The structure of a thiadiazole-containing expanded heteroazaporphyrinoid determined by gas electron diffraction and density functional theory calculations†

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Received (in Cambridge, UK) 12th March 2008, Accepted 28th April 2008
First published as an Advance Article on the web 9th June 2008
DOI: 10.1039/b804308f

The molecular structure of a macrocycle with a 24-membered ring, a thiadiazole-containing expanded heteroazaporphyrinoid, has been, for the first time, directly characterised by a synchronous gas electron diffraction and mass spectrometric experiment and DFT calculations; the molecule has the equilibrium structure of C_{3h} symmetry with a planar macrocycle.

The first study describing the synthesis of a macroheterocyclic compound containing 1,3,4-thiadiazole rings dates back to 1971.[1] Initially, its structure was represented as a four member ABAB type macrocycle.[2] In 1990 the substituted macrocycle containing *tert*-butyl groups[3] was obtained for the first time, but, because of lack of complete characterisation, the molecule was again described as an ABAB type macrocycle.

For the second time, the substituted macrocycle was synthesized in 2001 by two research groups[4] with the yield up to 50%. This time the compound obtained was characterised by mass spectrometry (MALDI, FAB), ^{1}H and ^{13}C NMR, IR and UV-Vis spectroscopy, and elemental analysis. Contrary to the earlier supposition of the ABAB type structure, it was determined that the macrocycle in question consists of three 1,3,4-thiadiazole rings and three 5-*tert*-butylisoindole subunits connected to each other *via* azabridges, and, therefore, is a macroheterocyclic system of the ABABAB type. Its structural analogue with three 4,5-bis(4-*tert*-butylphenyl)pyrroline rings instead of the substituted isoindole moieties was also described.[4] However, to our best knowledge, no direct method of structure investigation was ever applied to any of these compounds.

These expanded heteroazaporphyrinoids may be considered to be structural analogues of hexaphyrine[5] with the large inner cavity which is able to hold three metal ions such as Ni^{2+}, Cu^{2+}, or Co^{2+}. Their coordination properties are of great interest due to the unusual structure of the cavity. Recently, the acid–basic behaviour of these macrocycles in a proton-donating medium and their ability for complex formation were also studied.[6]

The principal questions about the structure of thiadiazole-containing expanded heteroazaporphyrinoids concern the planarity of the macrocycle and the orientation of the thiadiazole rings. Theoretical calculations using the AM1 method predicted that these molecules are non-planar and that configurations with the S atoms oriented outwards from the inner cavity are preferable (by *ca.* 70 kcal mol^{-1}) compared to those with an alternative orientation.[7]

In this study, we have used a synchronous gas electron diffraction and mass spectrometric experiment combined with density functional theory calculations to determine the structure of a thiadiazole-containing expanded heteroazaporphyrinoid containing three 1,3,4-thiadiazole rings and three 5-*tert*-butylisoindole subunits ($C_{42}H_{39}N_{15}S_3$, designated further as molecule **1**).

Theoretical studies on **1** and the unsubstituted macrocycle ($C_{30}H_{15}N_{15}S_3$, designated further as molecule **2**) have been carried out using density functional theory (DFT) calculations utilising the B3LYP hybrid functional (Becke + Slater + HF exchange and LYP + VWN5 correlation). In the final computations, all atoms were described by the triple-ζ valence correlation consistent cc-pVTZ basis sets[8] converted to the segmented contractions. The Gaussian elimination algorithm used to reduce the contraction lengths was described in ref. 9. The basis sets in their final (segmented contractions) form in the *GAMESS* format were obtained from the Extensible Computational Chemistry Environment Basis Set Database.[10] All calculations were performed using the *PC GAMESS* 7.0 version[11] of the *GAMESS* software[12] running under a Linux operating system.

According to the results of our theoretical study, molecules **1** and **2** have the equilibrium structures of C_{3h} and D_{3h} symmetry, respectively, with planar macrocycles. Force field calculations yielded no imaginary frequencies, indicating that the optimised configurations correspond to the minima on the potential energy hypersurfaces. The structure of **1** is presented in Fig. 1. Selected structural parameters of **1** are listed in Table 1; the labelling of atoms used in the table and in the text is given in Fig. 2.

Substitution of three hydrogen atoms by *tert*-butyl groups has negligible influence on the geometry of the inner macrocycle—the differences in bond lengths and in valence angles are within 0.001 Å and 0.1°, respectively. At the same time, this substitution has a prominent influence on the geometry of

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† Electronic supplementary information (ESI) available: Experimental and theoretical molecular intensity curves and radial distribution curves, Cartesian coordinates and energies of the optimised structures of **1** and **2** yielded by DFT calculations. See DOI: 10.1039/b804308f

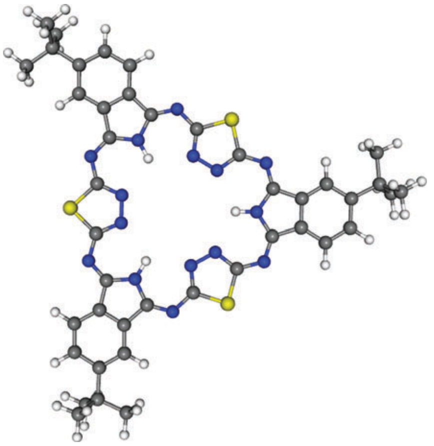

Fig. 1 Structure of the $C_{42}H_{39}N_{15}S_3$ macrocycle, a thiadiazole-containing expanded heteroazaporphyrinoid (**1**).

Table 1 Selected structural parameters of the $C_{42}H_{39}N_{15}S_3$ molecule yielded by B3LYP/cc-pVTZ study (distances in Å, angles in °).

	CW[a]	CCW[b]		CW[a]	CCW[b]
$r(N_p–C_{p1})$	1.385	1.384	$\alpha(N_p–C_{p1}–N_m)$	129.3	129.4
$r(C_{p1}–N_m)$	1.290	1.289	$\alpha(C_{p1}–N_m–C_t)$	122.4	122.4
$r(N_m–C_t)$	1.361	1.361	$\alpha(N_m–C_t–N_t)$	128.0	127.9
$r(C_t–N_t)$	1.316	1.316	$\alpha(N_m–C_t–S)$	119.2	119.2
$r(N_t–N_t)$	1.346		$\alpha(N_t–C_t–S)$	112.8	112.9
$r(C_t–S)$	1.752	1.752	$\alpha(N_p–C_{p1}–C_{p2})$	106.2	106.3
$r(C_{p1}–C_{p2})$	1.466	1.468	$\alpha(C_{p1}–C_{p2}–C_{p2})$	108.0	107.8
$r(C_{p2}–C_{p2})$	1.392		$\alpha(C_{p1}–C_{p2}–C_{b1})$	131.7	130.5
$r(C_{p2}–C_{b1})$	1.386	1.386	$\alpha(C_{p2}–C_{b1}–C_{b2})$	117.9	119.1
$r(C_{b1}–C_{b2})$	1.388	1.397	$\alpha(C_{b1}–C_{b2}–C_{b2})$	122.8	118.2
$r(C_{b2}–C_{b2})$	1.409		$\alpha(C_{b1}–C_{b2}–C_{bt})$		122.3
$r(C_{b2}–C_{bt})$		1.536			
$r(Z\cdots N_t)^c$	2.753		$r(Z\cdots N_p)^{[c]}$	3.880	
$r(N_t\cdots N_t)$	3.951		$r(N_p\cdots N_p)$	6.720	

[a] Clockwise part of the molecule, atoms labelled without stars (see Fig. 2). [b] Counter-clockwise part, starred atom labels. [c] Distance from the *z* axis, *i.e.* from the centre of the molecule.

the isoindole moieties, resulting in the elongation of two C–C bonds (C_{b1}–C_{b2} and C_{b2}–C_{b2}) by 0.006 and 0.011 Å, respectively. This is a well known effect with the introduction of an electron-donating substituent,[13] also reported, for example, in the theoretical study of several porphyrin complexes.[14]

The structure of the isomer of **1** with rotated thiadiazole rings, in which the sulfur atoms are inside the inner macrocycle (an alternative structure proposed in ref. 7), has also been studied using DFT computations. Force field calculations at the B3LYP/6-31(d) level indicated that this structure is a saddle point with a doubly degenerate imaginary frequency corresponding to the rotation of the thiadiazole rings around the C_t–N_m bonds. The energy difference between this configuration and the equilibrium structure shown in Fig. 1 is 232 kJ mol^{-1} (B3LYP/cc-pVTZ calculations).

This seemingly huge difference can possibly be attributed for the most part to the hydrogen bonding. Six strong hydrogen bonds between the H and N_t atoms exist in the equilibrium structure of **1** ($r(H\cdots N_t)$ = 2.19 Å), while the transition state structure lacks all of them ($r(H\cdots S)$ = 2.92–2.94 Å). The energy difference per bond, 232/6 = 38.7 kJ mol^{-1}, however, seems to be larger than the energy of a typical N–H···N hydrogen bond. Moreover, the hydrogen bond energies should be even larger than the energy difference between the two states because of some compensating distortions of the macrocycle frame. The structural parameters of the two structures are indeed distinct: $\alpha(C_{p1}–N_m–C_t)$ and $\alpha(N_p–C_{p1}–N_m)$ valence angles are smaller in the equilibrium structure and the thiadiazole rings are, therefore, "pulled" towards the centre of the macrocycle. Nevertheless, the existence of N–H···N hydrogen bonds with similar energies (8.2 kcal mol^{-1} or 34.3 kJ mol^{-1}) has been reported.[15]

The absence of a noticeable influence of the hydrogen substitution on the structure of the macrocycle allows study of its structural peculiarities (*e.g.* tautomerism) using **2** as a model, significantly saving computational resources. We have optimised the geometry of a tautomer of **2** with three hydrogen atoms bonded to the N atoms of the thiadiazole rings. According to the results of the B3LYP/6-31(d) force field calculation, this tautomer of C_{3h} symmetry is a local minimum. The energy of the second tautomer is, however, significantly higher than that of the D_{3h} structure (ΔE = 108 kJ mol^{-1}, B3LYP/cc-pVTZ calculations).

Again, this large difference is probably largely due to the existence of the strong hydrogen bonds: there are only three such bonds in the second tautomer, while the main structure has six. It is remarkable that the energy difference per bond, 108/3 = 36 kJ mol^{-1}, is very close to the per bond difference found when the two structures with the different orientations of the thiadiazole rings were compared.

Macrocycle **1** used in the experimental part of our study was synthesised by the condensation of 2,5-diamino-1,3,4-thiadiazole and 5-*tert*-butyl-1,3-diiminoisoindoline by the method described in ref. 4*a*.

A separate experiment has been carried out to study the process of sublimation of **1** by the Knudsen method with mass spectral monitoring of the vapour composition. At temperature T = 617–673 K, the molecular ion (m/z = 849.8) dominated, followed by several ions of weak (3–4%) intensity. No ions corresponding to the oligomeric species were detected. The enthalpy of sublimation calculated by the second law of thermodynamics is 300(6) kJ mol^{-1} for the average temperature.

The diffraction patterns of **1** were obtained in a synchronous gas electron diffraction (GED) and mass spectrometric (MS) experiment carried out using the *EMR-100/APDM-1* unit.[16]

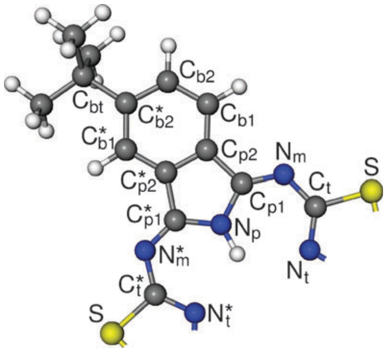

Fig. 2 Atom designations of $C_{42}H_{39}N_{15}S_3$.

The sample of $C_{42}H_{39}N_{15}S_3$ was evaporated at temperature $T = 742(10)$ K from a graphite cell with a cylindrical effusion nozzle of 0.6 × 1.2 mm size (diameter × length). The ratio of the evaporation area to the effusion orifice area was above 500. The mass spectra of the saturated vapour over the sample show a molecular ion of stable intensity, indicating the presence of the molecular species in the vapour at the temperature of the experiment. Vapour composition was monitored by mass spectrometry during the entire GED/MS experiment.

Electron diffraction patterns were obtained from short ($L_1 = 338$ mm) and long ($L_2 = 598$ mm) camera distances at accelerating voltages of 73 and 79 kV, respectively. Accurate wavelengths of electrons have been calibrated using polycrystalline ZnO. The diffraction patterns were recorded using Kodak SO-163 electron image films, which were scanned by a calibrated *Epson Perfection 3200 Photo* scanner. Least-squares structure refinement was performed using the modified version of the *KCED 35* program.[17]

Vibrational corrections k_{h1} and starting values of r.m.s. vibrational amplitudes u (which were later refined in groups in the least squares procedure) were calculated by the *SHRINK* program[18] (second approximation taking into consideration non-linear terms in the transformation between Cartesian and internal coordinates) using the force field from our B3LYP/cc-pVTZ theoretical study.‡ This approach of computing vibrational corrections was previously applied in studies of phthalocyanines[19] and may be considered the present state of the art for large molecules.

The experimental molecular intensity curves agree well with the theoretical curves calculated using the geometry and the vibrational corrections k_{h1} from the B3LYP/cc-pVTZ study (the disagreement factor $R_f = 5.5\%$). The theoretical and experimental radial distribution curves are also in excellent agreement. At the same time, the theoretical computations yielded no alternative structures which may be present in the vapour. The configuration with inverted thiadiazole rings is a saddle point, and the second tautomer has much higher energy. Moreover, the parameters of these structures differ significantly from the parameters of the main (*i.e.* global minimum) configuration, making the radial distribution curves distinct in the range of shorter interatomic distances.

Considering the results of our density functional theory and gas electron diffraction studies, we can conclude that the $C_{42}H_{39}N_{15}S_3$ molecule has the equilibrium structure of C_{3h} symmetry with a planar macrocycle and the sulfur atoms oriented outwards from the inner cavity, as presented in Fig. 1.

This work was supported by a grant of the President of Russian Federation for the State support of young Russian scientists (MK-9439.2006.3) and the Russian Foundation for Basic Research, grant no. 05-03-33003a.

Notes and references

‡ The initial processing of GED data as well as transferring the data between *GAMESS*, *SHRINK* and the least-squares analysis program were carried out by means of the software written by Dr A. V. Zakharov and Yu. A. Zhabanov. Further details can be requested from Dr A. V. Zakharov by e-mail: a_zakharov@isuct.ru.

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