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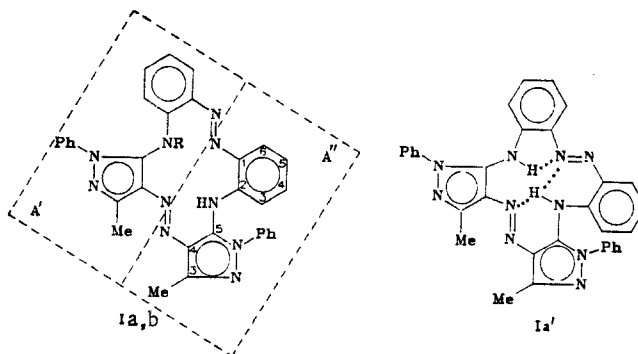
DETERMINATION OF THE CONFORMATION OF MACROCYCLIC 1,8,9,20-TETRAHYDRO-3,6,9-TRIMETHYL-1,8-DIPHENYLDIBENZO[c,m]DIPYRAZOLO[3,4-f:4',3'-j]-[1,2,5,8,9,12]HEXAAZACYCLOTETRADECENE

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UDC 543.422.25:547.773'778.4'898

The conformation of the macrocyclic skeleton of 1,8,9,20-tetrahydro-3,6,9-trimethyl-1,8-diphenyldibenzo[c,m]dipyrazolo[3,4-f:4',3'-j][1,2,5,8,9,12]-hexaazacyclotetradecene was determined by means of the ^{13}C NMR spectra with respect to the known conformations of the macrocyclic skeleton in isomeric Ni(II) complexes 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]hexaazacyclotetradecene.

The molecular and crystal structure of 1,8,9,20-tetrahydro-3,6-dimethyl-1,8-diphenyl-dibenzo[c,m]dipyrazolo[3,4-f:4',3'-j][1,2,5,8,9,12]hexaazacyclotetradecene (Ia) has been previously established by various methods [1, 2].

I a R=H; b R=CH₃; Ia' crystal structure

According to the IR spectral data, the conformations of the macrocyclic skeleton of Ia differ in the solid state and in solution. Only one of the three intramolecular hydrogen bonds (IMHB), viz., the one that forms a six-membered ring condensed with a pyrazole ring, that are observed in the crystal is retained in solution. However, the conformation of Ia in solution could not be investigated in greater detail because of exchange processes and the associated broadening of the resonance signals in the ^1H and ^{13}C NMR spectra. The NMR spectra of the mono-N-methyl derivative (Ib) of the ligand do not have this complication; this made it possible to make a more thorough study of the conformation of its macrocyclic skeleton in solution.

The signal of the proton of the NH group tied up by an IMHB in solution in CDCl₃ is observed at weaker field (12.10 ppm) for Ib than for Ia (11.78 ppm [1]); this constitutes evidence for a stronger NH...N IMHB in Ib. This is also confirmed by a comparison of the

TABLE 1. Data from the ^1H and ^{13}C NMR Spectra of Ligand Ib [$CDCl_3$, 30°C, $\delta(_1H)$ and $\delta(^{13}C)$ chemical shifts in parts per million relative to tetramethylsilane]

H or C atom	A' fragment		A" fragment	
	$\delta_{(^1H)}$	$\delta_{(^{13}C)}$	$\delta_{(^1H)}$	$\delta_{(^{13}C)}$
Benzene ring				
1	—	145,62	—	140,06
2	—	128,43	—	146,67
3	6,93	121,68	6,66	120,18
4	7,13	131,18	6,92	125,70
5	6,93	124,01	6,06	128,58
6	7,51	117,28	7,89	130,50
Pyrazole ring				
3	—	150,19	—	141,55
4	—	127,19	—	131,81
5	—	146,02	—	134,65
3-CH₃	2,66	16,26	2,54	11,47
1 (N—Ph)	—	142,59	—	139,96
2,6 (N—Ph)	7,16	122,93	7,94	122,52
3,5 (N—Ph)	7,16	128,78	7,54	129,53
4 (N—Ph)	7,16	127,04	7,46	127,04
NH/NCH₃	3,33	45,51	12,10	

frequencies of the band of stretching vibrations of the NH group tied up by an IMHB in the IR spectra of solutions of Ib and Ia in CCl_4 ($5 \cdot 10^{-3}$ M) of, respectively, 3162 cm^{-1} (molar extinction coefficient ε = 40 liters•mole^{-1}•cm^{-1}, half width $\Delta\nu_{1/2} \simeq 100$ cm^{-2}) and 3228 cm^{-1} (ε = 37 liters•mole^{-1}•cm^{-1} $\Delta\nu_{1/2} \simeq 90$ cm^{-1}).

Magnetic nonequivalence of the two N-phenyl substituents is observed in the PMR spectrum of Ib (Table 1). For one of them the AA'BB'C multiplet degenerates to a singlet, which is normal for the N-phenyl substituent in pyrazoles, which degeneracy is eliminated for the second; this constitutes evidence for closeness in space of the magnetically anisotropic group [3] — the azobenzene ring in this case. This closeness of the azobenzene ring to the N-phenyl substituent of the pyrazole ring in ligand Ib is more likely in fragment A" than in A' because of its greater coplanarity, which is stabilized by an IMHB with the NH group. In turn, the effect of the magnetic anisotropy of the N-phenyl substituent should be observed for the azobenzene ring adjacent to the NH group, and, of the two sets of signals of protons of o-substituted benzene rings, the signals located over a broader range of chemical shifts (CS) were therefore assigned to fragment A".

An analysis of the ^{13}C NMR spectra (Table 1) with complete and selective suppression of spin-spin coupling (SSC) with the protons of the 5-CH_3, NCH_3, and NH groups, as well as without suppression of SSC with the protons, made it possible to establish which of the two sets of signals of the pyrazole rings in the NMR spectra belongs to fragment A' and which belongs to fragment A".

According to [4], the transition from six-membered to five-membered metallochelate rings in both isomeric Ni(II) complexes of anionic o-(hetarylamino)arylazo ligand Ia and isomeric Ni(II) complexes of an anionic o-hydroxyarylazo ligand of the formazan type is accompanied by identical changes (deshielding by 10-13 ppm) of the ^{13}C chemical shift of the carbon adjacent to anionogenic heteroatom X (X = N, O). It is natural that a comparison of the effects of complexing $\Delta\delta(^{13}C) = \delta(^{13}C)^{ML} - \delta(^{13}C)^{HL}$ will lead to the same difference as a comparison of $\delta(^{13}C)^{ML}$. It may therefore be concluded that, regardless of the anionogenic heteroatom X, the effect of complexing $\Delta\delta(^{13}C)$ on the carbon atom adjacent to X is characterized by deshielding in the formation of a five-membered chelate ring (when X = O, $\Delta\delta$ ~ 10 ppm [5]), whereas it is characterized by shielding in the formation of a six-membered ring (when X = O, $\Delta\delta$ ~ —5 ppm [5]).

However, for a macrocyclic ligand of the I type, in contrast to open-chain ligands, one should expect an effect of the conformation of the skeleton of the macroring on the

C atom (hetaryl)[†]	Conformation of ligand Ib, ppm			
	IV	V	VI	VII
$C_{(2)}$ (5B)	−2,6	15,7	15,1	−3,2
$C_{(5)}$ (5P)	5,9	17,2	5,0	16,3
$C_{(2)}$ (6B)	4,4	−13,9	−16,7	1,6
$C_{(5)}$ (6P)	−0,5	−11,8	−3,7	−15,0

$^*\Delta\delta(^{13}C) = \delta(^{13}C)^{ML} - \delta(^{13}C)^{HL}$, where ML =
II for IV and V and ML = III for VI and VII.
[†]The designation of the hetaryl group in-
cludes the size (five- or six-membered) of
the metallochelate ring condensed with it,
the precursor of which is the given fragment
of the ligand.

^{13}C chemical shifts (CS). This is indicated, in particular, by the opposite-in-sign large
absolute values of the ^{13}C CS of the carbon atoms adjacent to the NH (fragment A'') and NCH_3
(fragment A') groups in Ib. These differences, which amount to 18 ppm for the $C_{(2)}$ atoms
of the benzene rings and −11 ppm for the $C_{(5)}$ atoms of the pyrazole ring, cannot be due
to the $N-CH_3$ substituent. Consequently, coincidence of the conformations of the hexaaza-
tetradecene skeleton of the ligand and its metal complex is a necessary condition for ful-
fillment of the above-indicated principle of reversal of the effects of the formation of
five-membered and six-membered metallochelate rings on the $\Delta\delta(^{13}C)$ value for the carbon
adjacent to the anionogenic N atoms. This, in turn, makes it possible to determine the
conformation of the macrocyclic skeleton of the corresponding ligands Ia and Ib from the
known conformation of the metal complexes, since, to a first approximation, the contribu-
tion of the $N-CH_3$ substituent to the ^{13}C CS of the carbon atoms adjacent to the N atom can
be disregarded [compare the ipso effects in monosubstituted benzenes for $NHCH_3$ (21.4 ppm)
and for $N(CH_3)_2$ (22.5 ppm) [6]].

Both possible conformations, viz., II [6B, 5B, 6P, 5P] and III [5B, 6B, 6P, 5P], with
[6,5,6,5] and [5,6,6,5] sequences of the five- and six-membered metallochelate rings vis-à-
vis an unchanged [B,B,P,P,] sequence of the hetarene rings condensed with them, where B
pertains to a benzene ring and P pertains to a pyrazole ring, have been previously identi-
fied for Ni(II) complexes of Ia [4].
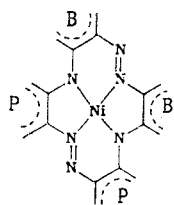
II
[6B,5B,6P,5P]
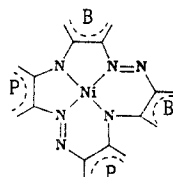
III
[5B,6B,6P,5P]

Two analogous doubly degenerate conformations of the macrocyclic skeleton can be real-
ized for starting ligand Ia (in the ligands we will consider the sequence of the four
fragments of the hexaazatetradecene skeleton that are precursors of the corresponding five-
and six-membered metallochelate rings). Degeneracy is eliminated for ligand Ib, and the
following four conformations are possible: IV [6B,5B,6P,5P], V [5B,6B,5P,6P], VI [5B,6B,
6P,5P], and VII [6B,5B,5P,6P] (the sequence of the precursors of the metallochelate rings
is reckoned from the Me-substituted nitrogen atom) on following page).

The values of the effect of complexing $\Delta\delta(^{13}C)$ on the carbon atoms adjacent to the
anionogenic N (or N-Me) atoms calculated from the experimental data for the benzene and
pyrazole rings that enter into fragments A' and A'' of each of the four possible conforma-
tions of Ib and for the corresponding Ni(II) complexes of Ia are presented in Table 2. It

IV	V	VI	VII
[6B, 5B, 6P, 5P]	[5B, 6B, 5P, 6P]	[5B, 6B, 6P, 5P]	[6B, 5B, 5P, 6P]
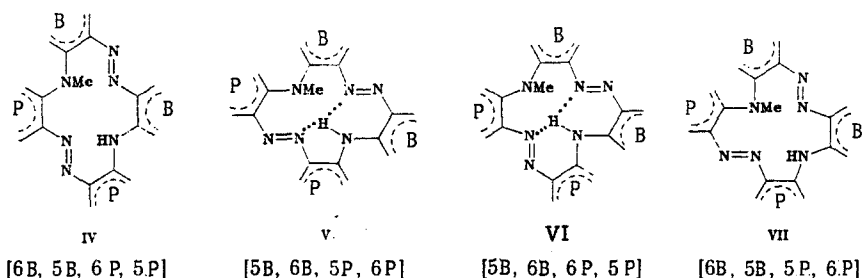
is apparent from Table 2 that only conformations V and VI lead to the expected (with respect to sign) $\Delta\delta(^{13}C)$ values in the formation of five- and six-membered metallochelate rings and, correspondingly, to deshielding and shielding.

The choice between conformations V and VI can be made on the basis of a comparison of the strengths of the IMHB expected for them and observed in Ib. In the case of Ia it was shown that the strength of the IMHB in the six-membered ring condensed with a pyrazole ring (6P) is higher than in the six-membered ring condensed with a benzene ring (6B) [1]. Consequently, the strengthening of the IMHB in Ib as compared with Ia, in which one IMHB (6P) is realized, can be explained by the formation of a forked IMHB in Ib. On passing from solution to the solid phase the ν_{NH} band for Ib remains virtually unchanged (ν_{NH} 3162 and 3156 cm^{-1}, respectively); this indicates retention of the conformation of the macrocyclic skeleton in solution and in the solid phase. On the other hand, in the case of Ia the transition from a solution to the solid phase gives rise to a 25-50 cm^{-1} shift* of the ν_{NH} band, i.e., weakening of the IMHB. As noted above, in the crystalline state Ia exists in a conformation of the VI type, which is stabilized by the almost planar five-membered ring with an IMHB (5B) and a forked IMHB with two acoplanar six-membered rings with IMHB [(6B) and (6P)] [2]. The acoplanarity of the adjacent six-membered rings with IMHB is evidently also retained for ligand Ib in the VI conformation; this does not make it possible to expect strengthening of the IMHB. On the other hand, for the V conformation one might expect greater coplanarity of the adjacent five- and six-membered rings with IMHB due to a smaller degree of overlapping of the benzene ring and N-phenyl substituent of the pyrazole ring that are condensed with them and, consequently, the observed strengthening of the IMHB.

The imporant role of the five-membered ring with an IMHB (5B) in the crystalline state of Ia for stabilization of the VI conformation with a forked IMHB (6B,6P) hence follows. The impossibility of realizing this IMHB in the case of mono-N-methylation in Ib leads to the V conformation with a stronger forked IMHB (6B,5P).

<center>EXPERIMENTAL</center>

The ^{1}H (100 MHz) and ^{13}C (25.16 MHz) NMR spectra of solutions of the compounds in CDCl$_3$ were recorded with a Varian XL-100 spectrometer with tetramethylsilane as the internal standard. The IR spectra of solutions in CCl$_4$ and suspensions in mineral oil and hexachlorobutadiene were obtained with a Specord IR-75 spectrometer. The assignment of the signals and the evaluation of the chemical shifts (CS) of the aromatic protons in the PMR spectra were accomplished by homonuclear and heteronuclear double-resonance methods. The assignment of the signals in the ^{13}C NMR spectra was made on the basis of an analysis of the spectra obtained in the case of complete and selective decoupling, as well as without decoupling, of the spin-spin coupling with the protons.

1,8,9,20-Tetrahydro-3,6,9-trimethyl-1,8-diphenyldibenzo[c,m]dipyrazolo[3,4-f:f',3'-j]-[1,2,5,8,9,12]hexaazacyclotetradecene (Ib). A mixture of 0.28 g (5·10^{-4} mole) of Ia [1], 4 ml of 50% NaOH, 0.02 g (6.2·10^{-5} mole) of tetrabutylammonium bromide, and 20 ml of benzene was heated with stirring to 80°C, 0.1 ml of dimethyl sulfate was added, and the mixture was maintained at 80°C for 0.25 h. It was then cooled to 25°C and treated with 50 ml of water. The aqueous layer was separated, and the organic phase was washed with 20 ml of water, dried over sodium sulfate, and evaporated. The residue was dissolved in 10 ml of chloroform, and the solution was applied to a column packed with silica gel and eluted with chloroform to give 0.27 g (95%) of Ib with mp 233-234°C (dec.) (from methanol).

*Evaluation with respect to the two principal components of the complex ν_{NH} absorption of Ia in a suspension in mineral oil, which consists of bands at 3280 and 3250 cm^{-1} that are overlapped and decrease in intensity and weak shoulders at 3225 and 3195 cm^{-1}.

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IDENTIFICATION OF RANDOMERS OF TETRA(tert-BUTYL)PORPHYRAZINE

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UDC 547.979.733:541.621:543.422.25'51

Randomers of tetra(tert-butyl)porphyrazine, the assignment of which was made on the basis of data from mass spectrometry and high-resolution PMR spectroscopy, were isolated by high-performance liquid column chromatography.

One of the important problems of the structural chemistry of macroheterocyclic compounds, particularly porphyrins and their aza and areno analogs, is the identification of the isomers with respect to the location of the substituents in the macroring (randomers) [1, 2]. This is associated with the fact that the common methods for the synthesis of such compounds, which are based on the template tetramerization of unsymmetrical porphyrinogens, lead to a mixture of randomers, the number of which is close to the number of possible connections of the fragments. The separation of the randomers is facilitated in the case of polar substituents. Thus they can be separated by paper or adsorption chromatography etc. and identified by spectral methods.

The identification of structures with alkyl or phenyl substituents is difficult and requires specific approaches.

We have investigated the possibility of the separation and identification of randomers of tetra(tert-butyl)porphyrazine obtained by tetramerization of tert-butylmaleonitrile in the presence of magnesium ethoxide with subsequent treatment of the intermediate complex of tetra(tert-butyl)porphyrazine with magnesium with boiling acetic acid [3]. Theoretically, one might expect the formation of four randomers, which, in conformity with the nomenclature of porphyrins [4, p. 101], can be assigned to the I-IV types (see scheme on following page).

High-performance liquid chromatography (HPLC) of this mixture revealed the presence in it of three randomers with identical electronic absorption spectra (λ_{max} 621, 547, and 334 nm). Calculation of the column efficiency with respect to each of the three peaks (~20,000 theoretical plates) shows that these compounds are individual. The yields of the randomers are 58.4% (fraction A), 25.2% (fraction B), and 16.4% (fraction C). The retention times of the isolated fractions differ markedly. Fraction A is eluted virtually with the free volume of the column ($K_A^1 = 0$), whereas capacity coefficients K_B^1 and K_C^1 for fractions B and C are 1.14 and 1.31, respectively. The retention of the isomer of fraction A under the investigated chromatographic conditions is characteristic for aromatic systems that do not contain strongly sorbed functional groups. On the basis of this we assumed