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Structures of Novel Macrocyclic Dipyridylmethaneamides

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Abstract. The structures of two 13-membered tetraaza ring compounds, (1*R*,17*R*)- (1) and (1*R*,9*r*,17*S*)-3,15-dioxo-4,5,6,7,8,10,11,12,13,14,22,23-dodecahydro-9-ethyl-9-methoxy-2,16,22,23-tetraazatetracyclo[15.4.0.$1^{4,8}$.$1^{10,14}$]tricosane (2) ($C_{22}H_{26}N_4O_3$, $M_r = 394·47$) have been studied by X-ray diffraction. (1): monoclinic, $P2_1$, $a = 10·2585$ (3), $b = 19·7992$ (7), $c = 9·9408$ (4) Å, $\beta = 92·009$ (4)°, $V = 2017·8$ (2) Å^3, $Z = 4$, $D_x = 1·2985$ (1) Mg m^{-3}, λ(Cu $K\alpha$) = 1·5418 Å, $\mu = 0·680$ mm^{-1}, $F(000) = 840$, $T = 291$ K, $R = 0·056$ for 1935 observed reflections; (2): triclinic, $P\bar{1}$, $a = 10·356$ (1), $b = 18·478$ (2), $c = 19·048$ (2) Å, $\alpha = 115·906$ (4), $\beta = 101·773$ (5), $\gamma = 98·575$ (4)°, $V = 3090·0$ (6) Å^3, $Z = 6$, $D_x = 1·2719$ (3) Mg m^{-3}, λ(Cu $K\alpha$) = 1·5418 Å, $\mu = 0·662$ mm^{-1}, $F(000) = 1260$, $T = 291$ K, $R = 0·058$ for 4412 observed reflections. The asymmetric units of (1) and (2) contain two and three molecules, respectively. These five macrocycles show very similar bowl-like overall shapes but also minor conformational differences. Intermolecular hydrogen bonds between the amide groups govern the packing in both compounds by linking the molecules into endless chains in (1) and by forming hexamer aggregates in (2).

Introduction. It has been known for a long time that macrocyclic ligand complexes are involved in a number of fundamental biological systems. Apart from the biological implications, there has recently been a remarkable expansion of research concerning the involvement of macrocycles in other areas of chemistry, such as metal ion catalysis, organic synthesis, metal ion discrimination and analytical methods as well as the investigation of a number of potential industrial, medical and other applications (Lindoy, 1989). Of particular importance are dissymmetric ligands capable of chiral recognition for use in asymmetric synthesis and chiral separations (Jolley, Bradshaw & Izatt, 1982). A novel class of 13-membered tetraaza rings containing dipyridylmethaneamide units was obtained by condensation of 1,2-diamines with 1,1-bis(6-chloroformyl-2-pyridyl)-1-methoxypropane (Moberg, Wärnmark, Csöregh & Ertan, 1991). By reaction with *trans*-1,2-diaminocyclohexane, a chiral macrocyclic amide (1) was obtained, while the *cis* isomer yielded two diastereoisomeric optically inactive (pseudochiral) forms, obtained in a ratio of 5:1. The structures of the major *meso* isomer (2) and of the chiral ligand (1) have been studied by spectroscopic methods (^{1}H and ^{13}C NMR, IR) and by X-ray diffraction. Here we present the results of the X-ray investigations, whereas the synthesis and results of the spectroscopic studies are reported elsewhere (Moberg, Wärnmark, Csöregh & Ertan, 1991).

Experimental. Crystals of (1) and (2) were grown from aqueous ethanol. Intensity data were collected using a Stoe AED-2 diffractometer with graphite-monochromated Cu $K\alpha$ radiation; ω–2θ scan, $\theta_{\max} = 70°$ for (1) and 60° for (2). Data collection details are given in Table 1. Data reduction included corrections for background, Lorentz and polarization effects, but the rather low absorption effects were ignored. The cell parameters were refined against the θ values of 38 and 90 carefully centered reflections ($35 < 2\theta < 70°$) for (1) and (2), respectively. Reasonable positions of the non-H atoms were derived by direct methods, using *SHELXS* for (1) (Sheldrick, 1990) and *MULTAN*80 for (2) (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). The structural models were refined on F with the full-matrix least-squares technique using the *SHELX* program system (Sheldrick, 1976, 1979). Most of the amide H atoms were located from $\Delta\rho$ maps and their positions were held riding on their 'parent' atoms during the subsequent calculations. The N(2*A*) H atom of (1) as well as the carbon-bonded H atoms in both structures were given geometrically predicted

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Table 1. *Details of data collection and refinement calculations*

	(1)	(2)
Crystal colour	Colourless	Colourless
Crystal size (mm)	0·17 × 0·30 × 0·32	0·09 × 0·09 × 0·09
Crystal shape	Irregular	Irregular
No. of collected reflections	4092	14886
Range of h, k and l	0→12, 0→24, −12→12	−11→11, −20→20, 0→21
No. of standard reflections	4	4
Intensity instability (%)	< 3	< 3
R_{int}	0·075	0·019
No. of unique non-zero reflections	3367	8299
No. of significantly observed reflections	1935	4412
Criterion for significance	$I > 2\sigma(I)$	$I > 3\sigma(I)$
No. of refined parameters	437	814*
Final agreement factors		
R	0·056	0·058
wR†	0·066	0·075
Final $(\Delta/\sigma)_{\max}$	0·52	0·36
Final $\Delta\rho_{\min}$ and $\Delta\rho_{\max}$ (e Å^{-3})	−0·17 and 0·09	−0·16 and 0·10

* In the case of (2) the 'blocked full-matrix' refinement technique (Sheldrick, 1976, 1979) had to be used due to the large number of variables: three blocks (each with 276 variables) were refined in consecutive cycles.

† Weights of the structure factors in *SHELX76* (Sheldrick, 1976) are estimated as $w = \text{constant}/[\sigma^2(F) + gF^2]$ with $g = 0{\cdot}00065$ and 0·00027 for (1) and (2), respectively.

positions. In the final cycles of refinement all H atoms in both (1) and (2) were treated as isotropic; anisotropic thermal parameters were refined for all non-H atoms of (2). For (1) the number of observed reflections with $I/\sigma(I) > 2$ was too low to allow anisotropic refinement of all non-H-atom positions. In order to reduce the number of variables the C atoms of the pyridine rings were refined with isotropic temperature factors. Final reliability indices together with selected details of the refinement calculations are listed in Table 1. The relatively high wR value for (2), 0·075, is probably due to the limited size and/or crystalline quality of that compound. Scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV).

The monochiral C(1)R,C(17)R compound (1) was prepared in the optically pure form starting from (−)-(1R,4R)-diaminocyclohexane (Moberg, Wärnmark, Csöregh & Ertan, 1991) (Figs. 1a and 1b). The absolute configuration, however, could not be proved by the X-ray analysis because the crystal

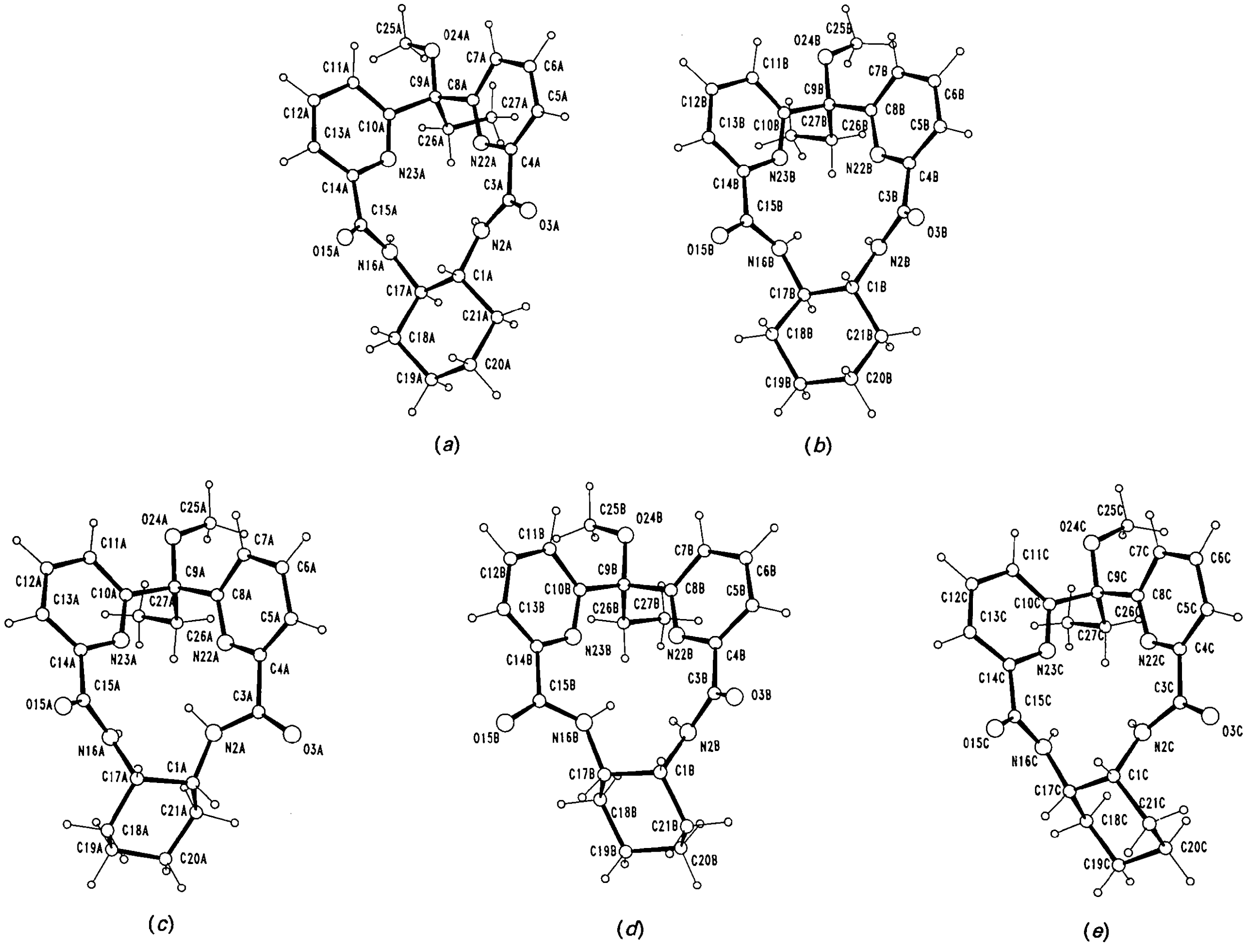

Fig. 1. (a), (b) Perspective views of the solid-state conformers of the monochiral 1R,17R compound (1) and (c)–(e) of the pseudochiral 1R,9r,17S isomer (2).

Table 2. *Fractional atomic coordinates and equivalent isotropic/isotropic temperature factors of the non*-H *atoms in compounds* (1) *and* (2), *with e.s.d.'s in parentheses*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}(Å^2)
Compound (1)				
C(1*A*)	0·3249 (9)	0·9228 (7)	0·7051 (9)	0·053 (3)
N(2*A*)	0·3941 (8)	0·9817 (6)	0·6547 (7)	0·055 (3)
C(3*A*)	0·3697 (9)	1·0448 (7)	0·6930 (9)	0·053 (4)
O(3*A*)	0·3098 (7)	1·0610 (6)	0·7931 (6)	0·070 (3)
C(4*A*)	0·4082 (9)	1·0983 (7)	0·5920 (9)	0·047 (4)
C(5*A*)	0·3923 (9)	1·1670 (7)	0·6116 (9)	0·056 (3)
C(6*A*)	0·4104 (9)	1·2075 (7)	0·5049 (10)	0·065 (3)
C(7*A*)	0·4411 (9)	1·1828 (7)	0·3774 (9)	0·052 (3)
C(8*A*)	0·4603 (8)	1·1123 (7)	0·3708 (8)	0·046 (2)
C(9*A*)	0·4854 (8)	1·0771 (7)	0·2358 (9)	0·048 (3)
C(10*A*)	0·3658 (8)	1·0304 (7)	0·2078 (8)	0·042 (2)
C(11*A*)	0·2685 (8)	1·0470 (7)	0·1092 (8)	0·051 (3)
C(12*A*)	0·1562 (9)	1·0080 (7)	0·1044 (10)	0·062 (3)
C(13*A*)	0·1376 (9)	0·9584 (7)	0·1982 (9)	0·059 (3)
C(14*A*)	0·2359 (8)	0·9470 (6)	0·2948 (8)	0·042 (2)
C(15*A*)	0·2190 (8)	0·9034 (7)	0·4155 (8)	0·042 (3)
O(15*A*)	0·1096 (5)	0·8963 (6)	0·4610 (6)	0·057 (3)
N(16*A*)	0·3305 (7)	0·8801 (6)	0·4724 (7)	0·051 (3)
C(17*A*)	0·3527 (9)	0·8624	0·6159 (9)	0·054 (4)
C(18*A*)	0·2765 (10)	0·8004 (7)	0·6634 (11)	0·073 (4)
C(19*A*)	0·3161 (15)	0·7842 (8)	0·8102 (14)	0·107 (6)
C(20*A*)	0·2945 (11)	0·8446 (7)	0·8998 (11)	0·082 (5)
C(21*A*)	0·3723 (10)	0·9059 (8)	0·8536 (10)	0·082 (5)
N(22*A*)	0·4478 (6)	1·0726 (6)	0·4752 (7)	0·042 (3)
N(23*A*)	0·3512 (6)	0·9797 (6)	0·2919 (6)	0·042 (3)
O(24*A*)	0·4954 (7)	1·1276 (6)	0·1385 (6)	0·059 (3)
C(25*A*)	0·5445 (10)	1·1056 (8)	0·0117 (9)	0·072 (5)
C(26*A*)	0·6098 (8)	1·0344 (7)	0·2548 (10)	0·057 (4)
C(27*A*)	0·7331 (9)	1·0745 (8)	0·2903 (12)	0·076 (5)
C(1*B*)	0·7874 (8)	0·9068 (7)	0·6049 (8)	0·052 (4)
N(2*B*)	0·8083 (6)	0·8942 (6)	0·4640 (6)	0·049 (3)
C(3*B*)	0·7098 (8)	0·8747 (7)	0·3774 (9)	0·045 (3)
O(3*B*)	0·5941 (6)	0·8820 (6)	0·4062 (6)	0·056 (3)
C(4*B*)	0·7456 (8)	0·8334 (7)	0·2581 (8)	0·045 (2)
C(5*B*)	0·6532 (8)	0·8186 (7)	0·1566 (8)	0·052 (3)
C(6*B*)	0·6824 (9)	0·7698 (7)	0·0678 (10)	0·064 (3)
C(7*B*)	0·7968 (9)	0·7328 (7)	0·0840 (9)	0·058 (3)
C(8*B*)	0·8843 (8)	0·7501 (7)	0·1854 (8)	0·044 (2)
C(9*B*)	1·0066 (9)	0·7094 (7)	0·2240 (9)	0·050 (3)
C(10*B*)	0·9753 (9)	0·6742 (7)	0·3573 (9)	0·049 (3)
C(11*B*)	0·9537 (9)	0·6072 (7)	0·3728 (10)	0·061 (3)
C(12*B*)	0·9207 (10)	0·5824 (8)	0·4977 (11)	0·072 (3)
C(13*B*)	0·9028 (10)	0·6276 (8)	0·6001 (11)	0·068 (3)
C(14*B*)	0·9262 (9)	0·6954 (7)	0·5802 (9)	0·051 (3)
C(15*B*)	0·8922 (9)	0·7485 (8)	0·6782 (9)	0·058 (4)
O(15*B*)	0·8331 (9)	0·7357 (7)	0·7793 (8)	0·112 (4)
N(16*B*)	0·9334 (9)	0·8099 (7)	0·6438 (9)	0·084 (4)
C(17*B*)	0·8986 (9)	0·8773 (7)	0·6889 (9)	0·062 (4)
C(18*B*)	0·8715 (11)	0·8844 (8)	0·8385 (10)	0·082 (5)
C(19*B*)	0·8544 (11)	0·9586 (9)	0·8733 (11)	0·091 (6)
C(20*B*)	0·7478 (12)	0·9907 (8)	0·7853 (11)	0·082 (5)
C(21*B*)	0·7697 (12)	0·9809 (7)	0·6363 (10)	0·077 (5)
N(22*B*)	0·8611 (7)	0·8023 (6)	0·2676 (7)	0·044 (3)
N(23*B*)	0·9674 (7)	0·7180 (7)	0·4604 (7)	0·066 (3)
O(24*B*)	1·0214 (6)	0·6553 (6)	0·1302 (6)	0·070 (3)
C(25*B*)	1·0717 (12)	0·6737 (8)	0·0013 (10)	0·081 (5)
C(26*B*)	1·1267 (8)	0·7546 (7)	0·2421 (10)	0·059 (4)
C(27*B*)	1·2514 (10)	0·7148 (8)	0·2848 (13)	0·084 (5)
Compound (2)				
C(1*A*)	−0·1189 (7)	0·1398 (4)	0·2714 (4)	0·066 (4)
N(2*A*)	−0·0663 (6)	0·1502 (4)	0·3520 (3)	0·083 (3)
C(3*A*)	−0·0916 (6)	0·1983 (4)	0·4222 (4)	0·060 (3)
O(3*A*)	−0·1690 (5)	0·2412 (3)	0·4294 (3)	0·060 (3)
C(4*A*)	0·0022 (6)	0·1943 (4)	0·4928 (4)	0·053 (3)
C(5*A*)	0·0359 (7)	0·2563 (4)	0·5727 (4)	0·069 (4)
C(6*A*)	0·1397 (8)	0·2548 (4)	0·6289 (4)	0·082 (4)
C(7*A*)	0·2091 (6)	0·1923 (4)	0·6063 (4)	0·068 (4)
C(8*A*)	0·1634 (6)	0·1300 (3)	0·5245 (4)	0·053 (3)
C(9*A*)	0·2346 (5)	0·0611 (3)	0·4889 (3)	0·051 (3)
C(10*A*)	0·3231 (6)	0·0881 (3)	0·4440 (3)	0·050 (3)
C(11*A*)	0·4638 (6)	0·1004 (4)	0·4644 (4)	0·061 (3)
C(12*A*)	0·5340 (6)	0·1322 (4)	0·4234 (4)	0·068 (4)
C(13*A*)	0·4636 (6)	0·1491 (4)	0·3669 (4)	0·062 (4)
C(14*A*)	0·3229 (6)	0·1326 (3)	0·3485 (3)	0·052 (3)
C(15*A*)	0·2378 (6)	0·1592 (4)	0·2951 (3)	0·057 (3)
O(15*A*)	0·2867 (4)	0·2197 (3)	0·2882 (3)	0·078 (3)
N(16*A*)	0·1051 (5)	0·1147 (3)	0·2593 (3)	0·061 (3)
C(17*A*)	−0·0005 (6)	0·1539 (4)	0·2387 (4)	0·067 (3)
C(18*A*)	−0·0464 (6)	0·1268 (4)	0·1468 (4)	0·073 (4)
C(19*A*)	−0·1322 (6)	0·0352 (4)	0·0987 (4)	0·072 (4)
C(20*A*)	−0·2582 (6)	0·0254 (4)	0·1254 (4)	0·075 (4)
C(21*A*)	−0·2216 (6)	0·0523 (4)	0·2147 (4)	0·067 (4)
N(22*A*)	0·0615 (5)	0·1315 (3)	0·4701 (3)	0·049 (3)
N(23*A*)	0·2535 (5)	0·1002 (3)	0·3849 (3)	0·050 (2)
O(24*A*)	0·3294 (4)	0·0578 (3)	0·5528 (2)	0·065 (2)
C(25*A*)	0·2704 (7)	0·0254 (4)	0·5978 (4)	0·075 (4)
C(26*A*)	0·1300 (5)	−0·0238 (3)	0·4280 (3)	0·052 (3)
C(27*A*)	0·1943 (6)	−0·0950 (4)	0·3916 (4)	0·067 (3)
C(1*B*)	0·3386 (6)	0·2739 (4)	0·1151 (4)	0·063 (3)
N(2*B*)	0·2339 (5)	0·2775 (3)	0·1568 (3)	0·054 (3)
C(3*B*)	0·1237 (6)	0·3037 (3)	0·1386 (4)	0·053 (3)
O(3*B*)	0·0754 (4)	0·2980 (3)	0·0709 (3)	0·075 (3)
C(4*B*)	0·0676 (5)	0·3488 (3)	0·2072 (3)	0·045 (3)
C(5*B*)	−0·0650 (6)	0·3567 (4)	0·1923 (4)	0·060 (3)
C(6*B*)	−0·1015 (6)	0·4095 (4)	0·2592 (4)	0·068 (4)
C(7*B*)	−0·0071 (6)	0·4526 (4)	0·3356 (4)	0·057 (3)
C(8*B*)	0·1223 (5)	0·4408 (3)	0·3448 (3)	0·047 (3)
C(9*B*)	0·2391 (5)	0·4904 (3)	0·4255 (3)	0·050 (3)
C(10*B*)	0·3476 (5)	0·5438 (3)	0·4126 (3)	0·048 (3)
C(11*B*)	0·3701 (6)	0·6296 (4)	0·4409 (4)	0·066 (3)
C(12*B*)	0·4662 (7)	0·6680 (4)	0·4186 (4)	0·079 (4)
C(13*B*)	0·5318 (6)	0·6215 (4)	0·3660 (4)	0·071 (4)
C(14*B*)	0·5015 (5)	0·5381 (3)	0·3380 (3)	0·052 (3)
C(15*B*)	0·5495 (6)	0·4785 (4)	0·2720 (4)	0·059 (5)
O(15*B*)	0·6432 (5)	0·4983 (3)	0·2496 (3)	0·088 (3)
N(16*B*)	0·4718 (6)	0·4018 (3)	0·2400 (3)	0·092 (3)
C(17*B*)	0·4798 (7)	0·3223 (4)	0·1774 (4)	0·072 (4)
C(18*B*)	0·5361 (6)	0·2760 (4)	0·2198 (4)	0·076 (4)
C(19*B*)	0·5328 (8)	0·1874 (5)	0·1592 (4)	0·093 (5)
C(20*B*)	0·3881 (8)	0·1391 (4)	0·1004 (4)	0·085 (4)
C(21*B*)	0·3353 (7)	0·1839 (4)	0·0557 (4)	0·073 (4)
N(22*B*)	0·1571 (4)	0·3874 (3)	0·2814 (3)	0·048 (2)
N(23*B*)	0·4151 (4)	0·5000 (3)	0·3637 (3)	0·050 (2)
O(24*B*)	0·1795 (4)	0·5433 (3)	0·4832 (2)	0·070 (2)
C(25*B*)	0·2655 (7)	0·5870 (5)	0·5678 (4)	0·086 (4)
C(26*B*)	0·2945 (6)	0·4292 (4)	0·4503 (3)	0·058 (3)
C(27*B*)	0·1882 (7)	0·3741 (4)	0·4641 (4)	0·082 (4)
C(1*C*)	−0·2536 (6)	0·1305 (4)	−0·1804 (4)	0·076 (4)
N(2*C*)	−0·2174 (5)	0·2219 (4)	−0·1582 (3)	0·076 (3)
C(3*C*)	−0·2698 (7)	0·2545 (4)	−0·2060 (4)	0·072 (4)
O(3*C*)	−0·3819 (5)	0·2234 (3)	−0·2592 (3)	0·092 (3)
C(4*C*)	−0·1683 (7)	0·3297 (4)	−0·1936 (4)	0·070 (4)
C(5*C*)	−0·1906 (8)	0·3584 (5)	−0·2500 (5)	0·096 (5)
C(6*C*)	−0·0810 (10)	0·4145 (5)	−0·2469 (5)	0·114 (6)
C(7*C*)	0·0447 (9)	0·4403 (4)	−0·1874 (5)	0·096 (5)
C(8*C*)	0·0547 (7)	0·4112 (4)	−0·1299 (4)	0·066 (4)
C(9*C*)	0·1898 (6)	0·4290 (4)	−0·0671 (4)	0·068 (4)
C(10*C*)	0·2332 (6)	0·3472 (4)	−0·1026 (4)	0·060 (3)
C(11*C*)	0·3408 (6)	0·3370 (5)	−0·1354 (4)	0·081 (4)
C(12*C*)	0·3603 (7)	0·2586 (5)	−0·1744 (4)	0·083 (5)
C(13*C*)	0·2688 (6)	0·1911 (4)	−0·1830 (4)	0·074 (4)
C(14*C*)	0·1634 (6)	0·2062 (4)	−0·1479 (3)	0·056 (3)
C(15*C*)	0·0490 (6)	0·1366 (4)	−0·1629 (4)	0·056 (3)
O(15*C*)	0·0177 (4)	0·0671 (3)	−0·2241 (3)	0·071 (2)
N(16*C*)	−0·0189 (5)	0·1580 (3)	−0·1078 (3)	0·067 (3)
C(17*C*)	−0·1594 (7)	0·1142 (4)	−0·1236 (4)	0·080 (4)
C(18*C*)	−0·1866 (8)	0·1452 (5)	−0·0392 (4)	0·105 (5)
C(19*C*)	−0·3320 (8)	0·1110 (6)	−0·0485 (5)	0·113 (5)
C(20*C*)	−0·4256 (9)	0·1349 (5)	−0·1030 (6)	0·120 (6)
C(21*C*)	−0·4044 (7)	0·0961 (5)	−0·1888 (5)	0·104 (5)
N(22*C*)	−0·0519 (5)	0·3588 (3)	−0·1331 (3)	0·062 (3)
N(23*C*)	0·1489 (5)	0·2826 (3)	−0·1070 (3)	0·055 (3)
O(24*C*)	0·2932 (5)	0·4895 (3)	−0·0664 (3)	0·094 (3)
C(25*C*)	0·2856 (9)	0·5747 (5)	−0·0262 (6)	0·122 (6)
C(26*C*)	0·1734 (6)	0·4511 (4)	0·0171 (4)	0·072 (4)
C(27*C*)	0·3089 (7)	0·4701 (4)	0·0801 (4)	0·093 (4)

contains only 'light' atoms which do not yield observable anomalous-dispersion effects. Nevertheless, the fractional atomic coordinates, listed in Table 2, refer to the expected correct enantiomer. The corresponding *cis*-fused macrocycle has different absolute configurations for the asymmetric centre at

Table 3. *Conformational features and selected torsion angles calculated for the solid-state conformers of the macrocyclic compounds* (1) *and* (2)

E.s.d.'s, where given, are in parentheses

		(1)		(2)		
		A	*B*	*A*	*B*	*C*
Pyridine rings planar to within (Å)		0·067 0·087	0·068 0·062	0·042 0·051	0·059 0·040	0·063 0·047
Dihedral angle* between pyridine rings (°)		99·0 (3)	99·4 (3)	101·9 (2)	77·1 (2)	84·2 (2)
Dihedral angle between pyridine ring and nearest amide group (°)		161·6 (6) 147·2 (6)	31·3 (8) 14·2 (7)	157·7 (7) 148·6 (5)	150·2 (5) 18·7 (4)	159·4 (7) 28·3 (4)
Ring-puckering parameters†						
q_2 (Å)		0·04 (2)	0·04 (2)	0·118 (7)	0·041 (8)	0·072 (10)
q_3 (Å)		0·62 (1)	0·58 (2)	−0·532 (7)	0·546 (7)	0·585 (9)
φ (°)		−73 (14)	−2 (17)	−19 (4)	−137 (10)	−119 (8)
Q (Å)		0·62 (1)	0·58 (2)	0·545 (7)	0·547 (7)	0·589 (9)
θ (°)		4 (1)	4 (2)	167·5 (7)	4·3 (8)	7·0 (9)
Torsional angles (°)‡§						
O(3)—C(3)—C(4)—N(22)		−167 (1)	−150 (1)	168·1 (6)	−148·2 (6)	178·6 (7)
O(3)—C(3)—C(4)—C(5)		7 (2)	18 (2)	−19·4 (1·0)	25·0 (9)	−9·4 (1·1)
N(2)—C(3)—C(4)—C(5)		−180 (1)	−172 (1)	156·8 (6)	−160·7 (6)	164·4 (7)
N(23)—C(14)—C(15)—O(15)		147 (1)	167 (1)	146·6 (6)	−167·0 (7)	149·6 (6)
C(13)—C(14)—C(15)—O(15)		−27 (2)	−5 (2)	−25·8 (9)	17·7 (1·0)	−23·0 (9)
C(13)—C(14)—C(15)—N(16)		159 (1)	175 (1)	157·1 (6)	−160·1 (6)	160·8 (6)
N(22)—C(8)—C(9)—O(24)		−180 (1)	180 (1)	−172·4 (5)	179·1 (5)	−176·5 (6)
C(7)—C(8)—C(9)—O(24)		5 (2)	6 (2)	13·7 (8)	2·9 (7)	10·4 (9)
O(24)—C(9)—C(10)—N(23)		178 (1)	176 (1)	−175·8 (5)	176·0 (5)	179·1 (5)
O(24)—C(9)—C(10)—C(11)		−11 (2)	−6 (2)	2·9 (7)	−10·2 (8)	−7·5 (9)
C(17)—C(1)—N(2)—C(3)	(1)¶	166 (1)	138 (1)	127·8 (7)	126·2 (6)	168·3 (7)
C(1)—N(2)—C(3)—C(4)	(2)	−156 (1)	−152 (1)	−173·7 (6)	−147·4 (6)	−147·9 (7)
N(2)—C(3)—C(4)—N(22)	(3)	7 (2)	20 (2)	−15·8 (8)	26·1 (8)	−7·6 (9)
C(3)—C(4)—N(22)—C(8)	(4)	167 (1)	161 (1)	168·0 (5)	168·8 (5)	164·2 (6)
C(4)—N(22)—C(8)—C(9)	(5)	−171 (1)	−168 (1)	−172·6 (5)	−172·3 (5)	−169·8 (6)
N(22)—C(8)—C(9)—C(10)	(6)	60 (1)	68 (1)	73·7 (6)	62·5 (6)	71·2 (7)
C(8)—C(9)—C(10)—N(22)	(7)	−66 (1)	−69 (1)	−58·1 (6)	−70·4 (6)	−65·1 (7)
C(9)—C(10)—N(23)—C(14)	(8)	164 (1)	173 (1)	172·6 (5)	171·1 (5)	169·7 (6)
C(10)—N(23)—C(14)—C(15)	(9)	−165 (1)	−167 (1)	−168·6 (5)	−169·5 (5)	−168·9 (6)
N(23)—C(14)—C(15)—N(16)	(10)	−26 (2)	−13 (2)	−30·4 (8)	15·2 (7)	−26·6 (8)
C(14)—C(15)—N(16)—C(17)	(11)	152 (1)	164 (1)	151·7 (6)	−177·0 (6)**	156·2 (6)
C(15)—N(16)—C(17)—C(1)	(12)	−58 (2)	−90 (2)	−129·6 (6)	−132·7 (7)	−70·6 (8)
N(16)—C(17)—C(1)—N(2)	(13)	−50 (1)	−44 (2)	41·3 (7)	−44·4 (7)	−44·1 (8)

* The least-squares planes through the non-H atoms and the dihedral angles between the planes were calculated according to Nardelli *et al.* (1965).
† The ring-puckering parameters were calculated according to Cremer & Pople. (1975).
‡ Right-hand rule according to Klyne & Prelog (1960).
§ E.s.d.'s of the torsion angles were calculated according to Stanford & Waser (1972).
¶ Numbering of the torsional angles within the 13-membered tetraaza rings (*cf.* Fig. 2).
** The sign of this angle is changed in the polar map from −177·0 to +183·0° (*cf.* Ounsworth & Weller, 1987).

C(1) and C(17) and also has a pseudochiral centre at C(9). The X-ray analysis showed the isomer (2), obtained in higher yield in the synthesis, to be 1*R*,9*r*,17*S* (Figs. 1*c*–*e*).

Discussion. Final fractional coordinates and equivalent isotropic/isotropic temperature parameters for the non-H atoms are listed in Table 2. The crystallographic labelling of the atoms is shown in Figs. 1(*a*)–(*e*). Selected conformation parameters, torsion angles and hydrogen-bonding dimensions are summarized in Tables 3 and 4.*

As seen in Figs. 1(*a*)–(*e*), the five crystallographically independent macrocycles show very similar overall shapes, but also small conformational variations. The methoxy C(9)—O(24) bond is approximately coplanar with the nearest C—C and C—N bonds of the pyridine rings in all five molecules, thus giving rise to a bowl-like form for these macrocycles. The mean values of the N—C—C(9)—O(24) and the C—C—C(9)—O(24) torsion angles (Klyne & Prelog, 1960; Stanford & Waser, 1972) (Table 3), with the r.m.s.d.'s $[=(\sum|\bar{x}-x|^2/n)^{1/2}]$ in parentheses are ±178 (2) and ±7 (4) in (1) and ±176 (3) and ±8 (4)° in (2), respectively. These values are similar to those previously observed for the corresponding angles in related macrocyclic compounds (Newkome, Taylor, Fronczek & Delord, 1984). The two pyridine rings are nearly perpendicular to each other. The dihedral angles (Nardelli, Musatti, Domiano & Andreetti, 1965) between the two aromatic ring planes are shown in Table 3. The mean deviation from 90° is 9·2 (2) and 10 (4)° for (1)

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* Lists of intramolecular bond lengths and bond angles involving non-H atoms, fractional atomic coordinates of the H atoms, equations of least-squares planes, atomic deviations from the planes, anisotropic thermal parameters of the non-H atoms, and observed and calculated structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54172 (76 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 4. *Bond distances* (Å) *and angles* (°) *in possible hydrogen bonds involving the amide groups in* (1) *and* (2)

E.s.d.'s, where given,* are in parentheses.

N—H···O	O-atom site	N···O	N—H	H···O	∠N—H···O
Compound (1)					
N(16*A*)—H(16*A*)···O(3*B*)	*x*, *y*, *z*	2·81 (1)	0·99	1·98	139
N(16*B*)—H(16*B*)···O(15*A*)	*x* + 1, *y*, *z*	3·11 (2)	0·89	2·36	143
N(2*B*)—H(2*B*)···O(15*A*)	*x* + 1, *y*, *z*	3·09 (1)	1·03	2·17	149
Compound (2)					
N(16*A*)—H(16*A*)···O(15*C*)	−*x*, −*y*, −*z*	3·125 (7)	0·96	2·18	169
N(2*B*)—H(2*B*)···O(15*A*)	*x*, *y*, *z*	3·108 (7)	1·08	2·22	138
N(16*C*)—H(16*C*)···O(3*B*)	*x*, *y*, *z*	3·071 (5)	1·11	2·06	150

* The H-atom positions are not refined (*cf.* the text).

and (2), respectively. The cyclohexane ring adopts a slightly distorted chair conformation in all five molecules, as shown *e.g.* by the ring-puckering parameters calculated according to Cremer & Pople (1975) (Table 3). In the ideal chair $\theta = 0$ or 180°, $q_2 = 0$ Å and $q_3 = \pm Q$ Å.

The complete set of endocyclic torsional angles will always uniquely define the conformation of a ring. Consequently, the conformation of the large tetraaza ring can most appropriately be characterized by a polar map of the torsional angles (Ounsworth & Weller, 1987, and references therein). The map, depicted in Fig. 2, proves that the 13-membered rings have very similar conformations in the five molecules presented here. There are only minor differences in the region of the N(16)—C(17)—C(1)—N(2) bonds.

The pseudosymmetric relationship between the two conformers of (1) (Figs. 1*a* and 1*b*) and also between molecules *A* and *B* of (2) (Figs. 1*c* and 1*d*) is easily seen from the orientations of the ethyl/methoxy and the amide groups. The conformational differences are described by the torsional angles listed in Table 3. Despite these differences, corresponding bond lengths and bond angles in the five conformers are identical within experimental error, with a few exceptions (see below), and generally also conform to expected values.

In the crystal structure of (1), depicted in Fig. 3, hydrogen bonds link the molecules together into endless chains perpendicular to the unique *b* axis. There is one hydrogen bond from molecule *A* to *B* and two somewhat longer ones from molecule *B* to *A* (Table 4) involving three N(H) groups, but only two O atoms. Accordingly, atom O(15*A*) seems to be the proton acceptor in two possible weak hydrogen bonds. The N(2*B*)···O(15*A*)···N(16*B*) angle is 52·2 (3)°. The distance from the fourth amide nitrogen [N(2*A*)] to the nearest potential proton acceptor oxygen [O(3*B*)] is 3·82 (2) Å, indicating only a weak van der Waals interaction between them. The unequal engagement of the amide groups in hydrogen-bond interactions in (1), and also in (2), gives

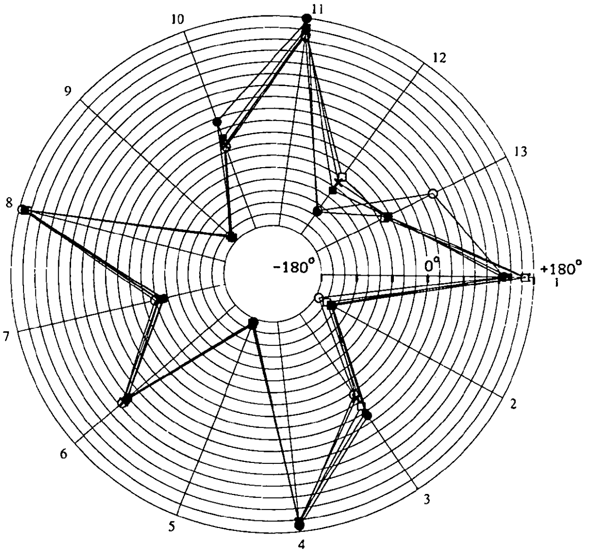

Fig. 2. Polar map of the endocyclic torsion angles of the 13-membered tetraaza rings in the different conformers of (1) and (2), respectively. The torsion angles are numbered as shown in Table 3. (1) *A* □, (1) *B* ■, (2) *A* ○, (2) *B* ●, (2) *C* ×.

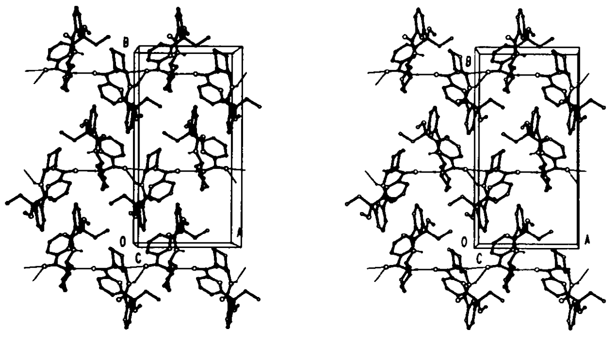

Fig. 3. Stereoview of the packing of the crystal structure of the 1*R*, 17*R* compound (1). The carbon-bonded H atoms are omitted for clarity. Hydrogen bonds are represented by thin lines.

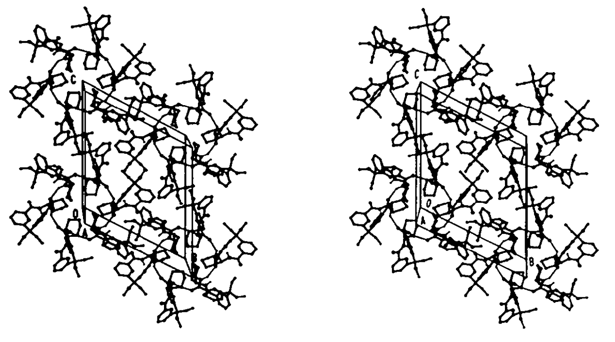

Fig. 4. Stereoview of the packing of the *meso* 1*R*,9*r*,17*S* compound (2). The carbon-bonded H atoms are omitted for clarity. Hydrogen bonds are represented by thin lines.

rise to a few significant differences between corresponding bond distances and bond angles involving these groups.

In the structure of (2), containing the *cis*-1,2-disubstituted cyclohexane moiety, the hydrogen bonds between the molecules form closed loops (Fig. 4) in which only one amide group of each conformer is involved. The crystal structure consists of hydrogen-bonded hexamers, held together by weak van der Waals forces.

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References

CREMER, D. & POPLE, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1367.

JOLLEY, S. T., BRADSHAW, J. S. & IZATT, R. M. (1982). *Heterocycl. Chem.* **19**, 3–19.

KLYNE, W. & PRELOG, W. (1960). *Experientia*, **16**, 521–523.

LINDOY, L. F. (1989). In *The Chemistry of Macrocyclic Ligand Complexes*. Cambridge Univ. Press.

MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1980). *MULTAN*80. *A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.

MOBERG, C., WÄRNMARK, K., CSÖREGH, I. & ERTAN, E. (1991). *J. Org. Chem.* **56**, 33–39.

NARDELLI, M., MUSATTI, A., DOMIANO, P. & ANDREETTI, G. (1965). *Ric. Sci.* **8**, 807–810.

NEWKOME, G. R., TAYLOR, H. C. R., FRONCZEK, F. R. & DELORD, T. J. (1984). *J. Org. Chem.* **49**, 2961–2971.

OUNSWORTH, J. P. & WELLER, L. (1987). *J. Chem. Educ.* **7**, 568–572.

SHELDRICK, G. M. (1976). *SHELX*76. Program for crystal structure determination. Univ. of Cambridge, England.

SHELDRICK, G. M. (1979). *SHELX* 400 *ATOM VERSION*. Updated by D. RABINOVICH & K. REICH, Department of Structural Chemistry, Weizman Institute of Science, Rehovot, Israel; and subsequently modified by G. M. SHELDRICK, Univ. of Göttingen, Germany.

SHELDRICK, G. M. (1990). *Acta Cryst.* **A46**, 467–473.

STANFORD, R. H. JR & WASER, J. (1972). *Acta Cryst.* **A28**, 213–215.

Acta Cryst. (1991). C**47**, 2176–2178

Structure of 7,8-Bis(3,3-dimethyl-1-butynyl)-*cis*-*anti*-*cis*-tricyclo[6.4.0.0^{2,7}]dodecane-3,12-dione

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Abstract. $C_{24}H_{32}O_2$, $M_r = 352{\cdot}52$, tetragonal, $P4_32_12$, $a = 11{\cdot}526\,(2)$, $c = 49{\cdot}982\,(7)$ Å, $V = 6640\,(3)$ Å^3, $Z = 12$, $D_x = 1{\cdot}06$ Mg m^{-3}, $\lambda(\mathrm{Cu}\ K\alpha) = 1{\cdot}5418$ Å, $\mu = 0{\cdot}47$ mm^{-1}, $F(000) = 2304$, $T = 110$ K, $R = 0{\cdot}048$, $wR = 0{\cdot}060$ for 5957 observed reflections. There are one and a half independent molecules of the title compound in the asymmetric unit cell. The cyclobutane ring shows a very similar degree of puckering ($\alpha = 147°$) compared to other tricyclo[6.4.0.0^{2,7}]dodecanes with analogous configuration and alkyl-substitution patterns.

Introduction. Cyclohex-2-enones undergo [2 + 2] photocycloaddition with alkenes affording bicyclo[4.2.0]octan-2-ones, while in the absence of alkenes irradiation in polar solvents leads to (dimeric) tricyclo[6.4.0.0^{2,7}]dodecan-3,12-diones (Anklam, König & Margaretha, 1983, and references cited therein). We have recently shown that 3-(alk-1-ynyl)cyclohex-2-enones afford both [2 + 2] and [3 + 2] photocycloadducts on iradiation in the presence of either 2,3-dimethylbut-2-ene (Margaretha, Rathjen, Wolff & Agosta, 1988) or 1,1-dimethoxy-2-methylpropene (Margaretha, Rathjen & Agosta, 1990), all products resulting from a common 1,4-alkylpropargyl biradical (1), which undergoes either 1,4- or 1,5-

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