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Thiaporphyrin with an Inverted Thiophene Ring – DFT Studies

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Abstract

The structure and electronic energy have been investigated applying the density functional theory (DFT) for two idealized 2-thia-21-carbaporphyrin, (SCP)H and (3H-SCP), 2-thia-21-carbaporphyrin anion $(SCP)^-$ and 21-thiaporphyrin (SP)H. The analysis of calculated total electronic energies, using the B3LYP/6-31-G* approach, demonstrates that the energy difference between 21-thiaporphyrin and its inverted isomer equals 10.34 kcal/mol [(SCP)H] and 52.08 kcal/mol [(3H-SCP)]. In contrast to 21-thiaporphyrin the thiophene fragments in (SCP)H and SCP^- present a geometry resembling that one of an isolated thiophene molecule.

Introduction

Core modifications of porphyrins by the introduction of various heteroatoms (O, S, Se, Te) in place of the nitrogen atoms resulted in the preparation of a series of macrocycles which have interesting properties both in terms of their aromatic character and their ability to bind metal ions or anions [1]. The search for their isomers yielded corresponding heteroporphycene analogs [2].

The recently synthesized 2-aza-21-carba-23-oxaporphyrin and 2-aza-21-carba-23-thiaporphyrin, i.e., isomers of 21-oxaporphyrin and 21-thiaporphyrin combine features of both inverted porphyrin and 21-heteroporphyrin [3]. A novel 5,10,15,20-tetraaryl-2-aza-21-carba-22-selenaporphyrin with an inverted pyrrole ring has been produced in addition to the expected 5,10,15,20-tetraaryl-21-selenaporphyrin in a [3 + 1] condensation of bis(arylhydroxymethyl)selenophene and 5,10-aryltripyrrin [4].

2-Thia-5,10,15,20-tetraphenyl-21-carbaporphyrin **2** [(SCTPP)H] has recently been synthesized [5]. It can be formally constructed by exchanging the sulfur atom and a β-CH unit in the thiophene ring in the isomeric 5,10,15,20-tetraphenyl-21-thiaporphyrin **1** [6]. Oxidation of **2** gave a new yellow species 2-thia-3-oxo-5,10,15,20-tetraphenyl-21-carbaporphyrin **3** [$(SCOTPP)H_2$]. The aromatic isomer of 5,10,15,20-tetra(*p*-tolyl)-21,23-dithiaporphyrin (S_2TTP) with an inverted pyrrole ring: 2-aza-5,10,15,20-tetra(p-tolyl)-21-carba-22,24-dithiaporphyrin (S_2CTTP) has been detected as well [7].

Here we comment on the relation between the mode of thiophene ring incorporation and the aromaticity of the regular and inverted monothiaporphyrin, and the derivatives of the latter.

Results and discussion

The considerable spectroscopic difference between (STPP)H and isomeric (SCTPP)H which merely differ by an orientation of the thiophene moiety in the macrocyclic structure, can be accounted for in terms of corresponding resonance structures presented in Scheme 2 [5]. The thiophene subunit attenuates conjugative pathways in (SCTPP)H **2** providing, however, a very efficient 18π delocalization path for (STPP)H. The less energetically accessible zwitterionic structure(s), which require charge separation, need to be included in order to provide the 18π delocalization route for (SCTPP)H which explains its relatively small aromaticity (Scheme 2).

Pursuing our interest in the difference in aromaticity determined for (SCTPP)H and (STPP)H as revealed by ^{1}H NMR spectra [5], we have used DFT calculations to probe the geometrical changes related to the aromaticity of 21-thiaporphyrin, two tautomers of inverted thiaporphyrin and its anion. The density functional theory methods and the high-level *ab initio* calculations have been recently applied to porphyrins, porphyrin isomers, metalloporphyrins and related systems [8–16]. These theoretical investigations addressed problems of geometry, NH tautomerisation, electronic spectra and substituent effect on the electronic structure. The interesting results have been reported for inverted porphyrin [11, 14], a series of carbaporphyrinoids [9, 10], sapphyrin and heterosapphyrin [15, 16].

In order of simplification all calculations have been carried out for structures where the *meso*-aryl groups of thiaporphyrins have been replaced by hydrogens yielding 2-thia-21-carbaporphyrin (SCP)H, its tautomeric form (3-HSCP) with the NH proton moved to the 3 position and its anion $(SCP)^-$. For the sake of comparison we have also included two extreme standard situations, feasible for the thiophene moiety inserted in to the macrocyclic struc-

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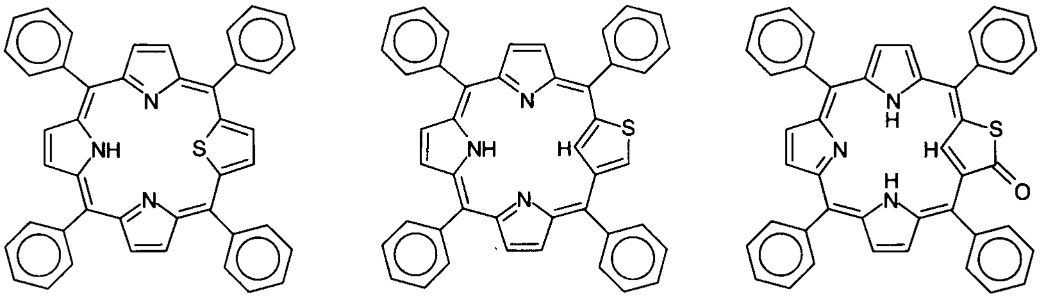
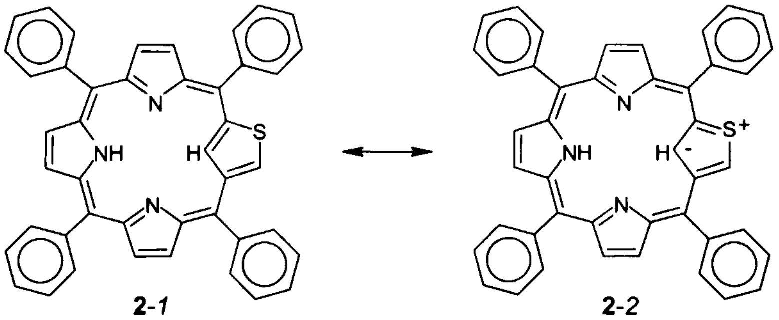


1 **2** **3**

Scheme 1.



2-*1* **2-*2***

Scheme 2.

ture, represented here by thiophene and 21-thiaporphyrin (SP)H. The first model presumes the preservation of the unperturbed thiophene molecular structure and has been exemplified by a regular thiophene molecule. In the case of 21-thiaporphyrin the essential involvement of the thiophene moiety into the 18π conjugation pathway could be expected. Previously it was experimentally established for 5,10,15,20-tetraphenyl-21-thiaporphyrin that the strong delocalization via the thiophene moiety has been reflected in the reverse of C_α—C_β and C_β—C_β bond lengths as compared to the unperturbed thiophene [6, 18].

The optimized geometries with peripheral phenyls replaced by hydrogens and the corresponding relative energies (B3LYP/6-31G*) are shown in Figures 1–4. In each case the macrocycle remains virtually planar. The DFT optimized bond lengths and angles of thiophene and 21-thiaporphyrin is in satisfactory agreement with the relevant X-ray crystallographic values [17, 18]. The calculated total electronic energies, using the B3LYP/6-31G* approach, demonstrate that 21-thiaporphyrin (−1332.3602 [Hartree]) is more stable than its inverted isomer (−1332.34369 [Hartree]) and its tautomer, (3H-SCP) (−1322.3437 [Hartree]). (The total energy is given in parentheses). The total electronic energy difference between the regular 21-thiaporphyrin (SP)H and its inverted isomer (SCP)H is calculated to be equal to 10.34 kcal/mol. The (SCP)H tautomer is more stable than (3H-SCP) (52.08 kcal/mol). The destabilization of (SCP)H vs (SP)H results from the inversion of the thiophene fragment and can be accounted for by reduction of aromaticity and, consequently, of aromatic stabilization energy.

A detailed comparison of bond distances within the pyrrole and thiophene portions demonstrates that extensive delocalization in the macrocycle is present in the (SP)H case and (SP)H extends on to the thiophene fragment. Bond distances of the regular pyrroles C_α—C_β > C_α—C_{meso} > C_α—N > C_β—C_β reproduce the pattern of the regular porphyrin macrocycle. There is an appreciable effect of the macrocyclic aromaticity on the thiophene moiety. In the (SP)H macrocycle the C_α—C_β distances are longer and the C_β—C_β distances are shorter than in free thiophene and the C_α—S bond lengths remain unchanged. Thus the pattern of C_α—C_β and C_β—C_β thiophene distances follows that seen in the porphyrin pyrrole rings and reflects the inclusion of the thiophene moiety in the π delocalization pathway of the macrocycle.

In contrast to (SP)H the thiophene fragments in (SCP)H and $(SCP)^-$ present a geometry resembling that of the individual thiophene molecule. However small although systematic changes in bond lengths have been noticed between (SCP)H and thiophene [$(SCP)^-$ and thiophene] S—C(20) 0.047 (0.039); S—C(3) −0.016 (−0.023); C(3)—C(4) 0.023 (0.027); C(4)—C(21) 0.008 (−006) (all values in Å). The optimised geometry of (SCP)H demonstrates modest bond length alternation in the complementary to the thiophene part of the macrocycle. For instance the lengths of C_α—C_{meso} bonds adjacent to thiophene are significantly unequal. The marked differences in bond distances have been found between the two C_α—N bonds for each of the unprotonated pyrrole rings. These observations suggest that structure **2** which isolates the 6π-delocalization framework with two simple σ-bonds from the overall macrocycle delocalization path should dominate the description of the (SCP)H properties. The N(23)-H proton dissociation of the N(23)-H proton of (SCP)H to form SCP^- pro-

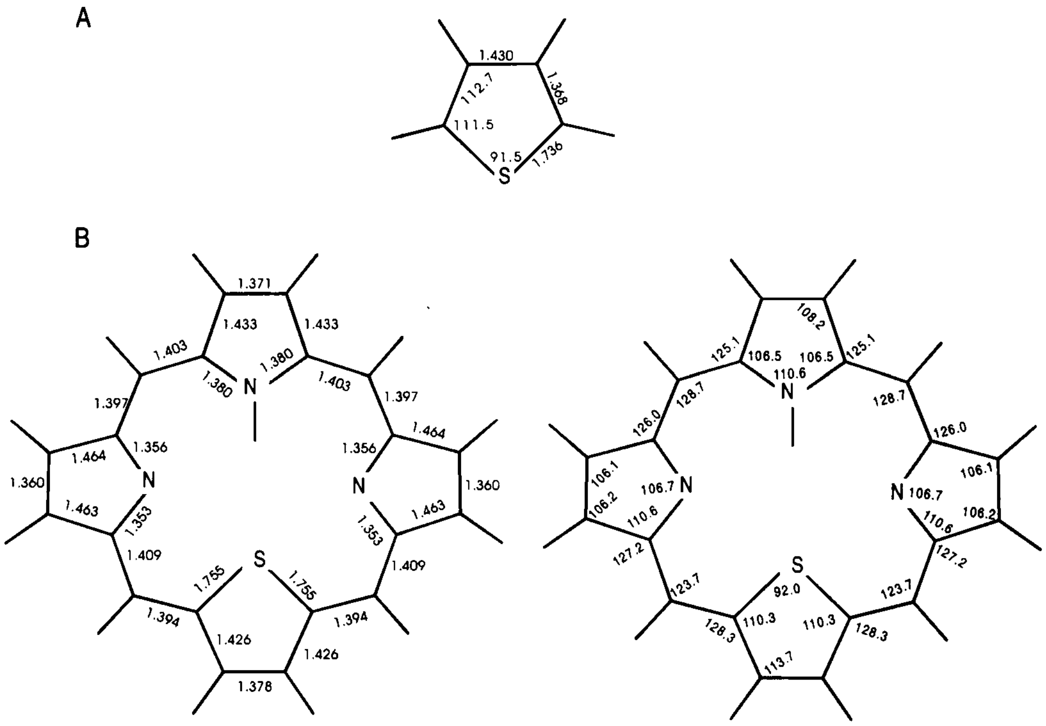

A
1.430
112.7
1.368
111.5
91.5
1.736
S
B
1.371
1.433
1.433
1.403
1.380
1.380
N
1.403
1.397
1.397
1.464
1.464
1.356
1.356
1.360
1.360
N
N
1.463
1.463
1.353
1.353
1.409
1.409
1.755
1.755
S
1.394
1.394
1.426
1.426
1.378
108.2
125.1
125.1
106.5
106.5
110.6
N
128.7
128.7
126.0
126.0
106.1
106.1
106.7
106.7
N
N
106.2
106.2
110.6
110.6
127.2
127.2
123.7
123.7
S
92.0
110.3
110.3
128.3
128.3
113.7

Figure 1. Optimized (B3LYP/6-31G) geometries of thiophene (A) and (SP)H (B). Bond lengths are in angstroms and the bond angles are in degrees.

duced some small but essential C_α—C_{meso} and C_α—N bond distance changes. The alternation of bond lengths in the C(6)N(22)C(9)C(10)C(11)N(23)C(14)C(15)C(16)-N(24)C(19), backbone has decreased as compared to (SCP)H. Altogether, the relatively small differences between the structural parameters of (SCP)H and $(SCP)^-$ have been determined by the DFT optimization.

Thus, bond alternation in (SCP)H is consistent with the pattern suggested by the standard valence structure **2**.

Root mean square deviations of bond lengths along the eight C_α—C_{meso} bonds can be considered as a useful measure of macrocyclic conjugation. These values equal respectively: (SP)H 0.006, $(SCOP)H_2$ 0.004 Å, (SCP)H 0.025 Å, (3H-SCP) 0.043 Å. Considering this criterion the (SP)H and $(SCOP)H_2$ molecules are aromatic. In contrast non aromatic properties are expected for (SCP)H. Bond distances within the tripyrrolic indicate that this part of the macrocycle is highly conjugated in all species. In all cases they are comparable to the corresponding distances calculated for porphine and inverted porphine [14].

The DFT calculations collaborate well with the ring current effect, which can be considered as the usual measure of the carbaporhyrinoid aromaticity. Thus ^{1}H NMR spectra of **1** and **3** are consistent with the aromatic nature of these molecules [1, 5]. One can consider the ^{1}H NMR shifts of the internally located CH (NH) proton and the β-4 pyrrole resonances as a convenient spectroscopic criterion of aromaticity [5, 6]. Consistently, the (SCTPP)H can be classified as a border-line case of the carbaporphyrinoid aromaticity. The thiophene subunit attenuates conjugative pathways in (SCTPP)H as shown by DFT calculations providing, however, a very efficient 18π delocalization path for (STPP)H, which is due to the difference of the orientation of the thiophene moiety in the macrocyclic structure [5].

Method

The DFT calculations were carried out with the GAUSSIAN94 program [19]. All structures were optimized within unconstrained C_1 symmetry of the system at the density functional theory (DFT) with Becke's three-parameter exchange functionals and the gradient-corrected functionals of Lee, Yang and Parr (DFT (B3-LYP)) [20]. Final estimations of the total electronic energies were performed at the B3-LYP level with the 6-31G* basis set using the B3-LYP/3-21G* reference structures.

Acknowledgments

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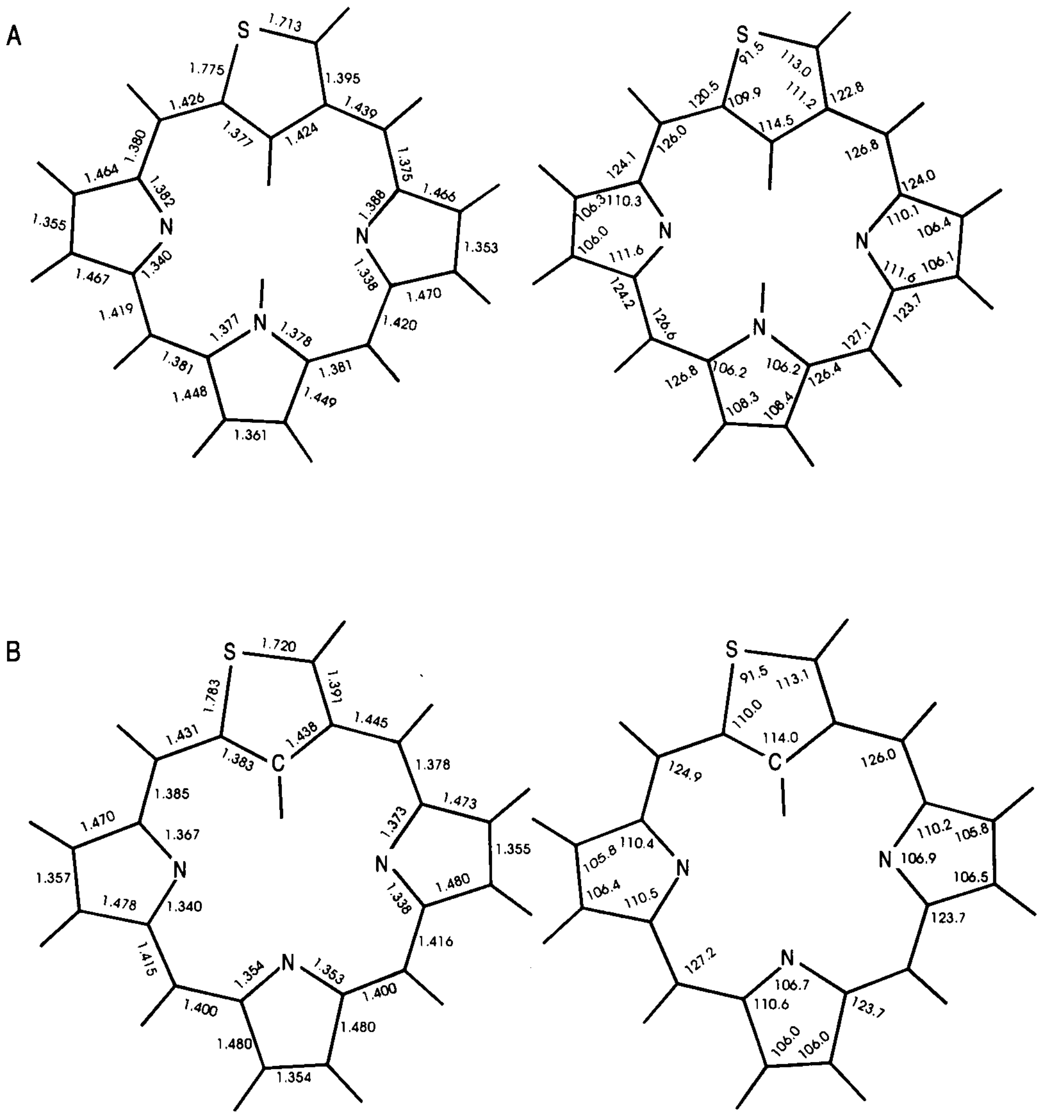
A
S
N
N
N
1.713
1.775
1.395
1.426
1.439
1.377
1.424
1.380
1.375
1.464
1.382
1.388
1.466
1.355
1.353
1.340
1.338
1.467
1.470
1.419
1.420
1.377
1.378
1.381
1.381
1.448
1.449
1.361
91.5
113.0
120.5
109.9
111.2
122.8
114.5
126.0
126.8
124.1
124.0
106.3
110.3
110.1
106.4
106.0
111.6
111.6
106.1
124.2
123.7
126.6
127.1
126.8
106.2
106.2
126.4
108.3
108.4
B
S
C
N
N
N
1.720
1.783
1.391
1.431
1.438
1.445
1.383
1.378
1.385
1.473
1.470
1.367
1.373
1.357
1.355
1.478
1.340
1.338
1.480
1.415
1.416
1.354
1.353
1.400
1.400
1.480
1.480
1.354
91.5
113.1
110.0
114.0
124.9
126.0
105.8
110.4
110.2
105.8
106.4
110.5
106.9
106.5
123.7
127.2
106.7
110.6
123.7
106.0
106.0

Figure 2. Optimized (B3LYP/6-31G) geometries of (SCP)H (A) and (SCP)$^-$ (B). Bond lengths are in angstroms and the bond angles are in degrees.

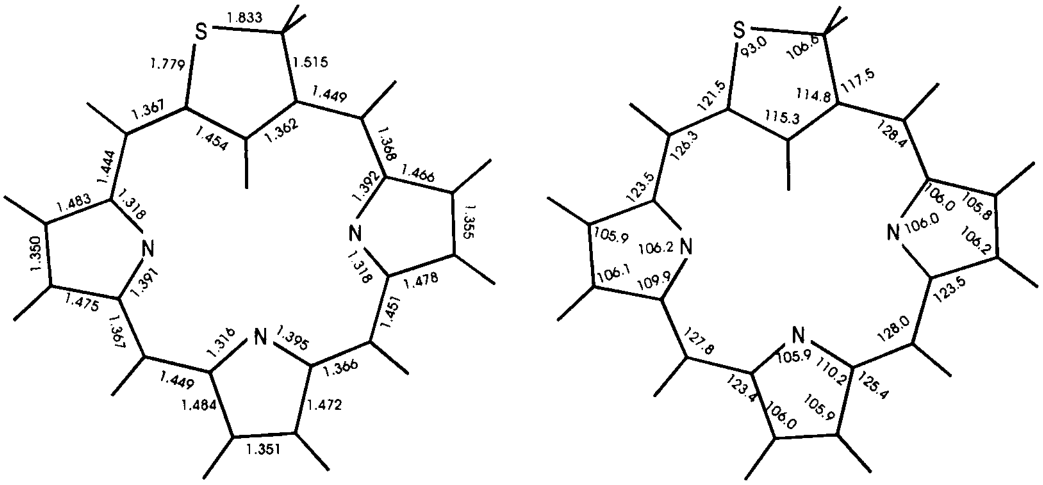
S
N
N
N
1.833
1.779
1.515
1.367
1.449
1.454
1.362
1.444
1.368
1.483
1.318
1.392
1.466
1.350
1.355
1.391
1.318
1.475
1.478
1.367
1.451
1.316
1.395
1.366
1.449
1.484
1.472
1.351
93.0
106.8
121.5
114.8
117.5
115.3
126.3
128.4
123.5
106.0
105.8
105.9
106.2
106.0
106.1
109.9
106.2
123.5
127.8
128.0
105.9
110.2
125.4
123.4
106.0
105.9

Figure 3. Optimized (B3LYP/6-31G) geometry of (3H-SCP). Bond lengths are in angstroms and the bond angles are in degrees.

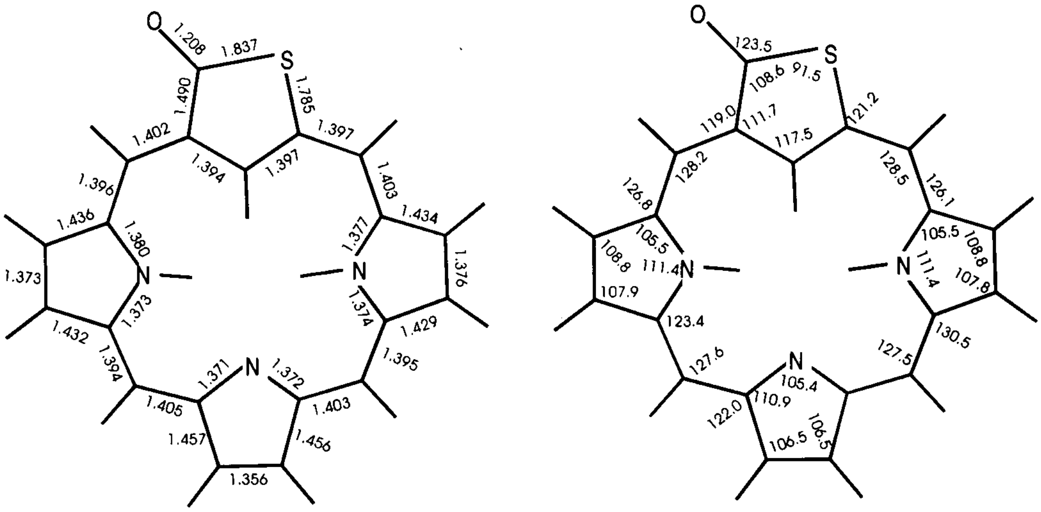
O
1.208
1.837
S
1.490
1.785
1.402
1.397
1.394
1.397
1.396
1.403
1.436
1.380
1.371
1.434
N
N
1.373
1.376
1.432
1.373
1.374
1.429
1.394
1.371
N
1.372
1.395
1.405
1.403
1.457
1.456
1.356
O
123.5
S
108.6
91.5
119.0
111.7
121.2
117.5
128.2
128.5
126.8
126.1
105.5
105.5
108.8
108.8
111.4
N
N
111.4
107.9
107.8
123.4
130.5
127.6
127.5
N
105.4
122.0
110.9
106.5
106.5

Figure 4. Optimized (B3LYP/6-31G) geometry (SCOP)H2. Bond lengths are in angstroms and the bond angles are in degrees.

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