	-2(1)	7(1)	3(1)
N(1)	33(1)	45(1)	27(1)	4(1)	9(1)	-8(1)
N(2)	33(1)	37(1)	24(1)	2(1)	8(1)	-6(1)
C(7)	26(1)	30(1)	28(1)	-1(1)	9(1)	-5(1)
C(8)	27(1)	31(1)	28(1)	1(1)	10(1)	0(1)
C(9)	41(1)	31(1)	33(1)	5(1)	15(1)	3(1)
C(10)	44(1)	42(1)	21(1)	5(1)	5(1)	12(1)
C(11)	34(1)	37(1)	21(1)	-2(1)	4(1)	2(1)
C(12)	25(1)	30(1)	21(1)	-1(1)	7(1)	1(1)
C(13)	26(1)	34(1)	24(1)	2(1)	7(1)	-1(1)
C(14)	21(1)	33(1)	21(1)	-2(1)	3(1)	-4(1)
O(2)	52(1)	36(1)	28(1)	-8(1)	10(1)	-7(1)
N(3)	25(1)	29(1)	23(1)	-1(1)	7(1)	-4(1)
C(15)	28(1)	34(1)	30(1)	1(1)	10(1)	-8(1)
C(16)	35(1)	28(1)	39(1)	2(1)	7(1)	-5(1)
O(3)	29(1)	45(1)	31(1)	8(1)	7(1)	-8(1)
C(17)	30(1)	34(1)	31(1)	6(1)	9(1)	-4(1)
C(18)	29(1)	26(1)	36(1)	7(1)	10(1)	2(1)
O(4)	26(1)	27(1)	33(1)	4(1)	5(1)	-2(1)
C(19)	28(1)	23(1)	40(1)	0(1)	4(1)	2(1)
C(20)	24(1)	23(1)	37(1)	-2(1)	10(1)	4(1)
C(21)	22(1)	36(1)	27(1)	-2(1)	9(1)	-2(1)
C(22)	27(1)	41(1)	26(1)	-5(1)	12(1)	-8(1)
O(5)	27(1)	37(1)	21(1)	-3(1)	7(1)	-7(1)
C(23)	29(1)	41(1)	21(1)	-5(1)	10(1)	-4(1)
C(24)	28(1)	33(1)	20(1)	0(1)	7(1)	-1(1)
O(6)	28(1)	41(1)	24(1)	4(1)	4(1)	-5(1)
C(25)	27(1)	38(1)	22(1)	-6(1)	5(1)	-4(1)
C(26)	25(1)	32(1)	24(1)	4(1)	3(1)	2(1)
N(4)	24(1)	22(1)	26(1)	-1(1)	8(1)	1(1)

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Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3).

	x	y	z	U(eq)
H(3)	7094	8426	6345	37
H(4)	6672	9061	5276	43
H(5)	5206	8264	4583	41
H(7)	4622	5967	6038	33
H(9)	2149	6684	3855	41
H(10)	803	5133	3312	45
H(11)	375	2714	3769	38
H(13)	2453	3772	5407	34
H(15A)	698	-1127	5491	37
H(15B)	1015	-319	6177	37
H(16A)	2005	-2587	6103	42
H(16B)	2288	-1557	5583	42
H(17A)	3150	1527	6093	38
H(17B)	3560	-118	5857	38
H(18A)	4257	920	7147	37
H(18B)	4743	-401	6811	37
H(19A)	6150	1085	6804	38
H(19B)	5901	1818	7392	38
H(20A)	6978	3550	7070	34
H(20B)	6152	3951	6435	34
H(21A)	217	2461	5775	34
H(21B)	852	3727	5540	34
H(22A)	1076	3854	6664	37
H(22B)	1565	2037	6726	37
H(23A)	3058	2861	7343	36
H(23B)	2586	4629	7418	36
H(24A)	4044	4503	6865	33
H(24B)	3678	6172	7120	33
H(25A)	5417	5941	8466	36
H(25B)	5074	6852	7797	36
H(26A)	6662	5688	8121	34
H(26B)	6195	3852	7997	34