A New Route to the Asymmetric Cylindrical Macrotricyclic Ligands

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New asymmeric cylindrical macrotricyclic ligands have been prepared containing two diaza-12-crown-4 units connected by diethyleneoxy or triethyleneoxy and *meta*- or *para*-xylylene bridges, **2-4**. These materials were prepared in three steps by first treating 6-tosyl-6-aza-3,9-dioxa-1,11-undecanediyl ditosylate with 3-oxa-1,5-pentanediamine or 3,6-dioxa-1,8-octanediamine to form ditosyl-substituted bis(diaza-12-crown-4)s connected by a diethyleneoxy or triethylencoxy bridge. These latter compounds were detosylated and treated with either *para*- or *meta*-α,α'-dibromoxylene to give new asymmetric cylindrical macrotricycles **2-4**. The solid state structure of one of these ligands, **3**, has been determined by X-ray diffraction methods.

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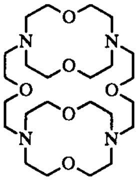
Cylindrical macrotricyclic polyethers are important ligands with strong affinities for cations [1-3]. For example, ligand **1** forms strong complexes with alkaline earth metal ions (log *K* = 6.52, 7.97, and 8.00 for Ca^{2+}, Sr^{2+}, and Ba^{2+}, respectively) [4]. These macrocycles form dinuclear complexes with Cu^{2+}, Zn^{2+}, and Ag^+ and mononuclear complexes with other cations [5-7]. Cylindrical macrotricyclic polyethers that have diazacrown units with appropriate bridge lengths form inclusion complexes with bisprimary alkylammonium salts [8-11]. Thus, the cylindrical macrotricyclic polyether ligands could be synthetic receptors for molecular recognition [2].



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It is important to find convenient syntheses for these interesting molecules. Three synthetic strategies have been used for the construction of cylindrical macrotricyclic polyethers containing diaza-12-crown-4 units. These are illustrated in Figure 1. In route 1, one nitrogen atom of aza-12-crown-4 was first protected and two of the protected-aza-12-crown-4 units were connected. After the protecting groups were removed, the second bridge was connected [12,13]. Route 2 often can be done in one step but the yields are low [11,14]. In route 3, bridging groups containing active and inactive (or protected) ends are treated with the diaza-12-crown-4. The second step consists of activation (or deprotection) of the terminal end of each bridge followed by reaction with another diaza-12-crown-4 [15]. Up to now, only route 1 has been used to prepare the asymmetric cylindrical macrotricyclic ligands.

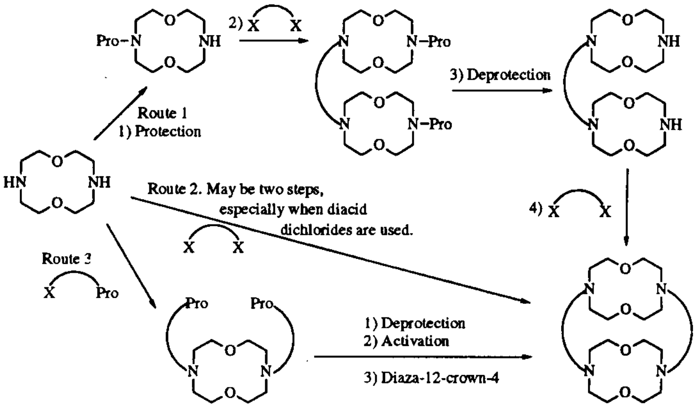
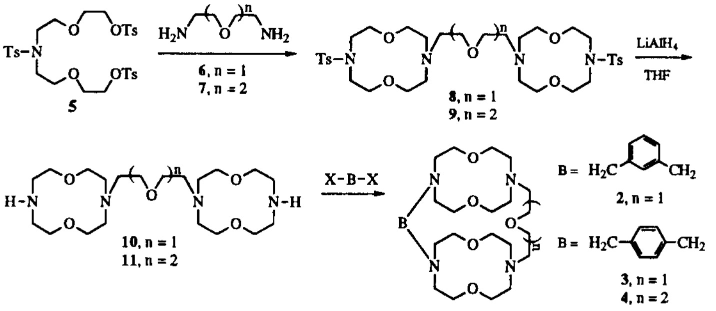


Figure 1. Published Methods to Prepare Macrotricyclic Ligands [1].

We present here a new strategy which does not use expensive diaza-12-crown-4 ($63 per 250 mg) for the preparation of asymmetric cylindrical molecules containing the diaza-12-crown-4 unit (Scheme 1). Starting reactant **5** was obtained after a two-step reaction from *p*-toluenesulfonamide and 2-(2-chloroethoxy)ethanol followed by tosylation [12]. After treating **5** with diaminoethers **6** and **7** in acetonitrile in the presence of potassium carbonate, two bis(*N*-tosyldiaza-12-crown-4) ethers **8** and **9** were obtained



Scheme I. New Preparation of Macrotricyclic Ligands.

wherein the two crown units are connected by ether chains. These types of products were first discovered in our initial attempts to prepare cryptands from diamines and the dihalide derivatives of tetraethylene glycol [16]. In the next step of our new synthetic route, the protecting tosyl groups were removed using lithium aluminum hydride in THF. In the last step, asymmetric cylindrical molecules **2-4** were produced by treating **10** and **11** with *meta*- or *para*-α,α'-dibromoxylene in acetonitrile in the presence of potassium carbonate.

A structural study of **3** was initiated in order to establish conclusively the structural formula of that compound and to examine the conformational features of the molecule. A computer drawing of **3**, which includes atom labels, is shown in Figure 2. The positional and thermal parameters of the atoms are listed in Table 1 and the bond lengths and angles are listed in Table 2. The two diaza-12-crown-4 rings have similar conformations as is indicated by the torsion angles which are listed in Table 3. It is interesting that the chemically similar torsion angles in the two rings have approximately the same absolute values but are opposite in sign. The least-square planes for the heteroatoms of the twelve membered rings were calculated. In each ring alternating donor atoms are above and below the planes. The average of the deviations of those atoms from each plane is the same, 0.3787 Å, but the individual deviations differ. The dihedral angle between the least-square planes of the crown rings is 27.2°.

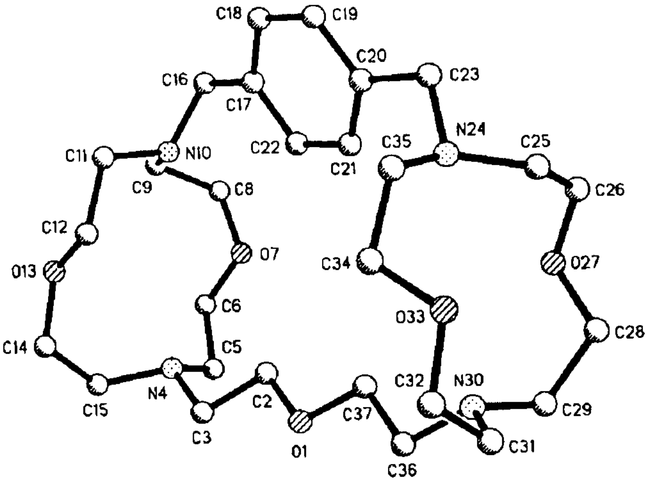


Figure 2. Computer drawing of **3** with hydrogens omitted for clarity.

The two crown rings are rather far apart. The bridges forming the rings differ considerably. The atoms N10 and N24 are linked by a benzene group and its para-carbons. This causes that bridge to be rigid. The nitrogen atoms linked by that group of atoms are slightly closer together than are the two nitrogens which are bridged by the

Table 1

Atomic Coordinates (x10^4) and Equivalent Isotropic Displacement Coefficients (Å^{2}x10^3) for **3**

atom	x	y	z	Ueq [a]
O1	8551(4)	1628(4)	4661(3)	61(2)
C2	7928(6)	1820(7)	3857(5)	72(4)
H2A	8127	1385	3494	80 [b]
H2B	8033	2485	3714	80
C3	6766(6)	1673(6)	3776(5)	59(4)
H3A	6560	2128	4122	80
H3B	6671	1017	3945	80
N4	6098(5)	1834(5)	2952(4)	45(3)
C5	6098(6)	1010(5)	2426(5)	54(4)
H5A	5547	558	2452	80
H5B	6774	674	2607	80
C6	5913(6)	1344(6)	1565(4)	55(4)
H6A	5323	1797	1416	80
H6B	5742	793	1205	80
O7	6849(4)	1809(4)	1522(3)	57(3)
C8	6662(6)	2431(6)	847(5)	63(4)
H8A	6164	2120	389	80
H8B	7324	2526	728	80
C9	6247(6)	3439(6)	974(4)	52(4)
H9A	5603	3344	1118	80
H9B	6070	3818	487	80
N10	7036(5)	3963(5)	1611(4)	46(3)
C11	6580(6)	4672(5)	2032(5)	56(4)
H11A	5956	4957	1654	80
H11B	7089	5189	2236	80
C12	6237(6)	4226(6)	2701(4)	55(4)
H12A	6204	4733	3075	80
H12B	6770	3757	2979	80
O13	5217(4)	3757(4)	2408(3)	54(3)
C14	4940(6)	3239(6)	3020(5)	60(4)
H14A	4228	3415	3013	80
H14B	5429	3407	3537	80
C15	5011(6)	2153(6)	2900(4)	55(4)
H15A	4770	1795	3286	80
H15B	4536	2001	2374	80
C16	7866(6)	4428(6)	1334(4)	59(4)
H16A	7635	5072	1128	80
H16B	7976	4041	906	80
C17	8931(5)	4519(5)	2020(4)	44(3)
C18	9576(7)	5334(6)	2102(4)	52(4)
H18A	9326	5896	1765	80
C19	10569(7)	5344(7)	2696(5)	60(5)
H19A	11032	5899	2727	80
C20	10925(6)	4566(7)	3212(5)	54(4)
C21	10271(7)	3771(7)	3137(5)	59(4)
H21A	10505	3229	3501	80
C22	9290(6)	3738(6)	2552(5)	54(4)
H22A	8843	3168	2506	80
C23	12037(6)	4585(7)	3812(5)	82(5)
H23A	12256	5256	3931	80
H23B	12521	4280	3569	80
N24	12114(6)	4086(6)	4560(4)	62(4)
C25	13141(7)	3597(8)	4906(5)	84(5)
H25A	13219	3438	5457	80
H25B	13720	4026	4897	80
C26	13189(8)	2648(9)	4487(6)	96(6)
H26A	13908	2394	4656	80
H26B	13002	2798	3923	80
O27	12497(5)	1924(5)	4606(4)	73(3)
C28	12904(7)	1416(7)	5338(5)	76(5)
H28A	13295	1863	5748	80
H28B	13380	901	5286	80

Table 1 (continued)

atom	x	y	z	Ueq[a]
C29	11988(7)	1012(6)	5579(5)	67(4)
H29A	12232	530	5997	80
H29B	11511	694	5115	80
N30	11401(5)	1782(5)	5835(4)	49(3)
C31	11907(6)	2092(7)	6654(5)	71(5)
H31A	12667	1993	6788	80
H31B	11648	1689	7006	80
C32	11726(7)	3133(8)	6794(5)	83(5)
H32A	12037	3291	7354	80
H32B	10966	3238	6653	80
O33	12164(5)	3758(5)	6329(4)	77(3)
C34	11371(8)	4257(7)	5708(6)	87(5)
H34A	11017	4738	5940	80
H34B	10844	3791	5417	80
C35	11831(8)	4742(6)	5128(6)	85(5)
H35A	11341	5230	4826	80
H35B	12467	5077	5442	80
C36	10263(6)	1562(5)	5658(4)	59(4)
H36A	9958	1932	6002	80
H36B	10175	876	5748	80
C37	9653(5)	1769(6)	4786(4)	67(4)
H37A	9781	2442	4677	80
H37B	9896	1354	4433	80

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor. [b] U values for all hydrogens are assigned isotropic displacement coefficients.

Table 2

Bond Lengths and Bond Angles for Nonhydrogen Atoms of **3**

1	2	3	1-2Å	1-2-3°
C37	O1	C2	1.406(8)	112.2(6)
O1	C2	C3	1.414(8)	109.0(7)
C2	C3	N4	1.499(11)	110.9(7)
C3	N4	C5	1.451(9)	113.2(6)
C15	N4	C3	1.466(10)	112.5(6)
C5	N4	C15	1.448(10)	112.3(5)
N4	C5	C6		111.4(6)
C5	C6	O7	1.518(11)	108.3(5)
C6	O7	C8	1.403(10)	112.8(5)
O7	C8	C9	1.410(10)	113.4(7)
C8	C9	N10	1.517(12)	110.8(6)
C9	N10	C11	1.452(9)	114.1(6)
C9	N10	C16		112.6(6)
C11	N10	C16	1.449(11)	110.2(6)
N10	C11	C12		113.2(6)
C11	C12	O13	1.503(12)	111.9(6)
C12	O13	C14	1.427(9)	112.4(5)
O13	C14	C15	1.419(10)	110.1(7)
C14	C15	N4	1.500(12)	112.6(6)
N10	C16	C17	1.465(11)	111.4(6)
C16	C17	C18	1.537(9)	121.8(6)
C16	C17	C22		119.7(6)
C18	C17	C22	1.376(11)	118.4(6)
C17	C18	C19		119.3(7)
C18	C19	C20	1.390(11)	112.1(8)
C19	C20	C21	1.375(13)	118.2(7)
C19	C20	C23		120.1(8)
C21	C20	C23	1.362(13)	121.6(8)
C22	C21	C20	1.374(10)	120.9(8)
C17	C22	C21	1.395(10)	121.1(7)
C20	C23	N24	1.508(10)	113.7(7)
C23	N24	C25	1.448(12)	112.8(8)
C35	N24	C23	1.465(13)	111.2(7)
C25	N24	C35	1.455(11)	113.2(7)
N24	C25	C26		111.4(7)
C25	C26	O27	1.496(16)	114.1(9)
C26	O27	C28	1.398(14)	113.7(6)
O27	C28	C29	1.405(11)	109.0(6)
C28	C29	N30	1.495(13)	111.7(7)
C29	N30	C31	1.450(11)	113.1(6)
C29	N30	C36		113.1(6)
C31	N30	C36	1.442(10)	113.4(7)
N30	C31	C32		113.6(7)
C31	C32	O33	1.470(14)	111.7(8)
C32	O33	C34	1.414(13)	113.3(7)
O33	C34	C35	1.422(10)	112.2(8)
C34	C35	N24	1.485(16)	115.6(8)
N30	C36	C37	1.458(10)	111.3(6)
C36	C37	O1	1.511(9)	109.1(6)

Table 3

Torsion Angles in the 12-crown-4 Rings of **3**

1	2	3	4	1-2-3-4°
C11 [a]	N10	C9	C8	-152.1(7)
N10	C9	C8	O7	63.3(9)
C9	C8	O7	C6	82.4(8)
C8	O7	C6	C5	-159.6(6)
O7	C6	C5	N4	72.9(8)
C6	C5	N4	C15	80.4(8)
C5	N4	C15	C14	-147.2(7)
N4	C15	C14	O13	62.0(7)
C15	C14	O13	C12	-108.1(6)
C14	O13	C12	C11	173.3(6)
O13	C12	C11	N10	-80.6(7)
C12	C11	N10	C9	84.7(7)
C35 [a]	N24	C25	C26	154.4(9)
N24	C25	C26	O27	-67.5(1.0)
C25	C26	O27	C28	-81.6(1.0)
C26	O27	C28	C29	155.1(8)
O27	C28	C29	N30	-71.1(8)
C28	C29	N30	C31	-80.8(9)
C29	N30	C31	C32	148.6(8)
N30	C31	C32	O33	-62.2(9)
C31	C32	O33	C34	110.9(8)
C32	O33	C34	C35	-168.2(8)
O33	C34	C35	N24	74.9(9)
C34	C35	N24	C25	-80.4(1.0)

[a] The torsion angles are arranged to show similarities between the two crown rings. Compare C11-N10-C9-C8 with C35-N24-C25-C26, N10-C9-C8-O7 with N24-C25-C26-O27, *etc.*

dietheleneoxy group. The N10 • • • N24 and N4 • • • N30 interatomic distances are 7.050 and 7.216 Å, respectively. This makes a large approximately rectangular cavity as shown in Figure 2. The N4 • • • N10 and N24 • • • N30 interatomic distances are 4.145 and 4.116 Å, respectively. The cavity is considerably larger than that found in many other similar structures. For example, in the Na^+ complex of a ligand in which the crown-4 rings are joined by a two

Table 4

Crystal and Solution Data for **3**

Formula	$C_{28}H_{48}N_4O_5$
Crystal size (mm)	0.12 x 0.14 x 0.36
Crystal system	Monoclinic
Space group	$P2_1/c$
a	13.106(8)Å
b	13.615(10)Å
c	17.462(10)Å
β	108.01(5)°
V	2962
Z	4
Dx(Mg/m^3)	1.168
Absorption coefficient (mm^{-1})	0.080
Index ranges	$0 \leq h \leq 14, 0 \leq k \leq 14, -18 \leq \ell \leq 17$
Data collected	4325
Independent data	3915 (R_{int} = 2.79%)
Observed data used in refinement	1444 (F > 4.0 σ (F))
Weighting Scheme	$w^{-1} = \sigma^2(F) + 2 \times 10^{-4}F^2$
R values	R = 6.51% Rw = 4.78%
Goodness of fit	1.32
Largest and mean Δ/σ	0.001, 0.000
Data to parameter ratio	4.3:1
Largest difference peak	0.30 eÅ^{-3}
Largest difference hole	-0.24 eÅ^{-3}

and a three carbon bridge, [12] the cation is sandwiched between the two crown rings and interacts with donor atoms of both rings. With the large distance separating the crown rings in **3**, any complexation of simple cations would likely involve the two rings acting independently, each complexing a metal ion similar to the Ag$^+$ complex in which the nitrogens of the 12-crown-4 rings are joined by two dietheleneoxy bridges [1]. If both rings would be involved in complexation of a single cation or molecule it would likely be a multi-atom species. No such complexes of **3** have been prepared.

EXPERIMENTAL

Proton and carbon nmr spectra were obtained at 200 MHz in deuteriochloroform. Molecular weights were determined by electron impact hrms. Starting material **5** was prepared as reported [12]. Compounds **6** and **7** were purchased from the Texaco Company. Kieselgel 60 (230-400 mesh) (Merck) and aluminium oxide (activated, neutral, Brockman 1,150 mesh) (Aldrich) were used for column chromatography. Ir spectra agreed with the structure of the compounds. Combustion analyses were obtained from MHW Labs, Phoenix, Arizona.

Preparation of *N,N'*-Ditosylbis(diaza-12-crown-4) Intermediates **8** and **9**.

Diamines **6** and **7** (0.01 mole), 0.02 mole of tritosyl **5** and 0.1 mole of potassium carbonate were refluxed in 400 ml of acetonitrile for 6 days. After cooling, the solvent was evaporated and water and methylene chloride were added and the mixture was thoroughly mixed. The organic layer was separated and dried using anhydrous magnesium sulfate. The solvent was evaporated and the residue was passed through an alumina column with THF/toluene: 5/1 as eluent and then it was purified on a silica gel column using methanol/ammonium hydroxide: 30/1, 20/1 and 10/1 as eluants. The collected fractions (first main spot) were combined and evaporated. Methylene chloride was added to the residue and the product was isolated after filtration and evaporation of the solvent. Yields of 35% and 32% were observed for **8** and **9**, respectively; ^{1}H nmr for **8**: (δ) 2.3 (s, 6 H), 2.7 (m, 12 H), 3.3 (t, 8 H), 3.55 (m, 12 H), 3.85 (t, 8 H), 7.3 (d, 4 H), 7.7 (d, 4 H), mp 87-88°; and for **9** (δ) 2.4 (s, 6 H), 2.7 (m, 12 H), 3.25 (t, 8 H), 3.55 (m, 16 H), 3.85 (t, 8 H), 7.25 (d, 4 H), 7.7 (d, 4 H). Satisfactory elemental analyses were obtained for **2-4**, derivatives of these intermediates.

Preparation of Bis(diaza-12-crown-4) Ligands **10** and **11**.

Compounds **8** and **9** (0.01 mole) were dissolved in 50 ml of THF and slowly added to 200 ml of THF containing 0.15 mole of lithium aluminum hydride. The mixture was refluxed for 72 hours under nitrogen. After cooling, 40 ml of water was slowly added and the resulting mixture was filtered and the organic solvents were evaporated. Methylene chloride (100 ml) was added and the resulting mixture was filtered and the organic solvents were evaporated. The residue was purified on a short silica gel column using methanol/ammonium hydroxide: 10/1 and 5/1 as eluants. The collected fractions were evaporated. Methylene chloride (50 ml) was added and the mixture was filtered and evaporated. Compounds **10** and **11** were obtained in yields of 78% and 87% respectively. Instead of column chromatography, it was possible to obtain crude products after decomposition of excess lithium aluminium hydride, filtration, and evaporation of the solvents. Hydrochloric acid was then added to *p*H = 1, followed by three extractions with chloroform. A solution of lithium hydroxide was added to the water layer until *p*H = 14. Three more extractions were done using chlorofom. The organic layer was dried over anhydrous magnesium sulfate, filtered and evaporated. The products had the following properties: **10**, mp 55-57°; ^{1}H nmr: (δ) 2.7 (m, 22 H), 3.6 (m, 20 H); **11**, mp 82-85°; ^{1}H nmr: (δ) 2.7 (m, 22 H), 3.6 (m, 24 H); ^{13}C nmr: (δ) 47.7, 53.7, 55.6, 67.8, 68.3, 69.3, 70.4. Satisfactory elemental analyses were obtained for **2-4**, derivatives of **10** and **11**.

Preparation of Macrotricyclic Ligands **2-4**.

Biscrowns **10** and **11** (0.01 mole) and 0.011 mole of *para*- or *meta*-α,α'-dibromoxylene were added to 200 ml of acetonitrile containing 10 g of potassium carbonate. The mixture was refluxed for 48 hours. After cooling, the crude product was filtered and the solvent was evaporated. Methylene chloride (30 ml) was added to the residue. The mixture was filtered and the solvent was evaporated. The residue crystallized from the mixture of methanol and ammonium hydroxide (20:1). Macrotricycle **3** was obtained in a 43% yield, mp 108-112°; ^{1}H nmr: (δ) 2.75 (m, 20 H), 3.6 (m, 24 H), 7.45 (s, 4 H); ^{13}C nmr: (δ) 55.8, 56.1, 60.8, 70.0, 70.8, 128.4, 139.1; ms: m/z 520, 521.

Anal. Calcd. for $C_{28}H_{48}N_4O_5$: C, 64.58, H, 9.29. Found: C, 64.71; H, 9.19.

Macrotricycles **2** and **4** were obtained using column chromatography instead of crystalization. They were purified on silica gel using methanol/ammonium hydroxide: 40/1, 20/1, 10/1 and 5/1 as eluants. To the combined evaporated fractions, 50 ml of methylene chloride was added and the resulting product was filtered and evaporated to give **2** and **4** as oils in 68% and 71% yields, respectively. The spectral properties for **2** are: ^{1}H nmr: (δ) 2.75 (m, 20

H), 3.6 (m, 24 H), 7.1 (m, 3 H), 7.7 (s, 1 H); ^{13}C nmr: (δ) 54.9, 56.4, 57.0, 61.6, 69.4, 69.8, 70.1, 127.5, 127.6, 129.5, 140.1.

Anal. Calcd for $C_{28}H_{48}N_4O_5$: C, 64.58; H, 9.29. Found: C, 64.54; H, 9.09.

The spectral properties for **4** are: ^{1}H nmr: (δ) 2.8 (m, 20 H), 3.7 (m, 28 H), 7.45 (s, 4 H); ^{13}C nmr (δ): 55.7, 56.2, 56.6, 61.6, 69.7, 70.1, 70.4, 128.6, 138.9.

Anal. Calcd. for $C_{30}H_{52}N_4O_6$: C, 63.80; H, 9.28. Found: C, 63.70; H, 9.16.

X-ray Structure Determination.

A suitable crystal was selected for the structure determination of **3**. The study was performed using a Siemens R3m/V automated diffractometer utilizing MoKα radiation (λ = 0.7071Å). Crystal data were obtained using a least-squares procedure involving 48 centered reflections. Intensity data were collected using a θ-2θ variable speed scanning mode. Crystal data and solution details are summarized in Table 4.

The trial structure was obtained using direct methods. Nonhydrogen atoms were refined using a full-matrix, least-squares procedure. Hydrogens were placed in calculated positions and assigned isotropic displacement coefficients. During the refinement process the hydrogens were allowed to ride on their neighboring atoms and their thermal parameters were fixed. All programs used in solution, refinement and display of the structure are contained in the SHELXTL-PLUS^{TM} program packaged [17]. Atomic scattering factors used are those contained in the program package.

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