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**CHARACTERIZATION AND CRYSTAL STRUCTURE OF A 17-MEMBERED  
MACROCYCLIC SCHIFF BASE COMPOUND MeO-sal-pn-bn****A.D. Khalaji<sup>1</sup>, S.H. Ghoran<sup>1</sup>, J. Rohlicek<sup>2</sup>, M. Dusek<sup>2</sup>**<sup>1</sup>*Department of Chemistry, Faculty of Science, Golestan University, Gorgan, Iran*

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The reaction of 1,4-diaminobutane with 2,2'-diformyl-6,6'-dimethoxy-diphenoxypropane in a mixed solvent of methanol and chloroform results in a new 17-membered macrocyclic Schiff base compound MeO-sal-pn-pn. The title compound is characterized by the elemental analysis (CHN), FT-IR, <sup>1</sup>H NMR spectroscopy, and powder X-ray diffraction. The crystal data are:  $M_r = 396.5$ , orthorhombic,  $P2_12_12_1$ , with unit cell parameters:  $a = 4.71769(3) \text{ \AA}$ ,  $b = 19.1524(2) \text{ \AA}$ ,  $c = 22.9418(2) \text{ \AA}$ ,  $V = 2072.90(3) \text{ \AA}^3$ , and  $Z = 4$ .

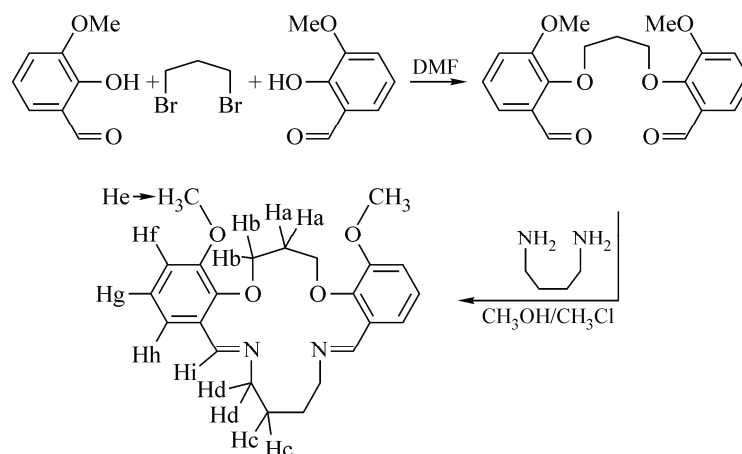
**Keywords:** macrocyclic, Schiff base, spectroscopy, powder diffraction, orthorhombic.

The macrocyclic Schiff base compounds and their transition metal complexes play a key role in coordination chemistry [1–5]. They are extensively studied for their capacity to bind and transport metal ions, for the possibility to act as models for metalloproteins [6, 7], and for their role in host-guest and supramolecular chemistry [8–10]. Macrocycles containing imine groups can form mono-, di-, and polynuclear transition metal complexes with various applications [11–14]. Among them a wide Schiff base macrocycles based on 2,6-diacetylpyridine and 2,6-diformylpyridine as building blocks evolved from the early studies [15].

Many synthetic methods for the preparation of Schiff base macrocyclic compounds use transition metal ions as templating agents [16–21]. However, this method yields stable macrocyclic complexes, thus making the preparation of a metal free ligand difficult [16–21]. Therefore, during the last decade, considerable effort has been made to develop metal free methods for the preparation of Schiff base macrocyclic compounds [15, 22–24]. Recently, many compounds in this field have been rapidly developed and studied [25]. Herein, we report the synthesis, characterization, and crystal structure of a 17-membered [1+1] macrocyclic Schiff base compound MeO-sal-pn-bn obtained by the condensation of 1,4-diaminobutane with 2,2'-diformyl-6,6'-dimethoxy-diphenoxypropane in a mixed solvent of methanol and chloroform (1:1 v/v) (Scheme 1).

**EXPERIMENTAL**

All reagents and solvents for synthesis and analysis were commercially available and used as received without further purifications. Elemental analyses were carried out using a Heraeus CHN—O—Rapid analyzer. Infrared spectra were recorded using KBr disks on a FT-IR Perkin—Elmer spectrophotometer. <sup>1</sup>H NMR spectra are measured on a BRUKER DRX-500 AVANCE spectrometer at 500 MHz. All chemical shifts are reported in  $\delta$  units downfield from TMS. 2,2'-Diformyl-6,6'-dimethoxy-diphenoxypropane used in this experiment was synthesized by the condensation of 1,3-



Scheme 1. Synthesis and chemical structure of the 17-membered [1+1] macrocyclic Schiff base compound MeO-sal-pn-bn

dibromopropane with 3-methoxysalicylaldehyde in *N,N*-dimethylformamide in the presence of anhydrous potassium carbonate according to the literature [16–21, 23].

**X-ray determination.** Single crystal experiment was performed on a Gemini diffractometer (Oxford Diffraction) at 120 K, using mirror-collimated  $\text{CuK}_{\alpha_{1,2}}$  radiation and an Atlas CCD detector. Because of too small single crystals only the orthorhombic unit cell with  $a = 4.662(5) \text{ \AA}$ ,  $b = 19.086(14) \text{ \AA}$ ,  $c = 22.53(10) \text{ \AA}$  could be obtained, but there were no sufficiently intense reflections for the reliable symmetry test and structure solution. Hence we decided to measure the powder diffraction data in order to find and refine the crystal structure from powder. The sample was ground and placed into a 0.3 mm borosilicate glass capillary which was measured at room temperature in the transmission mode on the PAN analytical Empyrean powder diffractometer from  $4^\circ$  to  $80^\circ$  ( $2\theta$ ) with  $\text{CuK}_{\alpha_{1,2}}$  radiation ( $\lambda = 1.54051 \text{ \AA}$ , focusing mirror, step size was  $0.013^\circ$   $2\theta$ ). The indexing in Crysfire2004 [26] and the subsequent Le Bail fitting in JANA2006 software [27] confirmed the orthorhombic unit cell with  $a = 4.71769(3) \text{ \AA}$ ,  $b = 19.1524(2) \text{ \AA}$ ,  $c = 22.9418(2) \text{ \AA}$ ,  $V = 2072.90(3) \text{ \AA}^3$ , previously found from single crystal study. The peak extinctions suggested the  $P2_12_12_1$  space group. Attempts to solve the crystal structure by direct methods failed. Hence, we finally used the parallel tempering algorithm (the direct space method) implemented in the FOX program [28] to determine the crystal structure from the powder diffraction data. The starting structure model was created in Chem Bio Office 2013 using the standard values for bond distances, angles and torsion angles. This model was transferred to the *z*-matrix and imported to the FOX software as a starting model. The resulting crystal structure was refined in the JANA2006 software. In the first step of the refinement we kept the model as a rigid fragment with one overall isotropic ADP parameter. In the final refinement we removed the rigid body constraint and allowed to refine the positions and one isotropic ADP parameter of all non-hydrogen atoms. Hydrogen atoms bonded to carbon were kept in their theoretical positions (ADP of each hydrogen atom =  $1.2 \cdot \text{ADP}$  of the parent atom). Profile parameters, zero shift, background, March-Dollase parameter, and unit cell parameters were refined together with the structure model. The final model was restrained with 31 bond and 39 bond angle restraints to get a result with a reasonable geometry. Each restrained bond and bond angle value was set individually by the help of the Mogul software [30] which explored the Cambridge Structural Database [31] and provided access to information on the preferred values of bond lengths and angles of similar fragments. The final agreement profile factors were  $R_p = 1.57\%$ ,  $R_{wp} = 2.17\%$  (the final Rietveld plot in Fig. 1), with details of the measurement and refinement given in Table 1.

**Synthesis of MeO-sal-pn-bn.** 2,2'-diformyl-6,6'-dimethoxy-diphenoxypropane (0.1 mmol) and 1,4-diaminobutane (0.1 mmol) were dissolved in a mixture of methanol-chloroform (1:1 *v/v*) at room temperature. The mixture was stirred and heated ( $50^\circ \text{C}$ ) for 1.5 h to give a clear solution. The mixture

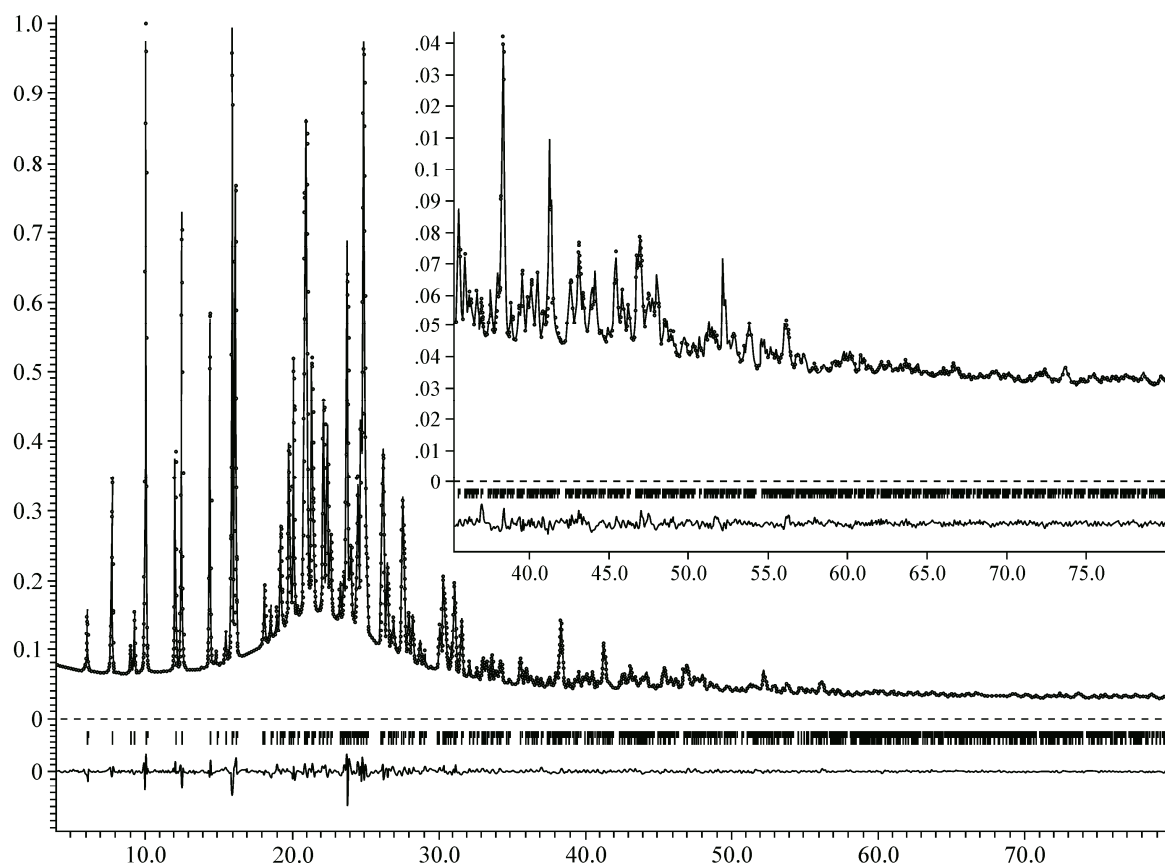


Fig. 1. Final Rietveld plot showing the measured data, calculated data and difference curve. Calculated Bragg positions are shown by vertical bars.

Table 1

Crystal data and summary of the experimental details for MeO-sal-pn-bn

Empirical formula	$C_{23}H_{28}N_2O_4$
Formula weight	396.5
Crystal system, space group	Orthorhombic, $P2_12_12_1$
$a, b, c, \text{\AA}$	4.71769(3), 19.1524(2), 22.9481(2)
$V, \text{\AA}^3$	2072.90(3)
$Z; \lambda$	4; 1.54056 $\text{\AA}$ ( $CuK_{\alpha 1,2}$ )
Density calc., $\text{g/cm}^3$	1.27
$F(000)$	458
Sample type / size, mm	Capillary 0.3 / 20
$2\theta$ range, deg.	4—79.98
Step size, deg.	0.013
March-Dollase coef. (direction)	1.11 (0 1 3)
$R_p, R_{wp}$	0.0157, 0.0217
GOOF	3.27
$R, R_w$	0.028, 0.038
Number of restraints	70 (31 distances, 39 angles)
Number of constraints	140 (28 isotropic ADPs, $28 \times 3 + 28$ coordinates and ADPs of hydrogen atoms)
Refined parameters	127 (29 $\times$ 3 of atoms coordinates, 1 isotropic ADPs, 3 unit cell, 3 profile, preferred orientation, shift, scale, 30 background points)
$\Delta\rho_{\min}, \Delta\rho_{\max}, e/\text{\AA}^3$	-0.10, 0.10

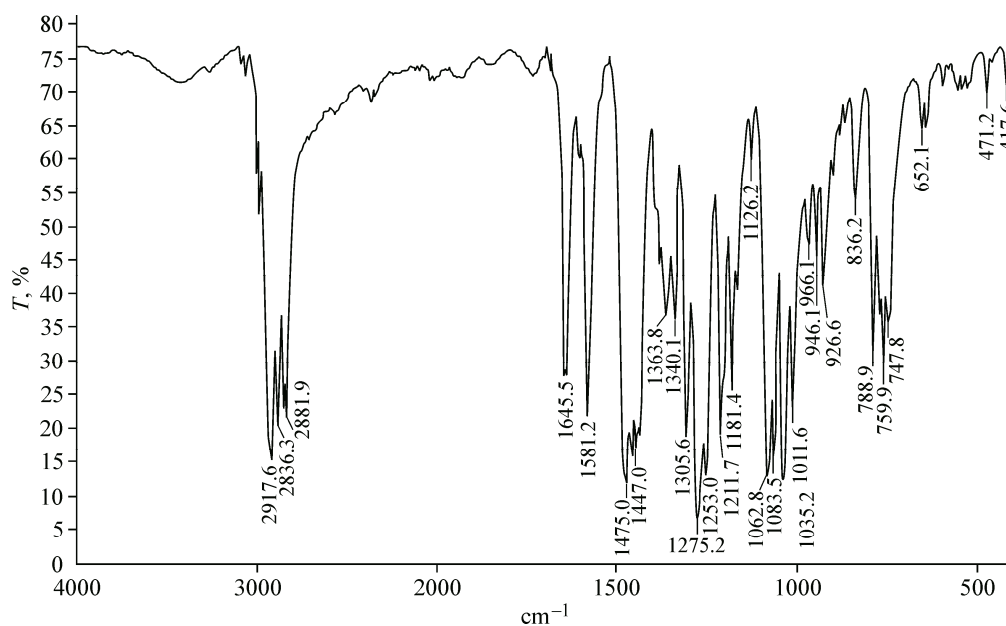


Fig. 2. FT-IR spectrum of MeO-sal-pn-bn

was cooled and allowed to crystallize at room temperature. After keeping the solution in air for several days by slow evaporation of the solvent, colorless crystals were formed at the bottom of the vessel. The resulting colorless crystals were collected by filtration and dried at room temperature. Yield: 76 %. Anal. Calc. for  $C_{23}H_{28}N_2O_4$ : C, 69.67; H, 7.12; N, 7.07 %. Found: C, 69.64; H, 7.18; N, 7.10 %. FT-IR (KBr pellet,  $cm^{-1}$ ): 1447, 1518, 1581 (m, C = C), 1645 (s, C = N), 2836 (—HC = N—), 2881 (CH aliphatic), 2917 (CH aromatic).  $^1H$  NMR ( $CDCl_3$ , ppm): 1.28 (s, 6He), 1.78 (q, 4Hc), 2.5 (q, 2Ha), 3.34 (t, 4Hb), 3.66 (t, 4Hd), 6.99 (d, 2Hh), 7.11 (t, 2Hg), 7.66 (d, 2Hf), 8.64 (s, 2Hi).

## RESULTS AND DISCUSSION

The title compound MeO-sal-pn-bn, contains different group such as the aromatic ring, methoxy and imino groups; it has 57 atoms and provides several normal vibrational modes. The Fourier transform infrared (FT-IR) experimental spectrum of MeO-sal-pn-bn is depicted in Fig. 2. The aromatic and aliphatic C—H vibrations are normally found in the range 2881—3917  $cm^{-1}$  [23—25]. In aromatic compounds, the C—H in-plane and out-of-plane bending vibrations appear in the range 1011—1305  $cm^{-1}$  and 747—966  $cm^{-1}$ , respectively. There are several C—C stretching vibrations in MeO-sal-pn-bn with very strong bands observed at 1447  $cm^{-1}$ , 1475  $cm^{-1}$ , and 1581  $cm^{-1}$ , which correspond to the range 1650—1450  $cm^{-1}$ , generally expected for the C—C stretching vibrations. The C=N stretching of Schiff base compounds appears in the range 1600—1630  $cm^{-1}$ . Singh *et al.* [28] assigned the C=N stretching vibration as a strong intense band in the FT-IR spectrum at about 1608—1632  $cm^{-1}$  in the case of 13- to 20-membered Schiff base macrocycles. We observed the C = N stretching vibration mode at 1645  $cm^{-1}$ .

The room temperature  $^1H$  NMR spectrum of MeO-sal-pn-bn in  $CDCl_3$  is presented in Fig. 3. The title compound shows five groups of aliphatic protons (Ha,b,c,d,e) at 1.28—3.66 ppm and three groups of aromatic protons (Hf,g,h) at 6.99—7.66 ppm. Also, the title compound shows one singlet in the region of 8.64 ppm which is assigned to —CH=N— (the imine proton).

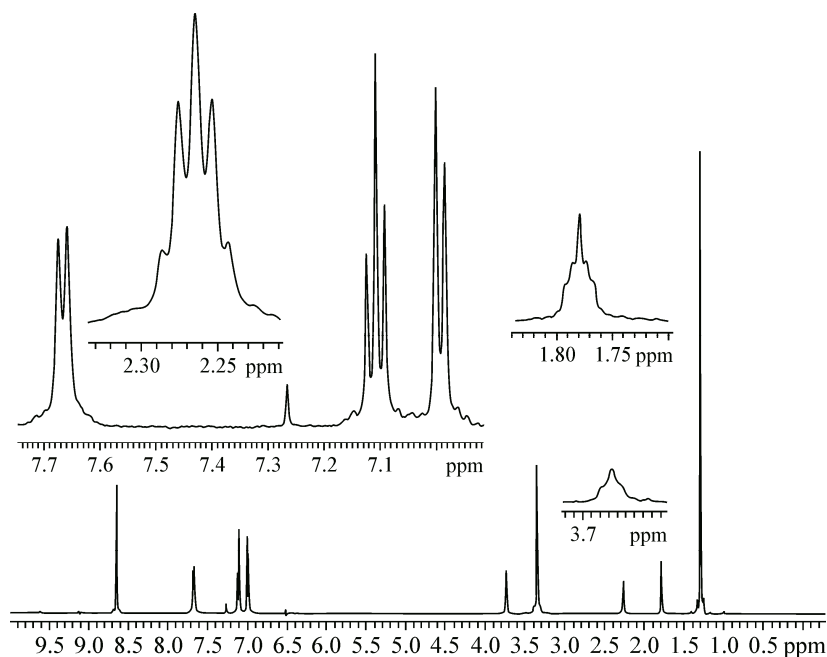


Fig. 3.  $^1\text{H}$  NMR spectrum of MeO-sal-pn-bn

**Molecular structure.** Fig. 4 depicts the isotropic ADP plot of Meo-sal-pn-bn with atomic numbering. Selected bond distances and angles are given in Table 2. The crystal structure analysis proves that the molecular structure of Meo-sal-pn-bn is very close to that of the similar compounds reported previously [ 23 ]. Although the bond lengths and angles had to be restraint in the refinement based on the laboratory powder diffraction data, the low profile and structure R values prove that the structure is correct. In Meo-sal-pn-bn, the C15—N16 and C22—N21 bond distances of 1.267(4) Å and 1.268(5) Å respectively, indicate the double character of these bonds, while the C20—N21 and C17—N16 bond distances of 1.461(5) Å and 1.462(4) Å respectively, indicate the single character of these bonds [ 23 ]. The N16—C15—C3, N21—C22—C23, C15—N16—C17, and C20—N21—C22 bond angles are 122.2(2)°, 122.2(3)°, 117.5(2)°, and 117.7(3)° respectively, which is consistent with the  $sp^2$  hybrid character of C15, C22, N16, and N21 atoms and are similar to other reported macrocyclic Schiff bases having these bond angles [ 23 ].

The geometrical details of the hydrogen bonds of Meo-sal-pn-bn are summarized in Table 3. The Meo-sal-pn-bn molecules are held together only by non-classical C—H $\cdots$ N and C—H $\cdots$ C intermolecular hydrogen bonds (Fig. 5 and Table 3).

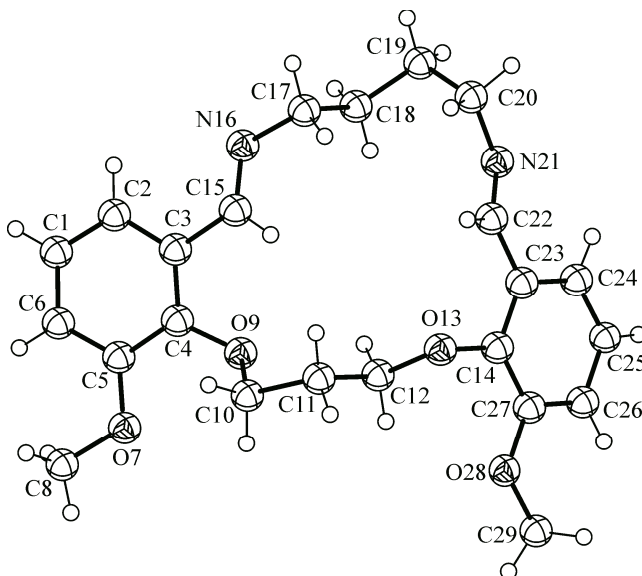
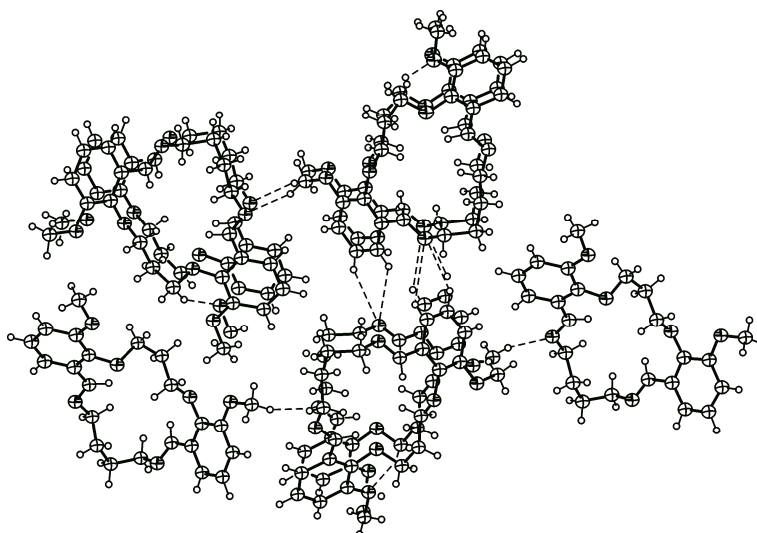


Fig. 4. Plot of isotropic displacement spheres of Meo-sal-pn-bn with atomic numbering

Table 2

*Selected bond distances and angles of Meo-sal-pn-bn based on restraints set by the Mogul software. Because of the small s.u. placed on the restraints, the refined bond lengths and angles are almost identical with the input values*

C4O9	1.391(2)	C5O7	1.371(3)	N21C22	1.268(5)
O9C10	1.436(3)	C27O28	1.365(3)	C15N16	1.267(4)
O13C14	1.386(2)	C12O13	1.433(4)	N16C17	1.462(4)
O7C8	1.424(6)	O28C29	1.423(6)	C20N21	1.461(5)
C11C12O13	107.5(2)	C4C5O7	117.98(17)	O13C14C23	118.0(2)
C3C4O9	117.96(18)	C5C4O9	121.97(18)	C15N16C17	117.5(2)
C6C5O7	122.0(2)	N16C17C18	110.8(2)	O9C10C11	108.00(18)
C5O7C8	117.5(3)	C4O9C10	113.51(17)	C26C27O28	122.0(3)
C12O13C14	113.50(19)	C19C20N21	110.9(3)	C27O28C29	117.5(2)
O13C14C27	122.00(17)	N21C22C23	122.2(3)	C20N21C22	117.7(3)
C3C15N16	122.2(2)	C14C27O28	117.98(19)	C14C27C26	119.99(19)



*Fig. 5. Intermolecular hydrogen bonds of Meo-sal-pn-bn. Dashed lines represent the hydrogen bonds*

Table 3

*Hydrogen bonds of the title compound*

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C6H1C6C8	0.96	2.46	2.778(6)	99.32
C12H1C12O28	0.96	2.46	3.049(5)	119.13
C12H2C12O9	0.96	2.39	2.765(5)	102.80
C22H1C22O13	0.96	2.50	2.779(4)	96.66
C26H1C26C29	0.96	2.44	2.767(4)	99.52



**Supplementary data.** Crystallographic data (excluding the structure factors) for the structure reported in this paper has been deposited with the Cambridge Crystallographic Center, CCDC No. 946159. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, fax: +44 1223 336 033, e-mail: deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>.

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