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Synthesis, characterization and crystal structure of a Phenol-functionalized diazamesocyclic derivative with unexpected configuration

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Abstract

A bis-substituent diazamesocyclic compound containing bulky phenolic donor pendants, 1,4-bis(3-*tert*-butyl-5-methyl-2-hydroxybenzyl)-1,4-diazacycloheptane, has been prepared from 1,4-diazacycloheptane (DACH) and 2-*tert*-butyl-4-methylphenol by the Mannich reaction, and structurally characterized by NMR, IR and X-ray diffraction techniques. The crystal structure of the title compound reveals that 1,4-diazacycloheptane (DACH) ring is folded up into unusual chair configuration, and the two phenol pendants of the compound are in unexpected *trans* positions, which is different from those in the transition metal complexes of DACH and its derivatives. There exist intra-molecular O–H···N hydrogen bonds between the phenolic O atoms and the DACH N donors which stabilize the crystal structure.

Keywords: Synthesis; Crystal structure; 1,4-Diazacycloheptane; Configuration

1. Introduction

Diazamesocyclic ligands occupy an important role in the coordination chemistry between acyclic and macrocyclic polyamine ligands due to their unique conformational feature [1–3] and the potential for further fuctionalization [4–6]. 1,5-Diazacyclooctane (DACO) and 1,4-Diazacycloheptane (DACH) are the most typical examples of such diazamesocyclic compounds. DACO and its derivatives usually exhibit the interesting 'boat/chair' configuration in their transition metal complexes, in which the hydrogen atoms of the trimethylene of DACO could effectively block the sixth-coordination to the metal centre to form penta-coordination complexes [7,8]. Recently, we have demonstrated that the configuration of DACO ring in its diprotonated salt $[H_2\text{-}DACO]Br{\cdot}ClO_4$ [9] and its imidazole-functionalized derivative (the two imidazole pendants are in *cis* positions) [10] is also 'boat/chair', which is consistent with those in their metal complexes.

However, relative to the special attention on DACO, studies on DACH are still rare and it always

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takes the boat configuration in its metal complexes [3,11,12]. In our efforts to systematically investigate the structures and properties as well as the coordination chemistry of diazamesocyclic ligands by modification of their backbone [6–16], we found that the study of structure and configuration on DACH derivatives in uncoordinated solid state is still unexplored. As a continuation of our work, we report herein the synthesis and crystal structure of a tetradentate DACH ligand containing bulky phenolic donor pendants, namely 1,4-bis(3-*tert*-butyl-5-methyl-2-hydroxybenzyl)-1,4-diazacycloheptane.

2. Experimental

2.1. Materials and general methods

All reagents for syntheses and analyses are of analytical grade and used as received. FT-IR spectra (KBr pellets) were taken on a FT-IR 170SX (Nicolet) spectrometer, and melting point was obtained without correction. Carbon, hydrogen and nitrogen analyses were performed on a Perkin–Elmer 240C analyser. ^{1}H NMR spectra were measured on a Bruker AC-P 400 spectrometer (400 MHz) at room temperature with TMS as the internal reference.

2.2. Synthesis of the title compound

Paraformaldehyde (0.70 g, 23 mmol) was added to a solution of 1,4-diazacycloheptane (1.00 g, 10 mmol) in methanol (40 ml). After heating the solution to reflux for ca. 1 h, 2-*tert*-butyl-4-methylphenol (3.45 g, 21 mmol) was added and heating at reflux for ca. 24 h. Then the solvent was removed by rotary evaporation, and the residue was dissolved in anhydrous ethanol. White crystalline solids were precipitated from this solution after standing at room temperature. Well-shaped colourless single crystals of the title compound suitable for X-ray diffraction were obtained by slow diffusion of CH_3OH/CH_2Cl_2 solution of the above solids at room temperature. Yield: 2.38 g (50%). mp: 126–128 °C. Found: C, 76.77; H, 9.78; N, 6.15. Calc. for $C_{29}H_{44}N_2O_2$: C, 76.94; H, 9.80; N, 6.19%. ^{1}H NMR ($CDCl_3$, δ): 1.40(s, 18H), 1.85(m, 2H), 2.23(s, 6H), 2.75(m, 4H), 2.80(s, 4H), 3.73(s, 4H), 6.64(s, 2H), 6.99(s, 2H). FT-IR (KBr pellet, cm^{-1}): 3431b, 2954vs, 2915s, 2870s, 1608w, 1462s, 1435vs, 1389m, 1302w, 1239s, 1147m, 864m, 774m.

2.3. Crystallographic data collection and structure determination

A block crystal with approximate dimensions of $0.35 \times 0.25 \times 0.15$ mm was mounted on a BRUKER SMART 1000 CCD diffractometer equipped with a graphite monochromator for data collection. The determination of unit cell parameters (17514 reflections with least-squares refinement) and data collections were performed with Mo Kα radiation ($\lambda = 0.71073$ Å). A total of 14668 independent reflections were collected in the range of $1.87 < \theta < 25.03°$ with $R_{\text{int}} = 0.0395$ by ω scan mode at 298(2) K. All data were corrected by semi-empirical method using SADABS program. The program SAINT [17] was used for integration of the diffraction profiles.

The structure was solved by direct methods using SHELXS program of the SHELXL-97 package and refined with SHELXL [18]. All the non-hydrogen atoms were located in successive difference Fourier syntheses. The final refinement was performed by full matrix least-squares methods with anisotropic thermal parameters for non-hydrogen atoms on F^2. The hydrogen atoms were added theoretically, riding on the concerned atoms and refined with fixed thermal factors. The weighting scheme was $W^{-1} = \sigma^2(Fo^2) + (0.0398P)^2$, where $P = (Fo^2 + 2Fc^2)/3$. The refinement converged to final $R = 0.0569$, $wR = 0.0884$, $S = 1.010$, $(\Delta/\sigma)_{\max} = 0.002$ and $(\Delta/\sigma)_{\min} = 0.000$. The maximum and minimum residual peaks are 0.245 and -0.240 e/Å^3, respectively. Molecular graphics were drawn with the program package XP. Further crystallographic data and experimental details for structural analyses are summarized in Table 1. Positional parameters and atomic coordinates are listed in Table 2, and selected bond lengths and angles with their estimated standard deviations in Table 3.

Table 1
Crystallographic data and structure refinement summary for the title compound

Formula	$C_{87}H_{132}N_6O_6$
Mr	1357.99
Crystal size (mm)	0.15 × 0.25 × 0.35
Crystal system	Triclinic
Space group	$P-1$
a (Å)	9.8502(16)
b (Å)	16.526(3)
c (Å)	27.243(5)
α (°)	94.371(4)
β (°)	98.420(4)
γ (°)	106.412(4)
V (Å^3)	4175.7(12)
Z	2
D_{calc} (g cm^{-3})	1.080
μ (cm^{-1})	0.67
F(000)	1488
Range of h,k,l	−11/11, −12/19, −32/32
Total reflections	17568
Independent reflections	14668
Parameters	893
R indices ($I > 2\sigma(I)$)	0.0569, 0.0884

3. Results and discussion

3.1. Synthesis and general characterization

The doubly substituted compound was produced by the reaction of paraformaldehyde, DACH and 2-*tert*-butyl-4-methylphenol in methanol through the Mannich reaction in satisfactory yield as shown in Scheme 1. The analytical and spectral data are in good agreement with the theoretical requirements. In the IR spectrum of the title compound, the bands in the 1400–1600 cm^{-1} region arise from the skeletal vibrations of the aromatic rings. The broad band centred at ca. 3400 cm^{-1} indicates the O–H stretching of the phenol group. The characteristic absorption band with strong intensity of C–O stretching of phenol appears at 1239 cm^{-1}, while the corresponding values in its metal complexes shift to higher frequencies (1260 ± 10 cm^{-1}), suggesting the deprotonation of the phenolic group when chelated with the metal ions [19].

3.2. Description of the crystal structure

The ORTEP structure of the title compound with atom labelling is shown in Fig. 1. It should be noted

Table 2
Atomic coordinates (×10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3)

Atom	x	y	z	U_{eq}
N(1)	4359(3)	9068(2)	6021(1)	65(1)
N(2)	4408(3)	7727(2)	5185(1)	73(1)
O(1)	6054(2)	9335(1)	6910(1)	74(1)
O(2)	2247(2)	7735(1)	4520(1)	76(1)
C(1)	3240(4)	8257(2)	6012(1)	86(1)
C(2)	3808(5)	7504(3)	6027(2)	108(2)
C(3)	4484(5)	7272(3)	5624(2)	127(2)
C(4)	5339(4)	8607(3)	5292(1)	86(1)
C(5)	4676(4)	9215(2)	5521(1)	77(1)
C(6)	3954(4)	9780(2)	6247(1)	76(1)
C(7)	3924(4)	9762(2)	6801(1)	58(1)
C(8)	5008(3)	9572(2)	7116(1)	55(1)
C(9)	5049(3)	9601(2)	7632(1)	54(1)
C(10)	3950(3)	9835(2)	7812(1)	60(1)
C(11)	2849(4)	10028(2)	7513(2)	63(1)
C(12)	2852(3)	9980(2)	7006(2)	65(1)
C(13)	6217(3)	9373(2)	7978(1)	59(1)
C(14)	7724(3)	9931(2)	7930(1)	92(1)
C(15)	6076(4)	8432(2)	7846(1)	90(1)
C(16)	6070(3)	9505(2)	8526(1)	82(1)
C(17)	1672(4)	10261(2)	7737(1)	94(1)
C(18)	4752(4)	7264(2)	4758(1)	90(1)
C(19)	4364(4)	7581(2)	4266(1)	63(1)
C(20)	3089(4)	7785(2)	4156(1)	57(1)
C(21)	2674(3)	8042(2)	3694(1)	55(1)
C(22)	3579(4)	8031(2)	3351(1)	68(1)
C(23)	4836(4)	7820(2)	3441(1)	67(1)
C(24)	5225(4)	7603(2)	3905(1)	69(1)
C(25)	1285(4)	8275(2)	3576(1)	70(1)
C(26)	−14(4)	7515(2)	3601(1)	102(1)
C(27)	1331(4)	9037(2)	3944(1)	100(1)
C(28)	1084(4)	8554(2)	3054(1)	108(1)
C(29)	5733(4)	7786(2)	3036(1)	101(1)
N(3)	1105(3)	6837(2)	8019(1)	57(1)
N(4)	−590(3)	7405(2)	7168(1)	55(1)
O(3)	2113(2)	8212(1)	8629(1)	77(1)
O(4)	−1797(2)	6313(1)	6348(1)	72(1)
C(30)	1517(4)	6492(2)	7569(1)	89(1)
C(31)	1729(4)	7088(3)	7179(1)	85(1)
C(32)	967(3)	7751(2)	7184(1)	71(1)
C(33)	−928(3)	7370(2)	7669(1)	62(1)
C(34)	−457(3)	6712(2)	7945(1)	65(1)
C(35)	1571(3)	6443(2)	8460(1)	70(1)
C(36)	1420(3)	6887(3)	8948(1)	60(1)
C(37)	1716(3)	7767(3)	9015(1)	59(1)
C(38)	1570(3)	8188(3)	9460(1)	65(1)
C(39)	1198(3)	7678(3)	9834(1)	78(1)
C(40)	951(4)	6810(3)	9784(2)	77(1)
C(41)	1057(3)	6422(2)	9330(2)	71(1)
C(42)	1816(4)	9144(3)	9541(2)	85(1)
C(43)	3330(4)	9629(2)	9453(2)	126(2)
C(44)	677(4)	9367(2)	9162(2)	107(1)

(*continued on next page*)

Table 2 (*continued*)

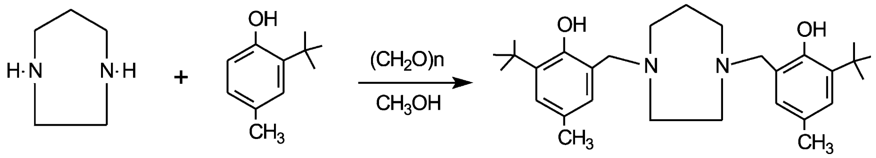
Atom	*x*	*y*	*z*	U_{eq}
C(45)	1646(5)	9464(3)	10060(2)	135(2)
C(46)	589(4)	6299(3)	10214(1)	115(2)
C(47)	− 1359(3)	7911(2)	6882(1)	64(1)
C(48)	− 1239(3)	7807(2)	6338(1)	53(1)
C(49)	− 1484(3)	7006(2)	6086(1)	55(1)
C(50)	− 1372(3)	6875(2)	5582(1)	58(1)
C(51)	− 1029(3)	7606(3)	5346(1)	68(1)
C(52)	− 774(4)	8416(3)	5582(2)	70(1)
C(53)	− 891(3)	8503(2)	6079(1)	66(1)
C(54)	− 1626(4)	5996(2)	5309(1)	75(1)
C(55)	− 537(4)	5580(2)	5556(1)	111(1)
C(56)	− 1468(4)	6028(3)	4756(1)	110(1)
C(57)	− 3155(4)	5438(2)	5315(2)	114(2)
C(58)	− 379(4)	9173(2)	5295(1)	110(2)
N(5)	5922(3)	7141(2)	9641(1)	63(1)
N(6)	5977(3)	5590(2)	8988(1)	55(1)
O(5)	7801(2)	7313(1)	10486(1)	72(1)
O(6)	4461(2)	5322(1)	8079(1)	66(1)
C(59)	6083(4)	7405(2)	9144(1)	92(1)
C(60)	7158(4)	7098(2)	8906(1)	86(1)
C(61)	7332(3)	6271(2)	9032(1)	70(1)
C(62)	5455(3)	5570(2)	9468(1)	69(1)
C(63)	4895(3)	6303(2)	9603(1)	72(1)
C(64)	5484(4)	7774(2)	9948(1)	79(1)
C(65)	5579(4)	7637(2)	10494(1)	59(1)
C(66)	6751(3)	7432(2)	10739(1)	55(1)
C(67)	6899(3)	7341(2)	11254(1)	51(1)
C(68)	5826(3)	7488(2)	11490(1)	54(1)
C(69)	4658(3)	7707(2)	11262(1)	59(1)
C(70)	4550(3)	7766(2)	10757(1)	67(1)
C(71)	8165(3)	7106(2)	11530(1)	55(1)
C(72)	8227(3)	6248(2)	11294(1)	74(1)
C(73)	9561(3)	7800(2)	11513(1)	84(1)
C(74)	8042(3)	7024(2)	12078(1)	80(1)
C(75)	3557(3)	7878(2)	11548(1)	85(1)
C(76)	6138(3)	4766(2)	8811(1)	67(1)
C(77)	6341(3)	4709(2)	8275(1)	56(1)
C(78)	5448(3)	4967(2)	7913(1)	52(1)
C(79)	5517(3)	4863(2)	7407(1)	52(1)
C(80)	6579(3)	4522(2)	7284(1)	64(1)
C(81)	7528(4)	4290(2)	7635(2)	64(1)
C(82)	7380(3)	4389(2)	8125(1)	65(1)
C(83)	4511(3)	5113(2)	7007(1)	60(1)
C(84)	4779(3)	6072(2)	7087(1)	80(1)
C(85)	2934(3)	4658(2)	7029(1)	81(1)
C(86)	4744(4)	4883(2)	6474(1)	93(1)
C(87)	8691(4)	3945(2)	7471(1)	100(1)

that three similar but different crystallographically independent neutral molecules were found to exist in the crystal structure of this compound. They have similar DACH configurations and phenol-pendants arrangements but only slight differences in bond distances and angles.

Table 3
Selected bond lengths (Å) and angles (°) for the title compound

Bond lengths			
N(1)–C(5)	1.465(4)	N(1)–C(6)	1.466(4)
N(1)–C(1)	1.472(4)	N(2)–C(3)	1.464(4)
N(2)–C(4)	1.464(4)	N(2)–C(18)	1.476(4)
O(1)–C(8)	1.375(3)	O(2)–C(20)	1.375(3)
C(1)–C(2)	1.502(4)	C(2)–C(3)	1.446(5)
C(4)–C(5)	1.491(4)	N(3)–C(30)	1.472(4)
N(3)–C(34)	1.475(3)	N(3)–C(35)	1.484(3)
N(4)–C(33)	1.453(3)	N(4)–C(32)	1.470(3)
N(4)–C(47)	1.471(3)	O(3)–C(37)	1.368(3)
O(4)–C(49)	1.379(3)	C(30)–C(31)	1.499(4)
C(31)–C(32)	1.493(4)	C(33)–C(34)	1.507(4)
N(5)–C(63)	1.451(4)	N(5)–C(59)	1.472(3)
N(5)–C(64)	1.485(4)	N(6)–C(61)	1.465(3)
N(6)–C(76)	1.468(4)	N(6)–C(62)	1.474(3)
O(5)–C(66)	1.374(3)	O(6)–C(78)	1.380(3)
C(59)–C(60)	1.501(4)	C(60)–C(61)	1.483(4)
C(62)–C(63)	1.509(4)		
Bond angles			
C(5)–N(1)–C(1)	111.8(3)	C(3)–N(2)–C(4)	111.7(3)
N(1)–C(6)–C(7)	113.1(3)	N(2)–C(18)–C(19)	112.9(3)
C(30)–N(3)–C(34)	110.9(3)	C(33)–N(4)–C(32)	111.1(2)
N(3)–C(35)–C(36)	112.5(3)	N(4)–C(47)–C(48)	110.9(3)
C(63)–N(5)–C(59)	111.2(3)	C(61)–N(6)–C(62)	110.2(3)
N(5)–C(64)–C(65)	113.3(3)	N(6)–C(76)–C(77)	112.3(3)

The title compound consists of a DACH ring substituted with two 3-*tert*-butyl-5-methyl-2-hydroxybenzyl groups on the N donors. The mesocyclic ring DACH is folded up into unusual chair configuration, and the folding angles in three independent molecules are 111.8(3) vs. 111.7(3)° for C(5)–N(1)–C(1) and C(3)–N(2)–C(4), 110.9(3) vs. 111.1(2)° for C(30)–N(3)–C(34) and C(33)–N(4)–C(32), and 111.2(3) vs. 110.2(3)° for C(63)–N(5)–C(59) and C(61)–N(6)–C(62), respectively. This is remarkably different from the reported results of the configuration of DACH ring in most of the metal complexes with DACH and its derivatives, even for the metal complexes with the title compound [19], in which the DACH ring always displays the normal boat configuration [3,11,12,15]. It is rather interesting that the two phenol pendant arms depart from the parent DACH ring in unexpected *trans*-position with the joint angles of 113.1(3) vs. 112.9(3)° for N(1)–C(6)–C(7) and N(2)–C(18)–C(19), 112.5(3) vs. 110.9(3)° for N(3)–C(35)–C(36) and N(4)–C(47)–C(48), 113.3(3) vs. 112.3(3)° for N(5)–C(64)–C(65) and



Scheme 1.

N(6)–C(76)–C(77) in three subunits, respectively. To the best of our knowledge, for all the bis-substituted functionalised DACH or DACO dervatives and their metal complexes the two pendent arms have the *cis*-arrangements. That is, the most stabilized configuration of the title compound in solid state is the DACH backbone in the unusual chair form and the two phenol pendants in unexpected *trans*-arrangement, and the configuration of the DACH ring spontaneously converted into the normal boat form and the two side-arms to the *cis*-positions when chelated to the metal centres. The dihedral angle between the two planes of the phenyl rings is 13.6°, 5.5° and 11.2° for three independent molecules. Two nitrogen atoms of the parent DACH ring and two oxygen donors of the pendant arms form a pseudo-torsion angle of 158.7° for N(1)···O(1) vs. N(2)···O(2), 162.4° for N(3)···O(3) vs. N(4)···O(4) and 169.7° for N(5)···O(5) vs. N(6)···O(6), respectively. All the bond distances and angles of DACH ring are in normal range with the mean C–C and C–N distances of 1.492 and 1.466 Å, and the bond angles ranging from 110.2(3) to 119.8(3)°. There exist intra-molecular O–H···N hydrogen bonds between the phenolic O atoms and the DACH N donors, which may further stabilize the crystal structure. The O···N separations are in 2.657–2.676 Å range with the H···N separations ranging of 1.968–2.013 Å, respectively, and the bond angles are from 135.0° to 142.1°, all being normal weak hydrogen bond interactions [20]. Further studies on the structure and configuration of other DACH derivatives are under way in our laboratory.

4. Supplementary materials

Crystallographic data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary materials (CCDC No. 190989). Copies of available material can be obtained free of charge on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033, e-mail: deposit@ccdc.cam.ac.uk).

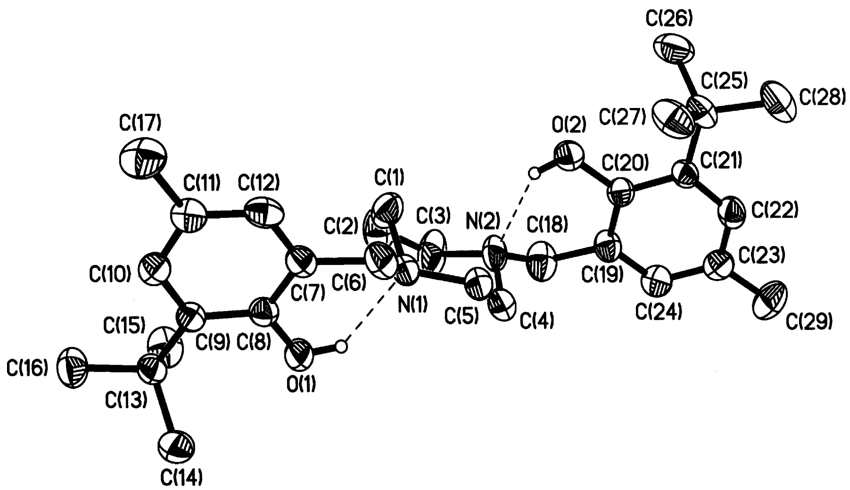


Fig. 1. ORTEP structure of the title compound with 30% probability thermal ellipsoids.

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