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CRYSTAL STRUCTURES OF *N,N'*-BIS(5-DODECYLOXYTROPON-2-YL)PIPERAZINE AND *N,N'*-BIS(4-BUTOXYPHENYL)PIPERAZINE[†]

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Abstract – The crystal structures of *N,N'*-bis(5-dodecyloxytropon-2-yl)piperazine (**1**) and *N,N'*-bis(4-butoxyphenyl)piperazine (**2**) were analyzed by X-ray crystallography. The molecules of **1** and **2** sit on a center of symmetry such that the two aromatic rings are in an *anti* conformation with respect to one another across the piperazine ring. The molecules (**1**, **2**) form a tilted layer structure via intermolecular C-H···O and C-H···π interactions in **1** and intermolecular C-H···O, C-H···N, and C-H···π interactions in **2**.

The synthesis, elucidation of crystal structures and investigation of physical properties of new liquid crystals are important for studying the relationship between molecular structures and mesophases.[1-6] Numerous studies have been dedicated to the structural investigation and the determination of the molecular aggregation mechanism. X-Ray crystallographic analysis plays an important role in obtaining information about intermolecular interactions controlling mesophases. The development of new type of crystals is an important and challenging subject from theoretical and practical view, because liquid crystalline materials are widely applied in communication and information processing systems. Recently

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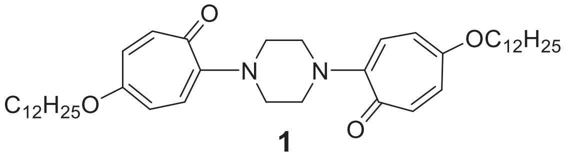
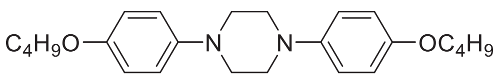
[†]Dedicated to Professor Dr. Lutz F. Tietze on the occasion of his 75th birthday.

we prepared liquid crystals with *N,N'*-bis(tropon-2-yl)piperazine core.[3] *N,N'*-Bis(5-dodecyloxytropon-2-yl)piperazines (**1**) had a smectic C phase while *N,N'*-bis(4-butoxyphenyl)piperazine (**2**) which had a smectic B phase. From the X-ray diffraction pattern of the mesophases of **1** and **2**, the smectic layer spacings (*d*) of **1** and **2** were observed to be 32.9 Å (118 °C) for the smectic C phase and 25.7 Å (215 °C) for the smectic B phase, respectively. However the crystal structures of **1** and **2** have not been reported. We now report on the structures of *N,N'*-bis(5-dodecyloxytropon-2-yl)piperazine (**1**) and *N,N'*-bis(4-butoxyphenyl)piperazine (**2**) with the aim of contributing to a deeper understanding of the relationships between mesomorphic properties and molecular packing in the crystal structure.



1



2

N,N'-Bis(5-dodecyloxytropon-2-yl)piperazine (**1**) was prepared by the condensation of piperazine and 5-dodecyloxy-2-methoxytropone in an ethanol-toluene solution, as reported in a previous paper.[3] Single crystals of **1** were obtained by recrystallization from chloroform and ethyl acetate (1:1 *v/v*) at room temperature. The molecular structures of **1** are shown in Figure 1. The selected bond distances and torsion angles are collected in Table 1.

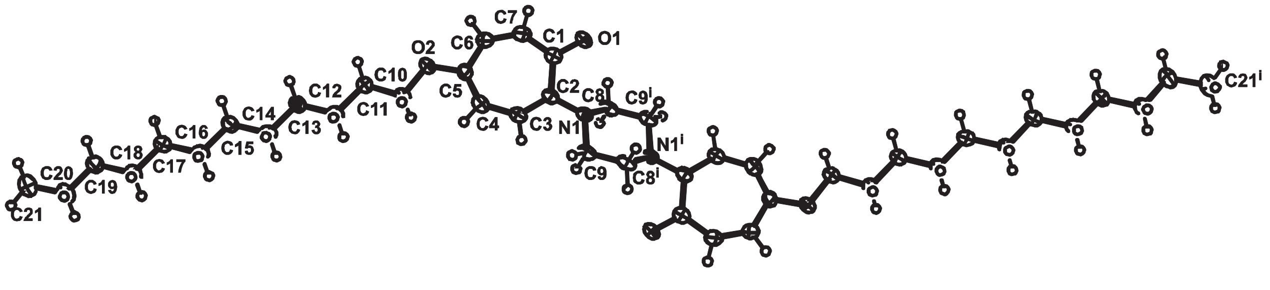


Figure 1. (a) ORTEP diagram of **1**, showing 50% probability ellipsoids. Symmetry codes: (i) -x, 2-y, 2-z.

Table 1. Selected bond distances and torsion angles (Å, º)

O1-C1	1.245(4)	N1-C2	1.397(4)
C1-C2	1.484(4)	C2-C3	1.371(4)
C3-C4	1.411(4)	C4-C5	1.345(4)
C5-C6	1.426(4)	C6-C7	1.360(4)
C1-C7	1.451(4)	O2-C5	1.384(4)
C8-N1-C9-C8^{i}	-53.5(3)	C9-N1-C8-C9^{i}	55.5(3)
N1-C8-C9^{i}-N1^{i}	-54.3(3)	C5-O2-C10-C11	168.90(18)
O2-C10-C11-C12	175.28(18)	C10-C11-C12-C13	177.3(2)
C11-C12-C13-C14	179.5(2)	C12-C13-C14-C15	-180.0(2)
C13-C14-C15-C16	179.8(2)	C14-C15-C16-C17	-179.5(2)
C15-C16-C17-C18	179.0(2)	C16-C17-C18-C19	-178.4(2)

Symmetry codes: (i) -x, 2-y, 2-z.

The molecule of **1** sat on a center of symmetry with the two tropone ring systems in an *anti* conformation with piperazine ring has a normal chair conformation. The angle between the least-squares tropone plane (defined by O1/C1/C2/C3/C4/C5/C6/C7) and piperazine plane (defined by N1/C8/C9/N1^{i}/C8^{i}/C9^{i}) is 145.5(1)°. The C-C, C-O, and C-N bond lengths (Table 1) of the aminotropone ring of **1** are similar to those of *N,N'*-bis(tropon-2-yl)piperazine[6] and *N,N'*-bis(tropon-2-yl)-1,7-dioxia-4,10-diazacyclododecane.[7] This result means that the aminotropone poiety of **1** forms a conjugated 10-electron system. Each paraffin chain of **1** has an *all*-trans conformation, thus forming an almost planar zigzag chain. The deviations of atom from the least-squares planes defined by atoms C10/C11/C12/C13/C14/C15/C16/C17/C18/C19/C18/C21 of **1** are within 0.076(3) Å. The molecular length of **1** is 42.944(4) Å for the C21···C21^{i} distance (symmetry code: (i) 2-x, 2-y, 2-z), which is longer than the smectic layer spacing (*d*=32.9 Å) of **1**. From the the *d*/*l* ratio of the smectic C phase, the tilt angle of **1** was 40° (118 °C), which was larger than that (27°) obtained by X-ray crystallographic analysis of **1**. The crystals of **1** form a tilted layer structure, such as a smectic C phase, as shown in Figure 2.

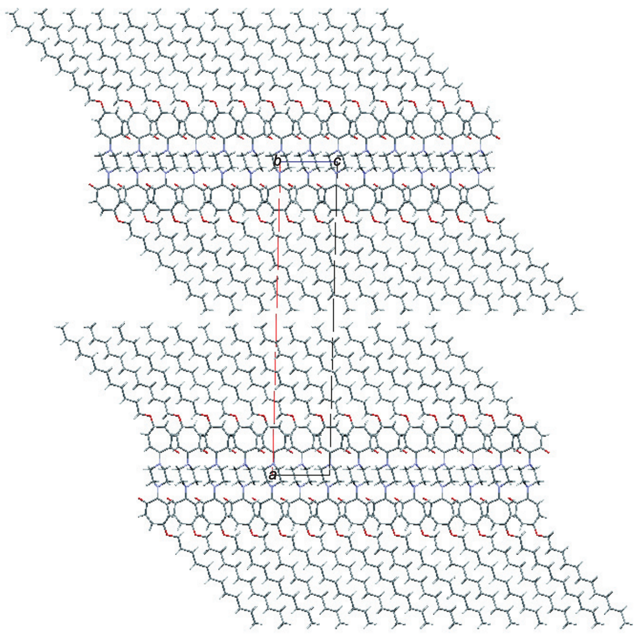


Figure 2. Packing diagrams of **1** viewed down the *b* axis

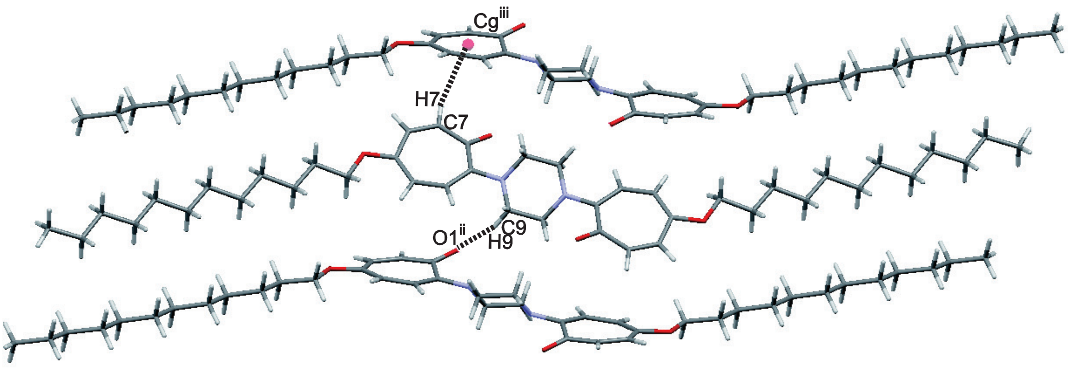


Figure 3. Intermolecular C-H···O and C-H···π interactions of **1**. Cg is the centroid of C1/C2/C3/C4/C5/C6/C7 ring. Symmetry codes: (ii) x, 5/2-y, z-1/2, (iii) x, 3/2-y, z-1/2

Intermolecular C-H···O and C-H···π interactions in the crystal structure of **1** are observed as shown in Figure 3 and Table 2, with distances typical these type of interactions: C-H···O=2.5–2.7 Å[5,6,8,9] and C-H···π=2.8−3.1 Å.[4,5,6,8,9] The combination of intermolecular C-H···O and C-H···πinteractions build up a three-dimensional network.

Table 2. Hydroge-bond geometry (Å, °) of **1**

D—H···A	D—H	H···A	D···A	D—H···A
C9-H9···O1^{ii}	0.970	2.653	3.555(4)	155
C7-H7···Cg^{iii}	0.970	2.941	3.646(4)	134

Symmetry codes: (ii) x, 5/2-y, z-1/2, (iii) x, 3/2-y, z-1/2.

N,N'-Bis(4-butoxyphenyl)piperazine (**2**) was synthesized by the reaction of 4-butoxyaniline and 1,2-dibromoethane in the presence of Na_2CO_3, as reported in a previous paper.[10] Single crystals of **2** were grown in a mixture of hexane-ethyl acetate (1:1 *v/v*) at room temperature. The selected bond distances and torsion angles are collected in Table 3.

Table 3. Selected bond distances and torsion angles of **2** (Å, º)

O1-C4	1.3748(17)	O1-C9	1.4326(19)
N1-C1	1.4291(19)	N1-C7	1.4672(19)
N1-C8	1.4616(18)	C1-C2	1.397(2)
C1-C6	1.3984(19)	C2-C3	1.390(2)
C3-C4	1.393(2)	C4-C5	1.387(2)
C5-C6	1.3872(19)	C7-C8	1.5132(19)
C9-C10	1.510(3)	C10-C11	1.520(3)
C11-C12	1.514(3)		
C9-C10-C11-C12	-179.54(12)	O1-C9-C10-C11	-173.66(11)
C4-O1-C9-C10	-176.49(10)	C7-N1-C8-C7^{i}	-56.52(13)
C8-N1-C7-C8^{i}	56.97(14)	N1-C7-C8^{i}-N1^{i}	-57.17(14)

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

An ORTEP drawing of molecule of **2** is shown in Figure 4. The molecule of **2** sits on a center of symmetry with the two phenyl ring systems in an *anti* conformation with piperazine ring has a normal chair conformation (Figure 4).

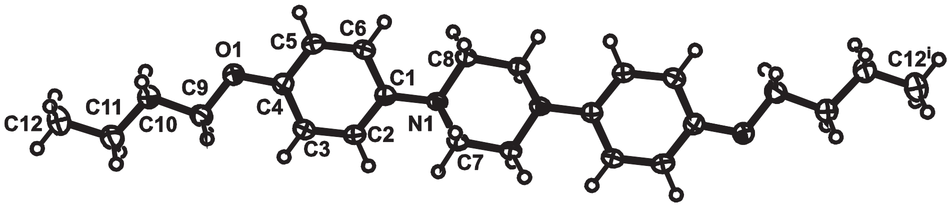


Figure 4. ORTEP structure of **2**, showing 50% probability ellipsoids. Symmetry code: (i) -x, 1-y, 1-z

Each paraffin chain has an *all*-trans conformation, thus forming an almost planar zigzag chain; the deviation of atom from the least-squares planes defined by atoms C9/C10/C11/C12 is within 0.005(2) Å.

The molecular length of **2** is 23.449(3) Å for the C12···C12[i] distance (symmetry code: (i) –x, 1-y, 1-z), which is close to that of smectic layer spacings (*d*=25.7 Å) of **2**. This suggested that the molecules were orthogonal to the layer. The angle between the benzene plane (defined by C1/C2/C3/C4/C5/C6) and the piperazine plane (defined by N1/C7/C8/N1[i]/C7[i]/C8[i]) is 152.12(5)°. Compound (**2**) has a tilted layer structure as shown in Figure 5.

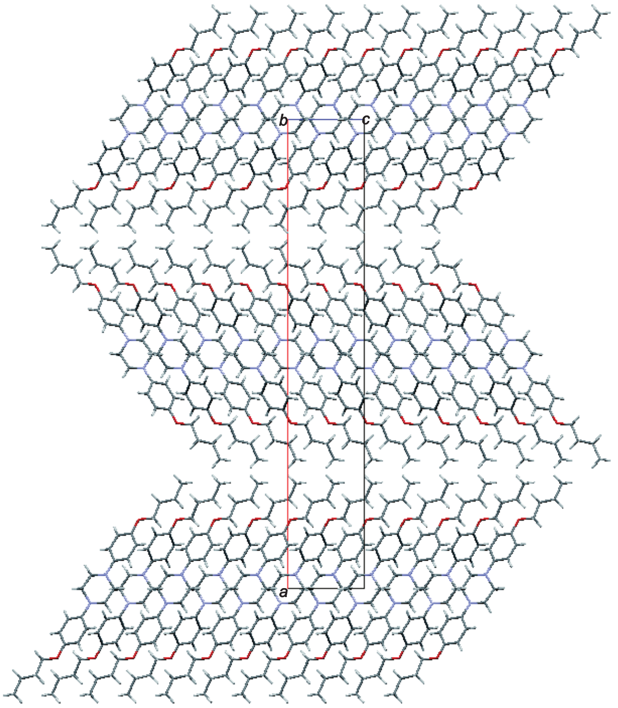


Figure 5. Packing diagrams of **2** viewed down the *b* axis

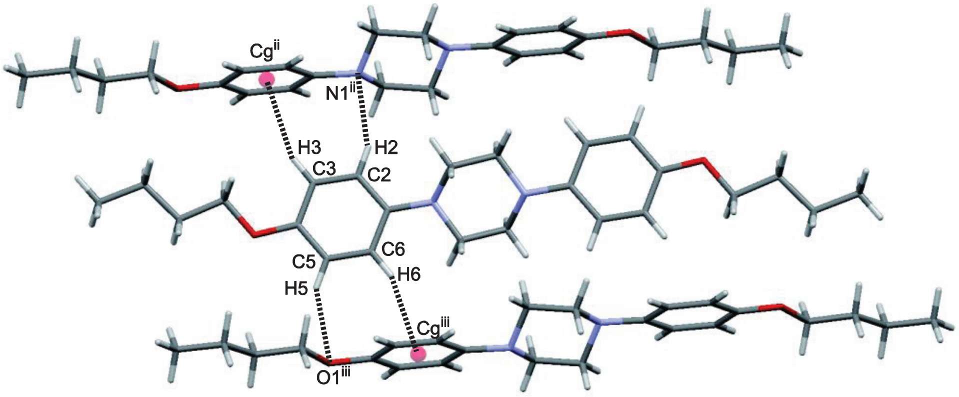


Figure 6. Intermolecular C-H···O, C-H···N, and C-H···π interactions of **2**. Cg is the centroid of C1/C2/C3/C4/C5/C6. Symmetry codes: (ii) x, 3/2-y, z-1/2, (iii) x, 1/2-y, z+1/2

Intermolecular C-H···O and C-H···N interactions are observed in the crystal structure of **2** (Table 4, Figure 6). The H···O distances are close to this type of interaction (2.5–2.7 Å).[5,6,8,9] The

Table 4. Hydroge-bond geometry (Å, °) of **1**

D—H···A	D—H	H···A	D···A	D—H···A
C2-H2···N1^{ii}	0.95	2.628	3.474(3)	149
C3-H3···Cg^{ii}	0.95	3.041	3.875(3)	147
C5-H5···O1^{iii}	0.95	2.651	3.490(3)	148
C6-H6···Cg^{iii}	0.95	2.996	3.841(3)	149

Symmetry codes: (ii) x, 3/2-y, z-1/2, (iii) x, 1/2-y, z+1/2.

H···N distance is shorter than that (2.739 Å) of 7-(diethylamino)-3-phenylcoumarin.[8] There is an intermolecular C-H···π interaction observed in the crystal structure of **2** (Table 4 and Figure 6), with distance for this type of interaction (2.8–3.1 Å).[4,5,6,8,9] These intermolecular C-H···O, C-H···N, and CH···π interactions help to stabilize the crystal packing.

In conclusion, the compounds (**1**, **2**) formed a tilted layer structure via intermolecular C-H···O and C-H···π interactions in **1** and intermolecular C-H···O, C-H···N, and C-H···π interactions in **2**. These intermolecular interactions would control the mesophases of **1** and **2**.

EXPERIMENTALS

Elemental analyses were performed at the elemental analysis laboratory of Kyushu University. The melting points were obtained using a Yanagimoto micro-melting-point apparatus and are uncorrected. The NMR spectra were recorded using JEOL Lambda 400 and 600 spectrometers and solutions in $CDCl_3$ at room temperature; the chemical shifts are expressed in δ units. The mass spectra were measured with JEOL 01SG-2 and JMS-700 spectrometers. The stationary phase used in column chromatography was Wakogel C-300. The transition temperatures were measured by differential scanning calorimetry (Seiko DSC 200) and the mesomorphic phases were observed by polarizing optical microscopy (Olympus BHSP BH-2 equipped with a Linkam TH-600MS hot stage).

Preparation of *N,N'*-bis(5-dodecyloxytropon-2-yl)piperazine (1)

A toluene-EtOH solution (1.5 cm^3, 1:1 *v/v*) of piperazine (15.6 mg, 0.18 mmol) and 5-dodecyloxy-2-methoxytropone (166.6 mg, 0.52 mmol) was refluxed for 7 h. The solvent was evaporated in vacuo. The residue was chromatographed on a silica-gel column using in hexane-EtOAc mixture to afford yellow crystals, which were recrystallized with hexane–EtOAc (1:1 *v/v*) to give yellow prisms (**1**, 104.1 mg, 87%). The physical and spectral data are given bellow.

1: yellow prisms, Cr·117·SmC·128·Iso. ^{1}H NMR ($CDCl_3$) δ 0.88 (6H, t, *J*=6.5 Hz), 1.27-1.60 (36H, m), 1.78 (4H, quint, *J*=6.5 Hz), 3.33 (8H, s), 3.89 (4H, t, *J*=6.5 Hz), 6.40 (2H, d, *J*=12.8 Hz), 6.78 (2H, d, *J*=10.9 Hz), 7.01 (2H, d, *J*=10.9 Hz), 7.09 (2H, d, *J*=12.8 Hz). ^{13}C NMR ($CDCl_3$) δ 14.1 (2C), 22.7 (2C), 26.0 (2C), 29.0 (2C), 29.28 (2C), 29.33 (2C), 29.5 (2C), 29.55 (2C), 29.60 (2C), 29.62 (2C), 31.9 (2C), 49.3 (2C), 68.4 (4C), 109.9 (2C), 121.8 (2C), 131.6 (2C), 137.5 (2C), 154.0 (2C), 159.1 (2C), 181.5 (2C). FAB-MS: *m/z,* 663 ($M+H^+$) Anal. Calcd for $C_{42}H_{66}N_2O_4$: C, 76.09; H, 10.03; N, 4.23% Found: C, 75.86; H, 9.97; N, 4.13%.

X-Ray crystallographic analysis of 1

Single crystals of **1** were grown in a mixture of $CHCl_3$-EtOAc (1:1 *v/v*) at room temperature. A yellow prism of $C_{42}H_{66}N_2O_4$ (approximately 0.200 x 0.200 x 0.030 mm^3) was mount on a glass fiber. All measurements were taken using a Rigaku R-AXIS RAPID diffractometer using monochromated Cu-*K*α radiation (λ=1.54187 Å) (Rigaku, Tokyo, Japan). The H atoms were positioned with the idealized geometry, and were refined to be isotropic (U_{iso}(H)=1.2U_{eq} (C)) using a riding model with C-H = 0.93 Å for aromatic H atoms C-H = 0.97 Å for methylene H atoms, and C-H = 0.96 Å for methyl H atoms. Data collection and cell refinement: *CrystalClear*.[11] Data reduction program: *Crystal Structure 4.0*.[12] Structure solving program: *SIR2008*.[13] Structure refinement program: *CRYSTALS*.[14] Molecular graphics: *ORTEPIII*[15] and *Mercury 3.3*.[16] Crystallographic data have been deposited with Cambridge Crystallographic Data Centre: Deposition number CCDC-1057078. Copies of the data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

Crystal data for **1**: $C_{42}H_{66}N_2O_4$, monoclinic, $P2_1/c$, a =38.288(9) Å, b = 7.187(2) Å, c = 6.924(2) Å, β = 91.42(2)°, V = 1904.6(8) Å^3, Z = 2, M_r = 662.99, D_x = 1.156 g cm^{-3}, μ = 5.659 cm^{-1}, T = 296(2) K, $R1[I > 2\sigma(I)]$ = 0.0764, wR = 0.1943, S = 1.011.

Preparation of *N,N'*-Bis(4-butoxyphenyl)piperaziene (2)

N,N'-Bis(4-butoxyphenyl)piperaziene (**2**) was synthesized by the reaction of 4-butoxyaniline and 1,2-dibromoethane in the presence of Na_2CO_3, as reported in a previous paper.[10]

2: Yield 48%, Cr·117·SmC·128·Iso, colorless prisms. ^{1}H NMR ($CDCl_3$) δ 0.97 (6H, t, *J*=7.4 Hz), 1.49 (4H, sext, *J*=7.4 Hz), 1.75 (4H, quint, *J*=7.4 Hz), 3.23 (8H, s), 3.92 (4H, t, *J*=7.4 Hz), 6.86 (2H, d, *J*=8.9 Hz), 6.95 (2H, d, *J*=8.9 Hz). ^{13}C NMR (CDCl3) δ 14.3 (2C), 19.7 (2C), 31.8 (2C), 51.4 (2C), 68.5 (4C), 115.5 (4C), 118.8 (4C), 145.9 (2C), 153.9 (2C). FAB-MS: *m/z*, 383 (M+H$^+$). Anal. Calcd for $C_{24}H_{34}N_2O_2$: C, 75.35; H, 8.96; N, 7.32% Found: C, 75.57; H, 9.13; N, 7.20%. Calcd for $C_{24}H_{34}N_2O_2$: C, 75.35; H, 8.96; N, 7.32%.

X-Ray crystallographic analysis of 2

Single crystals of **2** were grown in a mixture of hexane-EtOAc (1:1 *v/v*) at room temperature. A colorless prism of $C_{24}H_{34}N_2O_4$ (approximately 0.100 x 0.100 x 0.060 mm^3) was mount on a glass fiber. All measurements were taken using a Rigaku Saturn724 diffractometer using multi-layer mirror monochromated Mo-*K*α radiation (λ=0.71075 Å) (Rigaku, Tokyo, Japan). The H atoms were positioned with the idealized geometry, and were refined to be isotropic (U_{iso}(H)=1.2U_{eq} (C)) using a riding model with C-H = 0.95 Å for aromatic H atoms C-H = 0.99 Å for methylene H atoms, and C-H = 0.98 Å for methyl H atoms. Data collection & cell refinement program: *CrystalClear*.[11] Data reduction program: *CrystalStructure 4.0*.[12] Structure solving program: *SIR2008*[13] Structure refinement program: *CRYSTALS*.[14] Molecular graphics: *ORTEPIII*[15] *and Mercury 3.3*.[16]

Crystal data for **2**: $C_{24}H_{34}N_2O_4$, orthorhombic, P_{bca}, a =40.99(3) Å, b = 7.894(5) Å, c = 6.612 (4) Å, V = 2139(2) Å^3, Z = 4, M_r = 382.54, D_x = 1.188 g cm^{-3}, μ=0.750 cm^{-1}, T = 123(2) K, $R1[I > 2\sigma(I)]$ = 0.0530, wR = 0.1284, S = 1.134. CCDC-1057080.

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