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N,*N*′-Bis(2-methoxybenzylidene) adducts of ethane-1,2-diamine, propane-1,3-diamine and butane-1,4-diamine

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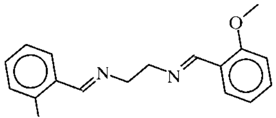
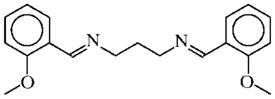
We have isolated and crystallographically characterized the three homologous compounds *N*,*N*′-bis(2-methoxybenzylidene)ethane-1,2-diamine (MeSalen), $C_{18}H_{20}N_2O_2$, *N*,*N*′-bis(2-methoxybenzylidene)propane-1,3-diamine (MeSalpr), $C_{19}H_{22}N_2O_2$, and *N*,*N*′-bis(2-methoxybenzylidene)butane-1,4-diamine (MeSalbu), $C_{20}H_{24}N_2O_2$. In contrast with MeSalpr, the molecules of MeSalen and MeSalbu, which have an even number of methylene units, have crystallographic $\overline{1}$ symmetry. Comparing these methoxy-substituted species with their hydroxy equivalents shows that the aryl rings rotate upon removal of the O—H···N hydrogen bonds. The packing of MeSalen and MeSalpr is controlled by C—H···π interactions, whereas that of MeSalbu has only van der Waals contacts.

Comment

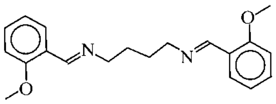
We have been investigating the structures adopted by the complexes of the late transition metals Ni, Cu and Zn (Reglinski *et al.*, 2002*a*,*b*) with symmetric salicylidene Schiff base ligands, as a function of the number of methylene units (n = 2, 3 or 4) between the two imine groups. As part of our ongoing study, we recently turned our attention to the preparation of the homologous compounds derived from *o*-anisaldehyde. As part of the characterization process, we have isolated and crystallographically characterized the three title compounds *N*,*N*′-bis(2-methoxybenzylidene)ethane-1,2-diamine (MeSalen), (I) (Billman & Dorman, 1963), *N*,*N*′-bis(2-methoxybenzylidene)propane-1,3-diamine (MeSalpr), (II) (Moneta *et al.*, 1988), and *N*,*N*′-bis(2-methoxybenzylidene)butane-1,4-diamine (MeSalbu), (III). A search of the December 2003 release of the Cambridge Structural Database (Allen, 2002) shows that no higher homologues have been reported to date. The availability of the structures of these three compounds has allowed us to make some simple but instructive observations regarding the effects of methylene chain lengths and the effects of hydrogen bonding in these systems compared with the parent salicylidene complexes *N*,*N*′-bis(2-hydroxybenzylidene)ethane-1,2-diamine (Salen; Pahor *et al.*, 1978), *N*,*N*′-bis(2-hydroxybenzylidene)propane-1,3-diamine (Salpr; Elderman *et al.*, 1991) and *N*,*N*′-bis(2-hydroxybenzylidene)butane-1,4-diamine (Salbu; Kennedy & Reglinski, 2001), respectively.



MeSalen, (I)



MeSalpr, (II)



MeSalbu, (III)

The three title molecules adopt extended conformations, as shown in Figs. 1(*a*), 1(*b*) and 1(*c*). In MeSalen, (I), and MeSalbu, (III), where there are an even number of C atoms in

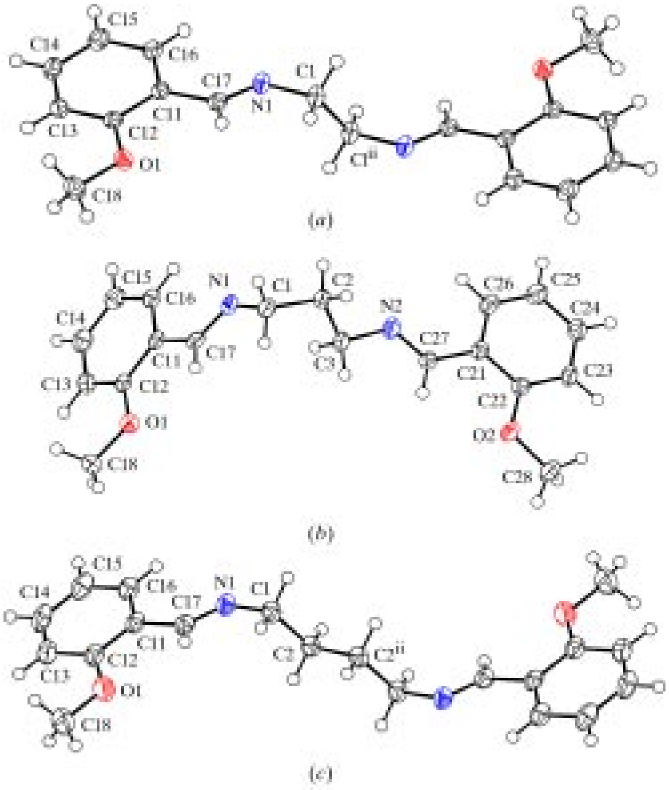


Figure 1
Views of (*a*) MeSalen, (*b*) MeSalpr and (*c*) MeSalbu, with the atom-numbering schemes and displacement ellipsoids drawn at the 50% probability level [symmetry code: (ii) $1 - x, 1 - y, 1 - z$].

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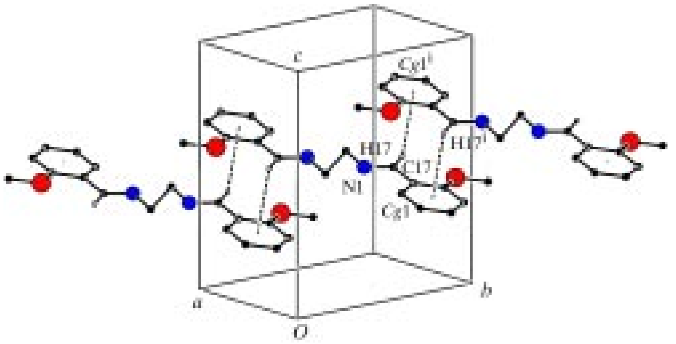

Figure 2
A chain of molecules in MeSalen. *Cg*1 denotes the centroid of the C11–C16 ring [symmetry code: (i) $1 - x, 2 - y, 1 - z$].

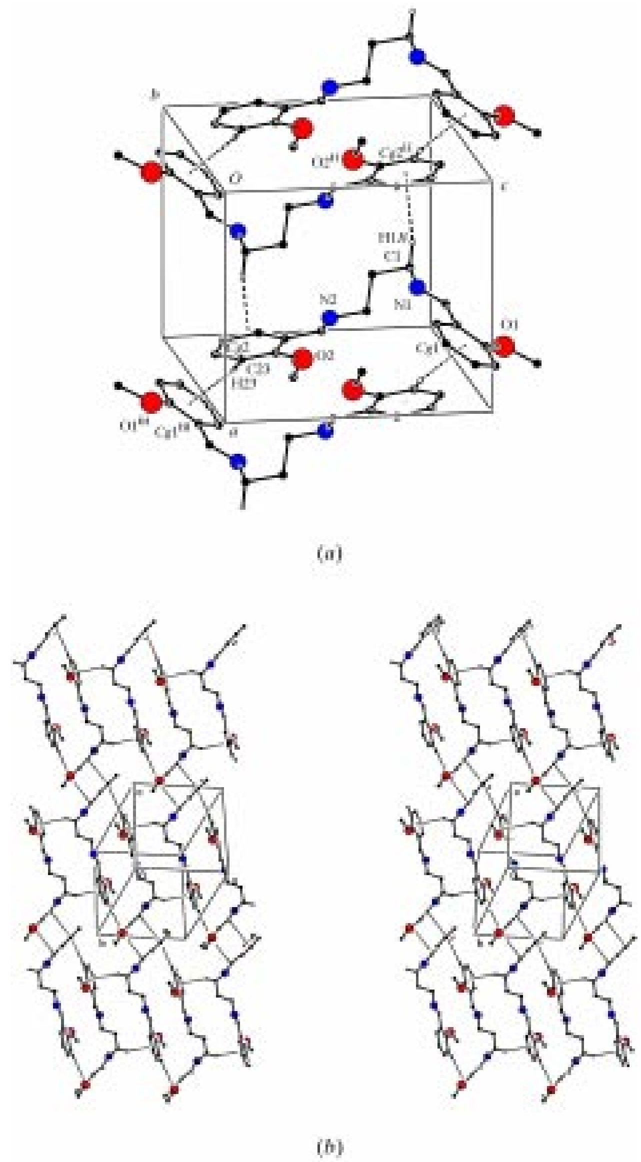

Figure 3
(*a*) The chains of molecules in MeSalpr. *Cg*1 denotes the centroid of the C11–C16 ring and *Cg*2 denotes the centroid of the C21–C26 ring [symmetry codes: (ii) $1 - x, 1 - y, 1 - z$; (iii) $2 - x, 1 - y, 1 - z$]. (*b*) A stereoview showing a sheet of molecules in MeSalpr.

the chain, the molecules lie about inversion centres and adopt an essentially planar extended conformation, with the methoxy moieties, of necessity, in a *trans* arrangement (Fig. 1*a* and *c*). However, for MeSalpr, (II), which has an odd number of C atoms in the linking chains, no symmetry is imposed by the $P\overline{1}$ space group and a markedly non-planar conformation is adopted, with the methoxy moieties in a *cis* arrangement (Fig. 1*b*).

In all three cases, replacement of the salicylidene OH moiety with the anisaldehyde OMe moiety has removed the stabilizing influence of intramolecular hydrogen bonding exhibited in the parent compounds (Pahor *et al.*, 1978; Elderman *et al.*, 1991; Kennedy & Reglinski, 2001), thus allowing a rotation of the aromatic ring such that the methoxy group is remote from the influence of the imine N atom. The lack of intramolecular hydrogen bonding does not alter the bond lengths or angles of the molecules. The largest systematic difference occurs in the angles to the O*R* group, where O1—C12—C11 is significantly smaller for the present methoxy compounds than for their hydroxy equivalents [116.66 (8), 116.29 (14) and 115.75 (12)° for (I), (II) and (III), respectively, compared with 121.23, 121.68 and 121.37° for the equivalent literature species]. This difference is simply explained by the steric effect of the Me group, which lies in the aryl ring plane.

Geometry calculations with *PLATON* (Spek, 2003) show that the packing of the three compounds is quite different. In MeSalen (Fig. 2), the molecules are linked by pairs of inversion-related C—H$\cdots\pi$ interactions to generate infinite chains extending in the *b* direction (details in Table 2). In MeSalpr, chains of inversion-related molecules are linked by two independent C—H$\cdots\pi$ interactions, as shown in Fig. 3(*a*) (details in Table 4). These chains are then linked to form sheets *via* pairs of inversion-related C17—H17$\cdots$*Cg*1^{iv} interactions similar to those observed in MeSalen [Fig. 2; *Cg*1 denotes the centroid of the C11–C16 ring; symmetry code: (iv) $1 - x, -y, 2 - z$]. In this way, the three independent C—H$\cdots\pi$ interactions generate sheets of molecules in the [011]

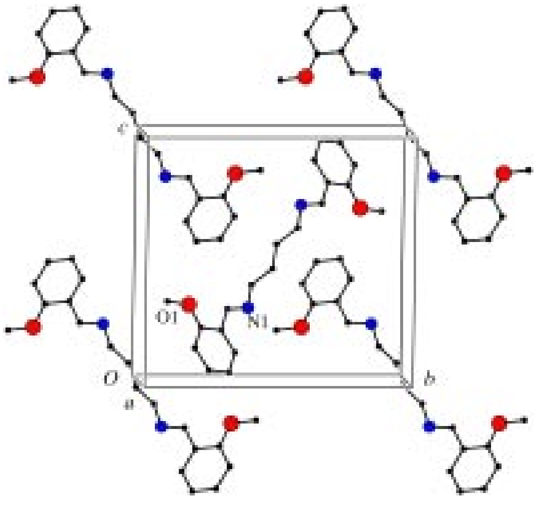

Figure 4
The crystal packing in MeSalbu.

plane, as shown in the stereopair (Fig. 3*b*). By contrast, in MeSalbu (Fig. 4), with a short *a* axis [4.6903 (2) Å], there are no signficant intermolecular interactions and contacts are all of the van der Waals type.

Experimental

MeSalen (Billman & Dorman, 1963) and MeSalpr (Moneta *et al.*, 1988) were prepared as previously reported and crystallized from chloroform–diethyl ether by vapour diffusion. MeSalbu was prepared by refluxing 1,4-diaminobutane with two equivalents of *o*-anisaldehyde in methanol for 4 h. The solvent was removed, giving a yellow oil which was dissolved in a small amount of diethyl ether. Storing the solution in the freezer (258 K) overnight produced pale-yellow crystals which were recrystallized from chloroform–diethyl ether by vapour diffusion. Analysis for MeSalbu found: C 74.06, H 7.37, N 8.39%; expected for $C_{20}H_{24}N_2O_2$: C 74.05, H 7.46, N 8.64%; ^{1}H NMR (270 MHz, $CDCl_3$, δ): 8.72 (*s*, 2H, C═N), 7.95 (*d*, 2H, aromatic), 7.39 (*t*, 2H, aromatic), 7.06 (*t*, 2H, aromatic), 6.91 (*d*, 2H, aromatic), 3.87 (*s*, 6H, OCH_3), 3.67 (*t*, 4H, N—CH_2–), 2.12 (*p*, 4H, –CH_2—CH_2–); ^{13}C NMR (270 MHz, $CDCl_3$, δ): 159, 157, 132, 128, 125, 121 (aromatic), 111 (C═N), 62 (MeO–), 56 (N—CH_2–), 29 (–CH_2—CH_2–); m.p. 332.5–334 K.

Compound (I)

Crystal data

$C_{18}H_{20}N_2O_2$
$M_r = 296.36$
Monoclinic, $P2_1/n$
$a = 7.8727$ (2) Å
$b = 8.9846$ (2) Å
$c = 11.3927$ (3) Å
$\beta = 96.345$ (1)°
$V = 800.90$ (3) Å^3
$Z = 2$

$D_x = 1.229$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 1815 reflections
$\theta = 3.5$–27.5°
$\mu = 0.08$ mm^{-1}
$T = 123$ (2) K
Prism, colourless
0.5 × 0.5 × 0.4 mm

Data collection

Nonius KappaCCD area-detector diffractometer
φ and ω scans
9458 measured reflections
1815 independent reflections
1627 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.037$
$\theta_{\rm max} = 27.5°$
$h = -10 \rightarrow 10$
$k = -11 \rightarrow 10$
$l = -14 \rightarrow 14$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.036$
$wR(F^2) = 0.098$
$S = 1.02$
1815 reflections
101 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0465P)^2 + 0.2339P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.001$
$\Delta\rho_{\rm max} = 0.26$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.17$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °) for (I).

O1—C12	1.3663 (11)	N1—C1	1.4579 (12)
O1—C18	1.4375 (12)	C11—C17	1.4759 (13)
N1—C17	1.2693 (13)	fmtv=top>	
C12—O1—C18	116.67 (8)	O1—C12—C13	123.21 (9)
C17—N1—C1	117.28 (8)	O1—C12—C11	116.66 (8)
C16—C11—C17	120.57 (9)	N1—C17—C11	121.40 (9)
C12—C11—C17	120.93 (8)		

Table 2
Hydrogen-bonding geometry (Å, °) for (I).

*Cg*1 denotes the centroid of the C11–C16 ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C17—H17···*Cg*1$^{\rm i}$	0.95	3.02	3.428	107

Symmetry code: (i) $1 - x, 2 - y, 1 - z$.

Compound (II)

Crystal data

$C_{19}H_{22}N_2O_2$
$M_r = 310.39$
Triclinic, $P\overline{1}$
$a = 8.8669$ (2) Å
$b = 9.9139$ (3) Å
$c = 10.2724$ (4) Å
$\alpha = 101.140$ (2)°
$\beta = 92.341$ (2)°
$\gamma = 109.442$ (2)°
$V = 830.05$ (5) Å^3

$Z = 2$
$D_x = 1.242$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3737 reflections
$\theta = 2.0$–27.5°
$\mu = 0.08$ mm^{-1}
$T = 123$ (2) K
Prism, yellow
0.4 × 0.3 × 0.2 mm

Data collection

Nonius KappaCCD area-detector diffractometer
φ and ω scans
12 958 measured reflections
3737 independent reflections
2279 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.063$
$\theta_{\rm max} = 27.6°$
$h = -11 \rightarrow 11$
$k = -12 \rightarrow 12$
$l = -12 \rightarrow 13$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.047$
$wR(F^2) = 0.122$
$S = 0.99$
3737 reflections
210 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0622P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.24$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.22$ e Å^{-3}

Table 3
Selected geometric parameters (Å, °) for (II).

O1—C12	1.3674 (17)	N1—C1	1.4609 (19)
O1—C18	1.4307 (17)	N2—C27	1.270 (2)
O2—C22	1.3674 (17)	N2—C3	1.4600 (18)
O2—C28	1.4404 (19)	C11—C17	1.475 (2)
N1—C17	1.2688 (18)	C21—C27	1.471 (2)
C12—O1—C18	117.86 (13)	O1—C12—C11	116.29 (14)
C22—O2—C28	116.49 (12)	N1—C17—C11	122.23 (14)
C17—N1—C1	117.99 (13)	C26—C21—C27	120.79 (14)
C27—N2—C3	118.37 (13)	C22—C21—C27	121.34 (14)
C16—C11—C17	120.75 (14)	O2—C22—C23	123.15 (14)
C12—C11—C17	120.55 (14)	O2—C22—C21	116.56 (13)
O1—C12—C13	123.50 (14)	N2—C27—C21	121.70 (14)

Table 4
Hydrogen-bonding geometry (Å, °) for (II).

*Cg*1 denotes the centroid of the C11–C16 ring and *Cg*2 denotes the centroid of the C21–C26 ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C1—H1*B*···*Cg*2$^{\rm ii}$	0.99	2.84	3.725	149
C23—H23···*Cg*1$^{\rm iii}$	0.95	3.05	3.944	157
C17—H17···*Cg*1$^{\rm iv}$	0.95	3.23	3.546	102

Symmetry codes: (ii) $1 - x, 1 - y, 1 - z$; (iii) $2 - x, 1 - y, 1 - z$; (iv) $1 - x, -y, 2 - z$.

Acta Cryst. (2004). C**60**, o169–o172 John Reglinski *et al.* • $C_{18}H_{20}N_2O_2$, $C_{19}H_{22}N_2O_2$ and $C_{20}H_{24}N_2O_2$ **o171**

Compound (III)

Crystal data

$C_{20}H_{24}N_2O_2$
$M_r = 324.41$
Monoclinic, $P2_1/n$
$a = 4.6903\ (2)$ Å
$b = 14.2387\ (6)$ Å
$c = 13.2170\ (5)$ Å
$\beta = 91.002\ (2)^\circ$
$V = 882.55\ (6)$ Å^3
$Z = 2$
$D_x = 1.221$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2004 reflections
$\theta = 2.1$–27.5°
$\mu = 0.08$ mm^{-1}
$T = 123\ (2)$ K
Needle, pale yellow
0.40 × 0.15 × 0.10 mm

Data collection

Nonius KappaCCD area-detector diffractometer
φ and ω scans
10 154 measured reflections
2004 independent reflections
1303 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.046$
$\theta_{\rm max} = 27.5^\circ$
$h = -6 \rightarrow 6$
$k = -18 \rightarrow 18$
$l = -17 \rightarrow 17$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.042$
$wR(F^2) = 0.103$
$S = 1.03$
2004 reflections
111 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0411P)^2 + 0.144P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.19$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.19$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.021 (4)

Table 5
Selected geometric parameters (Å, °) for (III).

N1—C17	1.2673 (17)	O1—C18	1.4279 (18)
N1—C1	1.4634 (17)	C11—C17	1.4719 (18)
O1—C12	1.3686 (17)	fmtv=top>	
C17—N1—C1	115.73 (12)	O1—C12—C13	124.01 (13)
C12—O1—C18	118.18 (11)	O1—C12—C11	115.75 (12)
C16—C11—C17	121.19 (13)	N1—C17—C11	123.01 (13)
C12—C11—C17	120.07 (13)		

All H atoms were clearly revealed in difference maps and were then allowed for as riding atoms with idealized geometry in the final refinement cycles. C—H distances were in the range 0.93–0.99 Å, and $U_{\rm iso}$(H) values were set at $1.2U_{\rm eq}$(C) for CH and CH_2 groups, and at $1.5U_{\rm eq}$(C) for CH_3 groups.

For all compounds, data collection: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT* (Nonius, 1998); cell refinement: *DENZO* and *COLLECT*; data reduction: *DENZO*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997) and *WinGX* (Farrugia, 1997); molecular graphics: *ORTEP*II (Johnson, 1976) and *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1727). Services for accessing these data are described at the back of the journal.

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