

***N,N',N'',N'''*-Tetrakis(1-naphthylmethyl)-1,4,8,11-tetraazacyclotetradecane****Kanji Kubo,<sup>a\*</sup> Emi Yamamoto,<sup>b</sup> Tadimitsu Sakurai<sup>c</sup> and Akira Mori<sup>a</sup>**<sup>a</sup>Institute of Advanced Material Study, 86, Kyushu University, Kasuga-koen, Kasuga, Fukuoka 816-8580, Japan, <sup>b</sup>Graduate School of Engineering Sciences, 39, Kyushu University, Kasuga-koen, Kasuga, Fukuoka 816-8580, Japan, and <sup>c</sup>Department of Applied Chemistry, Faculty of Engineering, Kanagawa University, Kanagawa-ku, Yokohama 221-8686, Japan

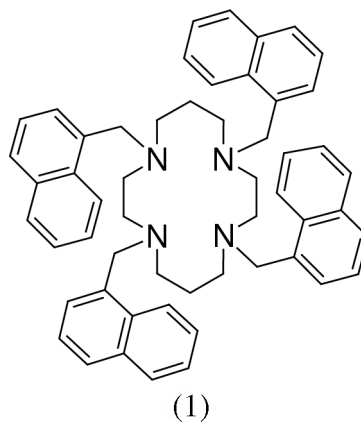
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**Key indicators**Single-crystal X-ray study  
 $T = 297\text{ K}$   
Mean  $\sigma(\text{C}—\text{C}) = 0.005\text{ \AA}$   
 $R$  factor = 0.052  
 $wR$  factor = 0.163  
Data-to-parameter ratio = 19.8For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

Molecules of the title compound,  $\text{C}_{54}\text{H}_{56}\text{N}_4$ , are centrosymmetric and adopt a conformation with two naphthylmethyl groups above the cyclam ring and the remaining two below. Packing with intermolecular  $\pi$ – $\pi$  interaction between naphthalene planes is observed.

Received 18 October 2000  
Accepted 13 November 2000  
Online 1 December 2000**Comment**

The development of photoinduced electron transfer (PET) systems for guest cations has gained much attention for their potential application to nanoscale devices for cation sensors and switches (Lehn, 1995). Recently we have reported the complexation and fluorescence behaviour of several PET fluoroionophores (Kubo & Sakurai, 2000). As an approach to the manipulation of PET sensors, we have investigated the complexation behaviour of the title compound (1) in the presence of metal salts using fluorescence spectroscopy. The compound (1) (when excited at 282 nm) gave a broad emission band at 460 nm in addition to an emission band at 337 nm. The intramolecular exciplex and excimer formation should be responsible for the appearance of the former band. The fluorescence intensity at 337 nm of (1) was reduced to approximately 1/80 of that of 1-methylnaphthalene. Complexation of (1) with  $\text{Zn}^{2+}$  increased the fluorescence intensity of the host by a factor of 8.1 (Kubo *et al.*, 1998). However, the structures of (1) and its complexes have not been elucidated. We now report the structure of (1) with the aim of contributing to a deeper understanding of PET systems.



Cyclic tetraamines such as cyclam and their derivatives can occur in several conformations. For instance, in [14]aneN<sub>4</sub> or R<sub>4</sub>[14]aneN<sub>4</sub> macrocycles with alternating five- and six-membered chelating rings a total of five combinations, such as four *trans* (I–IV) and one *cis* (V) configurations, can be

produced (Lydon, 1989). The crystal structure of (1) shows the conformation with two adjacent naphthylmethyl groups above the cyclam ring and the remaining two below the cyclam ring; the *trans*-IV configuration (Bosnich *et al.*, 1965) on a crystallographic centre of symmetry, is similar to that found in *N,N',N'',N'''*-tetramethyl-1,4,8,11-cyclam (Willey *et al.*, 1993) and *N,N',N'',N'''*-[4'-*p*-tolyl-(2,2':6',2''-terpyridyl)]-1,4,8,11-cyclam (Padilla-Tosta *et al.*, 2000). The angle of the intersection between the least-squares planes A (defined by C1, C2, C3, C4, C5, C6, C7, C8, C9, and C10) and B (defined by C21, C22, C23, C24, C25, N1, and N2), is 99.6 (1)°, while that between the least-squares planes B and C (defined by C11, C12, C13, C14, C15, C16, C17, C18, C19, and C20) is 69.6 (1)°.

The intermolecular distance between naphthalene rings is 3.428 (6) Å for C16–C17<sup>i</sup> (i: symmetry code  $\frac{3}{2} - x, \frac{1}{2} - y, 1 - z$ ) which is within the range associated with  $\pi$ – $\pi$  interaction [3.3–3.8 Å] (Prout *et al.*, 1973*a,b,c*; Nakasuji *et al.*, 1986, 1987; Lide, 1990; Hunter & Sanders, 1990; Munakata *et al.*, 1994).

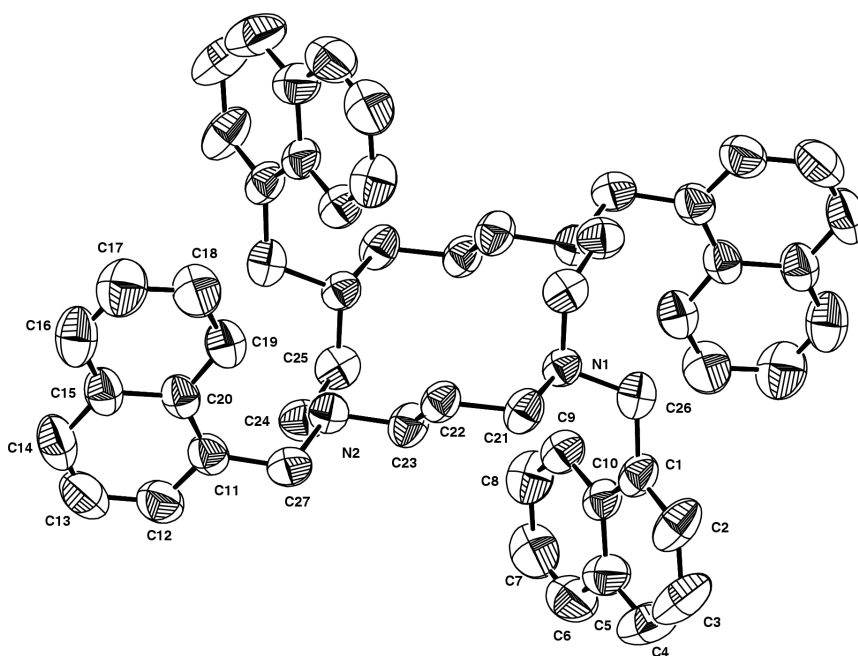
The N1<sup>i</sup>··N1<sup>ii</sup> and N2<sup>i</sup>··N2<sup>ii</sup> (ii: 1 – x, –y, –z) transannular distances are 4.90 Å and 5.63 Å, respectively. From the sum [1.5+1.5 = 3.0 Å] of van der Waals radii (Lide, 1990) of two N atoms, the cavity size of (1) is estimated as a smaller value than 1.9 Å, while the Zn<sup>2+</sup> diameter for six coordination is 1.76 Å (Shannon, 1976). The cavity of (1) fits with Zn<sup>2+</sup> cation. As a result, the PET fluoroionophore (1) exhibits high Zn<sup>2+</sup> selectivity.

## Experimental

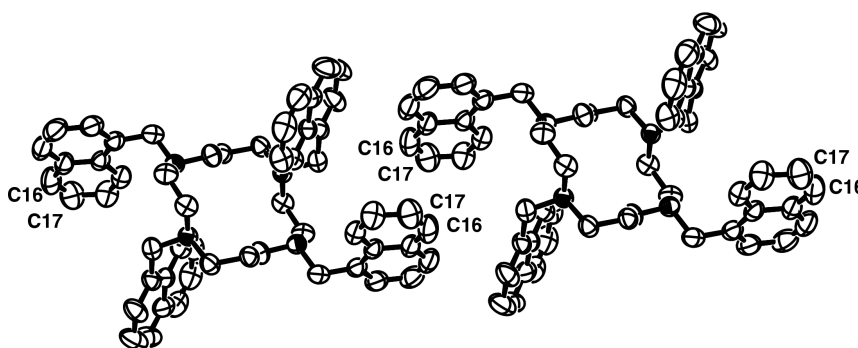
The compound (1) was synthesized by the *N*-alkylation of 1,4,8,11-tetraazacyclotetradecane with 1-chloromethylnaphthalene in tetrahydrofuran-triethylamine (Kubo *et al.*, 1998). The single crystals of (1) were obtained by recrystallization from chloroform.

### Crystal data

C <sub>54</sub> H <sub>56</sub> N <sub>4</sub>	$D_x = 1.171 \text{ Mg m}^{-3}$
$M_r = 761.02$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/a$	Cell parameters from 17 reflections
$a = 11.609 (5) \text{ \AA}$	$\theta = 9.5\text{--}18.1^\circ$
$b = 18.907 (5) \text{ \AA}$	$\mu = 0.07 \text{ mm}^{-1}$
$c = 9.878 (5) \text{ \AA}$	$T = 296 (2) \text{ K}$
$\beta = 95.462 (5)^\circ$	Prism, colourless
$V = 2158.3 (15) \text{ \AA}^3$	$0.35 \times 0.30 \times 0.25 \text{ mm}$
$Z = 2$	



**Figure 1**  
Molecular structure of (1) showing 50% probability displacement ellipsoids. H atoms are omitted.



**Figure 2**  
Two molecules showing the close intermolecular contact between C16 and C17<sup>i</sup> ( $\frac{3}{2} - x, \frac{1}{2} - y, 1 - z$ ).

### Data collection

Enraf–Nonius CAD-4 diffractometer	$R_{\text{int}} = 0.060$
$\omega$ – $2\theta$ scans	$\theta_{\text{max}} = 28.0^\circ$
Absorption correction: empirical via $\psi$ scans (North <i>et al.</i> , 1968)	$h = -15 \rightarrow 0$
$T_{\text{min}} = 0.952, T_{\text{max}} = 1.000$	$k = 0 \rightarrow 24$
5426 measured reflections	$l = -12 \rightarrow 13$
5183 independent reflections	3 standard reflections
1450 reflections with $I > 2\sigma(I)$	frequency: 120 min
	intensity decay: 2.0%

### Refinement

Refinement on $F^2$	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.052$	$w = 1/[\sigma^2(F_o^2) + (0.057P)^2]$
$wR(F^2) = 0.163$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.87$	$(\Delta/\sigma)_{\text{max}} = 0.004$
5183 reflections	$\Delta\rho_{\text{max}} = 0.13 \text{ e \AA}^{-3}$
262 parameters	$\Delta\rho_{\text{min}} = -0.14 \text{ e \AA}^{-3}$

**Table 1**

Selected geometric parameters (Å, °).

N1—C25 <sup>i</sup>	1.457 (3)	N2—C24	1.473 (3)
N1—C21	1.465 (3)	C21—C22	1.524 (4)
N1—C26	1.474 (3)	C22—C23	1.519 (4)
N2—C23	1.470 (3)	C24—C25	1.521 (4)
N2—C27	1.471 (3)		
C25 <sup>i</sup> —N1—C21—C22	77.8 (3)	C21—C22—C23—N2	−177.1 (3)
C26—N1—C21—C22	−159.8 (2)	C23—N2—C24—C25	−59.2 (3)
N1—C21—C22—C23	60.2 (3)	C27—N2—C24—C25	179.2 (3)
C24—N2—C23—C22	167.0 (2)	N2—C24—C25—N1 <sup>i</sup>	−47.0 (4)

Symmetry codes: (i) 1 − x, −y, −z.

All H atoms were located at ideal positions and were included in refinement, but restrained to ride on the atom to which they are bonded.  $U_{\text{iso}}$  of H atoms were held fixed to 1.2 times  $U_{\text{eq}}$  of the parent atoms.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *CAD-4 Software* (Enraf–Nonius, 1989); data reduction: *MolEN* (Fair, 1990); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *Xtal\_GX* (Hall & du Boulay, 1995); software used to prepare material for publication: *SHELXL97* (Sheldrick, 1997).

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