MOLECULAR AND CRYSTAL STRUCTURE OF 1,8,9,20-TETRAHYDRO-3,6-DIMETHYL-1,8-DIPHENYLDIBENZO[c, m]DIPYRAZOLO[3.4-f:4', 3'-j][1,2,5,8,9,12]-HEXAAZACYCLOTETRADECANE

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An X-ray structural study has been carried out of macroheterocycles constructed from azobispyrazole and azobisbenzene moieties linked by amino nitrogen atoms. The molecule exists as a 14-membered, highly nonplanar hexaaza-heterocycle. The hydrogen atoms of the amino-groups participate in two types of intramolecular hydrogen bonds of the N–H•••H type, one in a forked bond, and the other in a single bond.

Hitherto, macroheterocycles of the 1,2,5,8,9,12-hexaazacyclotetradecane type have been obtained only as their metal complexes. The non-template cyclization of 4,4'-azo-(5-chloro-2,3-dimethyl-1-phenyl-1H-pyrazolium) bismethylsulfate with 2,2'-diaminoazobenzene in an aprotic solvent has enabled us to obtain the free ligand 1,8,9,20-tetrahydro-3,6-dimethyl-1,8-diphenylbenzo[c, m]dipyrazolo[3,4-f:4',3'-j][1,2,5,8,9,12]hexaazacyclotetradecane (I), which is the first representative of compounds of this type [1]. We here describe an X-ray structural examination of this compound.

The structure of (I) is composed of discrete molecules. It consists of azobisbenzene and azobispyrazole fragments bonded to each other by amino-nitrogen atoms $N_{(7)}$ and $N_{(10)}$ (Fig. 1). This results in the formation of a 14-membered macroheterocycle with six nitrogen

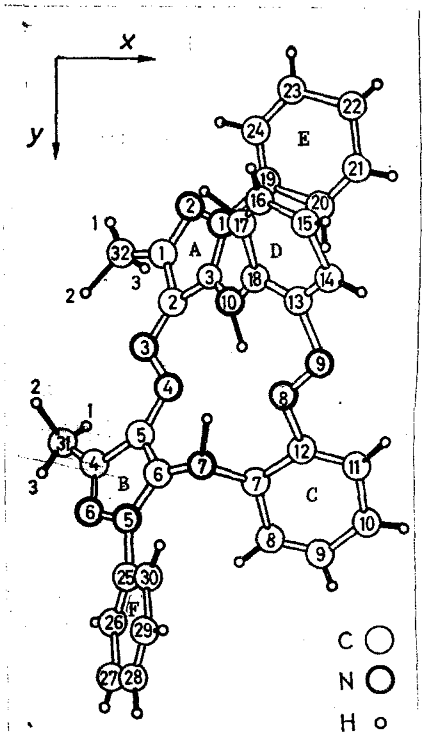

Fig. 1. Structure of the $C_{32}H_{26}N_{10}$ molecule.

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TABLE 1. Atom Coordinates (× 10^4, for H, × 10^3)

Atom	x	y	z	Atom	x	y	z
$N_{(1)}$	1986 (7)	1883 (1)	5494 (4)	$C_{(15)}$	5211 (8)	1905 (2)	10066 (8)
$N_{(2)}$	970 (5)	1768 (2)	4406 (3)	$C_{(16)}$	4024 (8)	1656 (3)	9481 (4)
$N_{(3)}$	36 (4)	3035 (2)	5105 (5)	$C_{(17)}$	3163 (8)	1906 (2)	8487 (6)
$N_{(4)}$	728 (6)	3335 (2)	5905 (5)	$C_{(18)}$	3431 (7)	2368 (2)	8019 (4)
$N_{(5)}$	−10 (6)	4580 (2)	6738 (6)	$C_{(19)}$	3101 (8)	1539 (2)	5811 (5)
$N_{(6)}$	−1196 (4)	4516 (2)	5820 (5)	$C_{(20)}$	4453 (8)	1712 (2)	6100 (5)
$N_{(7)}$	2070 (4)	4097 (2)	7692 (4)	$C_{(21)}$	5502 (7)	1370 (3)	6380 (5)
$N_{(8)}$	4108 (6)	3411 (2)	8026 (3)	$C_{(22)}$	5267 (8)	860 (4)	6282 (4)
$N_{(9)}$	5113 (7)	3114 (1)	8363 (5)	$C_{(23)}$	3937 (9)	688 (3)	5985 (8)
$N_{(10)}$	2588 (6)	2601 (2)	6967 (4)	$C_{(24)}$	2819 (6)	1016 (2)	5743 (5)
$C_{(1)}$	186 (7)	2178 (2)	4217 (9)	$C_{(25)}$	194 (11)	5043 (2)	7385 (9)
$C_{(2)}$	673 (7)	2556 (2)	5110 (5)	$C_{(26)}$	−369 (8)	5474 (3)	6803 (8)
$C_{(3)}$	1831 (7)	2352 (2)	5943 (5)	$C_{(27)}$	−151 (12)	5937 (2)	7461 (12)
$C_{(4)}$	−1121 (6)	4047 (2)	5369 (5)	$C_{(28)}$	655 (9)	5962 (2)	8658 (8)
$C_{(5)}$	125 (5)	3809 (3)	5999 (5)	$C_{(29)}$	1162 (7)	5526 (3)	9256 (7)
$C_{(6)}$	787 (7)	4166 (2)	6822 (5)	$C_{(30)}$	970 (9)	5068 (2)	8607 (5)
$C_{(7)}$	3273 (6)	4234 (2)	7327 (4)	$C_{(31)}$	−2246 (7)	3871 (3)	4348 (6)
$C_{(8)}$	3407 (8)	4692 (3)	6740 (7)	$C_{(32)}$	−1046 (11)	2200 (2)	3101 (5)
$C_{(9)}$	4644 (8)	4825 (2)	6536 (7)	$HC_{(8)}$	263 (5)	491 (2)	654 (4)
$C_{(10)}$	5767 (6)	4518 (2)	6875 (6)	$HC_{(9)}$	464 (5)	513 (2)	603 (5)
$C_{(11)}$	5678 (6)	4052 (2)	7414 (8)	$HC_{(10)}$	664 (5)	457 (2)	674 (4)
$C_{(12)}$	4420 (5)	3907 (2)	7632 (6)	$HC_{(11)}$	654 (6)	382 (2)	789 (6)
$C_{(13)}$	4658 (6)	2618 (3)	8630 (3)	$HC_{(14)}$	662 (5)	253 (2)	1003 (5)
$C_{(14)}$	5551 (8)	2373 (2)	9643 (4)	$HC_{(15)}$	599 (6)	179 (2)	1077 (6)
$HC_{(16)}$	358 (6)	139 (2)	984 (5)	$HC_{(29)}$	179 (6)	555 (2)	1010 (6)
$HC_{(17)}$	232 (4)	173 (2)	810 (4)	$HC_{(30)}$	131 (6)	479 (2)	907 (6)
$HC_{(20)}$	466 (5)	207 (2)	633 (5)	$HN_{(7)}$	222 (6)	378 (3)	816 (6)
$HC_{(21)}$	650 (5)	153 (2)	660 (5)	$HN_{(10)}$	267 (7)	297 (3)	692 (6)
$HC_{(22)}$	609 (5)	64 (2)	647 (5)	$H_{(1)}C_{(31)}$	−205 (7)	380 (3)	347 (7)
$HC_{(23)}$	368 (6)	32 (2)	597 (5)	$H_{(2)}C_{(31)}$	−267 (6)	359 (2)	458 (6)
$HC_{(24)}$	191 (5)	90 (2)	549 (5)	$H_{(3)}C_{(31)}$	−302 (6)	404 (2)	408 (6)
$HC_{(26)}$	−98 (5)	548 (2)	595 (5)	$H_{(1)}C_{(32)}$	−138 (6)	187 (2)	275 (6)
$HC_{(27)}$	−45 (6)	623 (2)	697 (6)	$H_{(2)}C_{(32)}$	−73 (6)	244 (3)	322 (6)
$HC_{(28)}$	89 (6)	623 (2)	911 (6)	$H_{(3)}C_{(32)}$	−75 (7)	227 (3)	247 (7)

atoms. Compounds incorporating macroheterocycles of this type have not hitherto been investigated structurally.

The resulting heterocycle is highly nonplanar (Table 4). Its configuration is shown diagramatically in Fig. 2 with the values of the torsion angles at the C–C, C–N, and N–N bonds The $HN_{(7)}$ atom is considerably displaced from the mean plane of the ring (by 1.1 Å), although the other atom $HN_{(10)}$ is almost coplanar (0.1 Å).

The conformations of cyclic systems are often represented by the numerical system of Dale [2], developed for cycloalkanes with large numbers of carbon atoms. This system consists of a series of numbers (starting with the smallest) corresponding to the number of bonds on one of the 'sides' of a polygon used to represent the ring. The 'side' of the polygon is taken to mean the sum total of the bonds connected to the 'true' angles, i.e., the angles formed by two gauche-bonds of the same sign.

In the molecule of (I), only two bonds ($C_{(6)}$–$N_{(7)}$ and $N_{(7)}$–$C_{(7)}$) (−88 and −137° respectively) can form the 'true' angle from gauche-bonds of the same sign, i.e., in this case it is not possible to distinguish the sides of the polygon in the ring and describe its conformation in the numerical representation of Dale. This is evidently due to the fact that the atoms of the 14-membered ring are in the sp^2-hybridized state, in contrast to the sp^3-hybridized state of the carbon atoms in cycloalkanes. Therefore, in describing the ring, it can only be said that both the groups ($N_{(3)}$–$N_{(4)}$and $N_{(8)}$–$N_{(9)}$) possess the trans-structure.

The pyrazole rings A and B, and the aromatic rings C, D, E, and F are nearly planar (Table 4). In the azobispyrazole fragment, rings A and B are almost coplanar (the dihedral angle AB is 9°), and the benzene rings E and F are inclined to the plane of 'their own' pyrazole ring by 43 and 30° respectively. In the azobisbenzene fragment, rings C and D are highly noncoplanar with each other (the angle CD is 43°).

The interatomic distances $N_{(3)}$–$N_{(4)}$ and $N_{(8)}$–$N_{(9)}$ in the azo-groups are almost identical (1.257 and 1.26 Å), and correspond to the N=N bonds (1.20 and 1.28 Å) in azo-groups bonded to aromatic hydrocarbon radicals [3], i.e., as expected, the π-bond therein is almost completely localized. The N–C bonds in the macrocycle, both those with the amino-nitrogen atoms and the azo-group nitrogens, are characterized by a large contribution of the single N–C bond (Table 2). The interatomic distances in the pyrazole and the aromatic rings have the usual values.

TABLE 2. Interatomic Distances

Bond	d, Å	Bond	d, Å	Bond	d, Å
$N_{(3)}-N_{(4)}$	1,257 (7)	$N_{(5)}-N_{(6)}$	1,37 (1)	$C_{(17)}-C_{(18)}$	1,37 (1)
$N_{(8)}-N_{(9)}$	1,26 (1)	$N_{(6)}-C_{(4)}$	1,34 (1)	$C_{(13)}-C_{(18)}$	1,41 (1)
$N_{(3)}-C_{(2)}$	1,41 (1)	$C_{(4)}-C_{(5)}$	1,42 (1)	$C_{(19)}-C_{(20)}$	1,40 (2)
$N_{(4)}-C_{(5)}$	1,400 (9)	$C_{(5)}-C_{(6)}$	1,36 (1)	$C_{(20)}-C_{(21)}$	1,36 (1)
$N_{(7)}-C_{(6)}$	1,418 (9)	$N_{(5)}-C_{(6)}$	1,34 (1)	$C_{(21)}-C_{(22)}$	1,36 (1)
$N_{(7)}-C_{(7)}$	1,412 (8)	$C_{(7)}-C_{(8)}$	1,39 (1)	$C_{(22)}-C_{(23)}$	1,37 (1)
$N_{(8)}-C_{(12)}$	1,43 (1)	$C_{(8)}-C_{(9)}$	1,362 (9)	$C_{(23)}-C_{(24)}$	1,39 (1)
$N_{(9)}-C_{(13)}$	1,44 (1)	$C_{(9)}-C_{(10)}$	1,363 (9)	$C_{(19)}-C_{(24)}$	1,40 (1)
$N_{(10)}-C_{(3)}$	1,36 (1)	$C_{(10)}-C_{(11)}$	1,37 (1)	$C_{(25)}-C_{(26)}$	1,36 (1)
$N_{(10)}-C_{(18)}$	1,40 (1)	$C_{(11)}-C_{(12)}$	1,40 (1)	$C_{(26)}-C_{(27)}$	1,40 (1)
$N_{(1)}-N_{(2)}$	1,404 (8)	$C_{(7)}-C_{(12)}$	1,41 (1)	$C_{(27)}-C_{(28)}$	1,37 (2)
$N_{(2)}-C_{(1)}$	1,320 (9)	$C_{(13)}-C_{(14)}$	1,40 (1)	$C_{(28)}-C_{(29)}$	1,36 (2)
$C_{(1)}-C_{(2)}$	1,40 (1)	$C_{(14)}-C_{(15)}$	1,38 (1)	$C_{(25)}-C_{(30)}$	1,38 (1)
$C_{(2)}-C_{(3)}$	1,40 (1)	$C_{(15)}-C_{(16)}$	1,38 (1)	$C_{(1)}-C_{(32)}$	1,52 (1)
$N_{(1)}-C_{(3)}$	1,35 (1)	$C_{(16)}-C_{(17)}$	1,38 (1)	$C_{(4)}-C_{(31)}$	1,46 (1)
$N_{(1)}-C_{(19)}$	1,414 (9)				

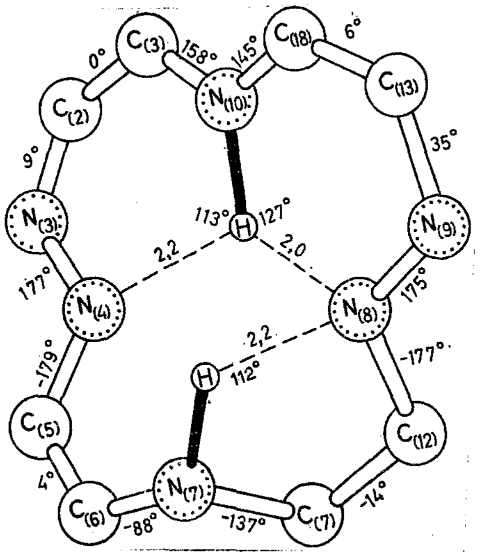

Fig. 2. Diagram of the formation of the 14-membered hexaaza-heterocycle in the $C_{32}H_{26}N_{10}$ molecule.

The azo-groups in the ring are situated in such a way that the distance between $N_{(3)}$ and $N_{(9)}$ (5.48 Å) is much greater than that between $N_{(4)}$ and $N_{(8)}$ (3.63 Å). The latter function as acceptors in the formation of intramolecular hydrogen bonds with the amino-nitrogen $N_{(7)}$ and $N_{(10)}$: $N_{(7)}-H\cdots N_{(8)}$ 2.69(1) Å, $N_{(10)}-H\cdots N_{(4)}$ 2.74(1) Å, $N_{(10)}-H\cdots N_{(8)}$ 2.72(1) Å (Table 5). The $R_{H\cdots N}$ values for these (2.2, 2.2, and 2.0 Å respectively) satisfy the condition for the formation of $N-H\cdots N$ hydrogen bonds ($R_{H\cdots N} \leqslant 2.44$ Å [4]. Consequently, $HN_{(10)}$ forms a forked hydrogen bond with $N_{(4)}$ and $N_{(8)}$ of the two azo-groups, and the second atom $HN_{(7)}$ forms only one hydrogen bond with $N_{(8)}$ of one azo-group. Consequently, within the 14-membered ring one five-membered [$HN_{(7)}$, $N_{(7)}$, $C_{(7)}$, $C_{(12)}$, $N_{(8)}$] and two six-membered slightly puckered fragments [$HN_{(10)}$, $N_{(10)}$, $C_{(18)}$, $C_{(13)}$, $N_{(9)}$, $N_{(8)}$, and $HN_{(10)}$, $N_{(10)}$, $C_{(3)}$, $C_{(2)}$, $N_{(3)}$, $N_{(4)}$] are formed (Table 4). The dihedral angle between the planes of the two six-membered fragments is 27°, and those between the five-membered and six-membered fragments are 52 and 68° respectively.

In the formation of complexes, the metal atom will in all probability be coordinated with, in addition to the amino-nitrogens $N_{(7)}$ and $N_{(10)}$, atoms $N_{(4)}$ and $N_{(8)}$ which are involved in hydrogen bond formation. If the mean plane is constructed through these four nitrogen atoms, it will be seen to be tetrahedrally distorted, the amino-nitrogens $N_{(7)}$ and $N_{(10)}$ being situated on one side of this plane, and two azo-nitrogens $N_{(4)}$ and $N_{(8)}$ on the other (Table 4).

$N-H\cdots N$ hydrogen bonds of similar magnitude have been found in tetraazaheterocycles such as 5,6,7,8,15,16,17,18-octahydrodibenzo[e, o][1,4,8,13]-tetraazacyclotetradecane [5]; 2.71 and 2.75 Å, $R_{H\cdots N}$ 1.92 and 2.04 Å.

TABLE 3. Valence Angles

Angle	ω, deg	Angle	ω, deg	Angle	ω, deg
$C_{(2)}N_{(3)}N_{(4)}$	112,5 (6)	$C_{(5)}C_{(6)}N_{(5)}$	109,1 (7)	$C_{(10)}C_{(11)}C_{(12)}$	118,3 (8)
$N_{(3)}N_{(4)}C_{(5)}$	115,7 (7)	$N_{(9)}C_{(13)}C_{(14)}$	113,8 (8)	$C_{(7)}C_{(12)}C_{(11)}$	121,1 (7)
$C_{(12)}N_{(8)}N_{(9)}$	116 (1)	$N_{(9)}C_{(13)}C_{(18)}$	127,5 (8)	$N_{(7)}C_{(7)}C_{(8)}$	122,8 (6)
$N_{(8)}N_{(9)}C_{(13)}$	110,4 (8)	$N_{(10)}C_{(18)}C_{(13)}$	118 (1)	$N_{(7)}C_{(7)}C_{(12)}$	119,0 (7)
$C_{(6)}N_{(7)}C_{(7)}$	118,5 (6)	$N_{(10)}C_{(18)}C_{(17)}$	124 (1)	$N_{(8)}C_{(12)}C_{(7)}$	113,5 (9)
$C_{(3)}N_{(10)}C_{(18)}$	125 (1)	$C_{(20)}C_{(19)}C_{(24)}$	120,3 (9)	$N_{(8)}C_{(12)}C_{(11)}$	125,0 (8)
$N_{(2)}N_{(1)}C_{(3)}$	112,5 (7)	$C_{(19)}C_{(20)}C_{(21)}$	119,7 (9)	$C_{(14)}C_{(13)}C_{(18)}$	120 (1)
$N_{(1)}N_{(2)}C_{(1)}$	104,0 (6)	$C_{(20)}C_{(21)}C_{(22)}$	121 (1)	$C_{(13)}C_{(14)}C_{(15)}$	120,6 (9)
$N_{(2)}C_{(1)}C_{(2)}$	112,1 (7)	$C_{(21)}C_{(22)}C_{(23)}$	119 (1)	$C_{(14)}C_{(15)}C_{(16)}$	121 (1)
$C_{(1)}C_{(2)}C_{(3)}$	106,1 (8)	$C_{(22)}C_{(23)}C_{(24)}$	122,4 (9)	$C_{(15)}C_{(16)}C_{(17)}$	117 (1)
$C_{(2)}C_{(3)}N_{(1)}$	105,3 (9)	$C_{(19)}C_{(24)}C_{(23)}$	117,0 (9)	$C_{(16)}C_{(17)}C_{(18)}$	125 (1)
$N_{(2)}N_{(1)}C_{(19)}$	116,2 (6)	$N_{(6)}N_{(5)}C_{(25)}$	118,3 (7)	$C_{(13)}C_{(18)}C_{(17)}$	117 (1)
$C_{(3)}N_{(1)}C_{(19)}$	130,3 (9)	$C_{(6)}N_{(5)}C_{(25)}$	131,3 (8)	$N_{(1)}C_{(19)}C_{(20)}$	121,3 (8)
$N_{(2)}C_{(1)}C_{(32)}$	119,8 (7)	$N_{(6)}C_{(4)}C_{(31)}$	118,3 (7)	$N_{(1)}C_{(19)}C_{(24)}$	118,3 (8)
$C_{(2)}C_{(1)}C_{(32)}$	128,1 (8)	$C_{(5)}C_{(4)}C_{(31)}$	131,3 (9)	$C_{(26)}C_{(25)}C_{(30)}$	119 (1)
$C_{(1)}C_{(2)}N_{(3)}$	123,4 (8)	$C_{(4)}C_{(5)}N_{(4)}$	134,6 (8)	$C_{(25)}C_{(26)}C_{(27)}$	119 (1)
$C_{(3)}C_{(2)}N_{(3)}$	130,5 (8)	$C_{(6)}C_{(5)}N_{(4)}$	120,8 (7)	$C_{(26)}C_{(27)}C_{(28)}$	121 (1)
$N_{(1)}C_{(3)}N_{(10)}$	131 (1)	$C_{(5)}C_{(6)}N_{(7)}$	125,4 (8)	$C_{(27)}C_{(28)}C_{(29)}$	119 (1)
$C_{(2)}C_{(3)}N_{(10)}$	124 (1)	$N_{(5)}C_{(6)}N_{(7)}$	125,4 (8)	$C_{(28)}C_{(29)}C_{(30)}$	120 (1)
$N_{(6)}N_{(5)}C_{(6)}$	110,4 (7)	$C_{(8)}C_{(7)}C_{(12)}$	118,1 (8)	$C_{(25)}C_{(30)}C_{(29)}$	121 (1)
$N_{(5)}N_{(6)}C_{(4)}$	105,6 (6)	$C_{(7)}C_{(8)}C_{(9)}$	119,6 (7)	$N_{(5)}C_{(25)}C_{(26)}$	119,6 (9)
$N_{(6)}C_{(4)}C_{(5)}$	110,4 (8)	$C_{(8)}C_{(9)}C_{(10)}$	122,2 (7)	$N_{(5)}C_{(25)}C_{(30)}$	120,9 (9)
$C_{(4)}C_{(5)}C_{(6)}$	104,5 (8)	$C_{(9)}C_{(10)}C_{(11)}$	120,6 (8)		

TABLE 4. Coefficients of the Equation Ax + By + Cz−D = 0 for the Mean Square Planes of Some Fragments of the Structure, and the Departures of Atoms (× 10²) in Å from These Planes

	Atoms and their Δ values	*A*	*B*	*C*	*D*
I A	$N_{(1)}$, $N_{(2)}$, $C_{(1)}$, $C_{(2)}$, $C_{(3)}$ 0 1 −1 1 −1	0,7330	0,3796	−0,5644	−1,0521
II B	$N_{(5)}$, $N_{(6)}$, $C_{(4)}$, $C_{(5)}$, $C_{(6)}$ −1 1 0 −1 1	0,6273	0,3699	−0,6854	−1,6111
III C	$C_{(7)}$, $C_{(8)}$, $C_{(9)}$, $C_{(10)}$, $C_{(11)}$, $C_{(12)}$ −2 1 1 −2 1 1	−0,0404	−0,4312	−0,9013	−11,8780
IV D	$C_{(13)}$, $C_{(14)}$, $C_{(15)}$, $C_{(16)}$, $C_{(17)}$, $C_{(18)}$ −1 1 −1 1 −1 1	0,6404	−0,4502	−0,6222	−7,3063
V E	$C_{(19)}$, $C_{(20)}$, $C_{(21)}$, $C_{(22)}$, $C_{(23)}$, $C_{(24)}$ 0 2 −3 1 0 −1	0,2508	0,0051	−0,9680	−5,5885
VI F	$C_{(25)}$, $C_{(26)}$, $C_{(27)}$, $C_{(28)}$, $C_{(29)}$, $C_{(30)}$ 1 0 −2 3 −3 1	0,9326	0,1480	−0,3296	−2,3143
VII	$N_{(4)}$, $N_{(7)}$, $N_{(8)}$, $N_{(10)}$, $N_{(3)}$*, $N_{(9)}$* 20 −21 22 −22 36 30	0,5965	0,2607	−0,7591	−3,2121
VIII	$N_{(3)}$, $N_{(4)}$, $N_{(7)}$, $N_{(8)}$, $N_{(9)}$, $N_{(10)}$, $C_{(2)}$, 26 1 −64 7 27 −12 49 $C_{(3)}$, $C_{(5)}$, $C_{(6)}$, $C_{(7)}$, $C_{(12)}$, $C_{(13)}$, $C_{(18)}$, 32 −29 −56 53 84 −46 −72 $HN_{(7)}$*, $HN_{(10)}$* −112 10	0,6259	0,1354	−0,7680	−4,2042
IX	$N_{(7)}$, $N_{(8)}$, $C_{(7)}$, $C_{(12)}$, $HN_{(7)}$ 5 8 5 −10 −9	−0,1686	−0,3804	−0,9093	−11,616
X	$N_{(3)}$, $N_{(4)}$, $N_{(10)}$, $C_{(2)}$, $C_{(3)}$, $HN_{(10)}$ −4 −4 −18 7 1 17	0,7080	0,2683	−0,6533	−2,3301
XI	$N_{(8)}$, $N_{(9)}$, $N_{(10)}$, $C_{(13)}$, $C_{(18)}$, $HN_{(10)}$ −25 27 14 −4 −16 14	0,6736	−0,1980	−0,7121	−6,2945

Angles between Planes

Plane	II	III	IV	V	VI	X	XI
I	9	72	51	43			
II		64	50		30		
III			43				
IX						68	52
X							27

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*Atoms not included in the plane calculations.

TABLE 5. Intramolecular Distances and Angles Involving $HN_{(7)}$ and $HN_{(10)}$

A—H···B	A—H	A···B	H···B	Angle A—H...B (deg)
$N_{(7)}$—H ··· $N_{(4)}$	1,0	2,899(8)	2,8	85
$N_{(7)}$—H ··· $N_{(8)}$	1,0	2,69(1)	2,2	112
$N_{(10)}$—H ··· $N_{(4)}$	1,0	2,74(1)	2,2	113
$N_{(10)}$—H ··· $N_{(8)}$	1,0	2,71(1)	2,0	127
$N_{(10)}$—H ··· $N_{(9)}$	1,0	2,95(1)	2,6	101

Thus, the presence of different types of intramolecular hydrogen bonds and the considerable degree of nonplanarity of the macroheterocycle appear to give rise to asymmetry in the potentially symmetrical molecule of (I), and to facilitate coordination by the metal of those nitrogen atoms which are involved in hydrogen bonding, in the formation of complexes.

EXPERIMENTAL

Dark red crystals of $C_{32}H_{26}N_{10}$, of prismatic habit, were grown by slow evaporation of the acetone solution. The density of the compound was measured by flotation in zinc chloride solution. The crystals of (I) were monoclinic: $a = 10.058(1)$, $b = 26.272(3)$, $c = 11.007(2)$, Å, $\beta = 104.15(1)°$, $V = 2820(3)$ Å^3, $M = 550.63$ $d_{meas} = 1.29(1)$, $d_{calc} = 1.297(1)$ g/cm^3, $Z = 4$, sp. grp. $P2_1/c$, $F_{000} = 1152$.

A three-dimensional set of intensities, including 4678 independent reflections of which 2234 had $I_{hkl} \geqslant 3\sigma(I)$, was obtained on an automatic CAD-4SDP diffractometer (λMoK_α, graphite monochromator, $\omega/2\theta$ scan, $\Delta\omega = 0.392 \pm 0.347 \tan\theta$), dimensions of single crystal 0.30 × 0.50 × 0.60 mm, $\theta_{max} = 24°$, absorption disregarded. All structural calculations were carried out on a PDP-11/55t minicomputer using the ENX-SDP programs.

The structure was calculated by the direct method (Multan-78). The positions of all the nonhydrogen atoms were found from the E-synthesis, constructed from the best set of signs. The structural model was refined by least squares, initially in isotropic, then in anisotropic approximation. The positions of the hydrogen atoms bonded to the carbon atoms of the aromatic rings were found from geometric considerations, and those attached to the amino-nitrogens and the methyl carbons from the electron density difference synthesis. The coordinates of all the located hydrogen atoms were then refined by least squares in isotropic approximation. Finally, the structure model was refined in anisotropic approximation (without refinement of H) to $R = 0.072$, $R_W = 0.069$. In the structural refinement, a single weighting was used, $w_i = 1/\sigma(F_i)^2$.

The atom coordinates are given in Table 1. The values of B_{ij} for the nonhydrogen atoms are not given here, but they were within the normal range of values. The interatomic distances and angles are given in Tables 2 and 3 respectively. The C—H bond lengths were found to lie within the range 0.84-1.13 Å.

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