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Supporting Information for

On the Flexibility of Carboranylalkylthio Substituents in Porphyrazines and Its Relevance to the Photophysical Properties

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Experimental Details

Materials

All chemical and solvents (Aldrich Chemicals Ldt.) were of reagent grade and used in the syntheses as supplied. *o*-carborane was purchased from KATCHEM. Solvents used in physical measurements were of spectroscopic or HPLC grade. THF was freshly distilled from sodium benzophenone ketyl under nitrogen.

Physical Measurements

(a) Room Temperature NMR Measurements. ^{1}H (^{11}B) and ^{13}C (^{1}H) NMR spectra were recorded on an INOVA Varian 500 MHz spectrometer and on a Varian VNMRS 400 MHz spectrometer, respectively. ^{11}B (^{1}H) NMR spectra were recorded on a Varian VNMRS 400 MHz spectrometer. Chemical shifts (δ) are expressed in parts per million (ppm). Coupling constants (*J*) are in Hz. The ^{1}H and ^{13}C NMR chemical shifts are relative to tetramethylsilane. The ^{11}B NMR chemical shifts are relative to external $BF_3{\cdot}OEt_2$. All measurements were carried out at 298 K. Abbreviations used in the description of the NMR data are as follows: b, broad; s, singlet; d, doublet; t, triplet; q, quartet; qt, quintet; dd, double doublet; m, multiplet.

(b) Dynamic ^{1}H NMR Measurements. Variable temperature (VT) ^{1}H NMR spectra were recorded with a Varian INOVA spectrometer operating at 600 MHz and 14.09 T. In the VT experiments the sample, dissolved in CD_2Cl_2, was cooled at the appropriate temperature by a flow of dry nitrogen precooled in the standard spectrometer heat exchanger immersed in liquid nitrogen. In the coalescence range, the temperature was let to equilibrate at least for 20 minutes before acquiring the experimental measure.

The temperature calibration was checked before experiments using a calibrated Cu/Ni thermocouple immersed in a dummy sample tube filled with *iso*-pentane in order to obtain nearly identical conditions. The uncertainty in the temperatures was estimated from a calibration curve to be in the range of ± 0.5 °C.

Line shape simulation of the ^{1}H traces were performed by using a PC version of the QCPE program[1] and the best fit was visually judged by superimposing the simulated and experimental traces.

(c) IR and GC-MS Spectra. IR spectra were measured with a FT/IR-460-Plus JASCO spectrometer. GC-MS spectra were measured with an Hewlett-Packard 6890.

(d) UV/vis Absorption Spectra. The ground state electronic absorption spectra were recorded at room temperature on a Varian Cary 50 Bio (Varian Corporation) UV/vis single beam spectrophotometer using 10 mm or 2 mm path length quartz cuvettes.

(e) Fluorescence Spectra. Fluorescence spectra were acquired with a Q-switched Nd:YAG laser (Spectra Physics Quanta Ray GCR-230) using 8 ns excitation pulses. The laser operated in the frequency tripled mode at 355 nm (10 Hz, 5 mJ) and an homebuilt nanosecond laser flash photolysis system, which was described elsewhere.[2-4]For the detection of the emission, the probe white light continuum was blocked and appropriate filters were used to avoid scattered light from laser beam entering the photomultiplier tube (PMT). To obtain emission spectra, solutions were Ar saturated prior to the experiment. The concentration of the samples was *ca*. 15 μM providing $A_{355} = 0.5$ in a 10 mm cuvette. Absolute fluorescence quantum yield for H_2HEHCSPz and H_2OESPz was estimated using the Strickler-Berg equation.

(e) Ultrafast Pump-probe Measurements. The pump-probe instrument for ultrafast transient absorption measurements available in the Ohio Laboratory for Kinetic Spectrometry was employed to characterize the excited state deactivation of the studied compounds. [3, 4] In the current experiments, the excitation wavelengths at 340 or 640 nm were generated with an optical parametric amplifier (OPA 800, Spectra Physics), pumped with 800 nm light from an amplified, mode-locked Ti:Sapphire laser (Hurricane, Spectra-Physics). The white light continuum generation was accomplished by focusing the 800 nm fundamental into either a CaF_2 crystal (350-780 nm effective spectral range) or a sapphire plate (450-810 nm effective spectral range). The linear polarization of the pump beam was set at an angle 54.7° with

respect to that of the probe beam, in order to eliminate the influence of molecular reorientation on the observed dynamics. The instrument response time of the ultrafast spectrometer was ca. 200 fs. Typical pump energy at the sample was 1 μJ per pulse. The sample cell had an optical path of 2 mm. The absorption spectra of the solutions were measured before and after the experiment to check for possible sample degradation.

(f) Mass Spectra. Matrix Assisted Laser Desorption Ionization Mass Spectra (MALDI-MS) spectra were obtained with a Perspective Biosystems/CISESMA instrument or with a Micro-MX/Waters Maldi instrument. Samples for mass spectrometric analyses were prepared by dissolving 2–3 mL of porphyrazine solution ($< 10^{-4}$ M in CH_2Cl_2 or $CHCl_3$) directly in the matrix. The matrix was deposited on the probe tip by placing 3 mL of a solution of α-cyano-4-hydroxy cinnammic acid in a 4:1 CH_2Cl_2/isopropyl alcohol mixture, or 2 mL of a solution of α-cyano-4-hydroxy cinnammic acid (10 mg) in a 1:1 H_2O/acetonitrile mixture (1 mL) added by 1% trifluoroacetic acid (TFA), and allowing the solution to evaporate. Time-of-flight (ToF) mass spectra were obtained by irradiating the sample with 10 ns pulses of a Nd(YAG) laser operating at 530 nm. The spectra from 50 laser shots were averaged to obtain better statistics. Mass spectral data were elaborated using the Masslynx software (Waters).

Computational Details

All calculations were performed with the Amsterdam Density Functional (ADF) program package, release 2013,[5-8] employing the all-electron TZ2P basis set. The calculations were performed on the model compound H_2OMSPz in which the alkyl chains are replaced by methyl groups. Only the most stable, nearly degenerate, C_{2h} and C_{2v} symmetry conformers of H_2OMSPz were considered. To model the electronic effects of the twisting of the methyl groups around the C_β–S bond, for each conformer two structures were considered, the equilibrium structure, **a**, and a structure of the same symmetry as **a** with the methyl groups constrained to be nearly coplanar with the Pz ring, **b**. The C_{2h} and C_{2v} equilibrium structures were optimized in CH_2Cl_2 solution using both, the pure GGA BP86[9, 10] functional, and the hybrid B3LYP[11-13] functional. The optimized structures were verified to be true minima by frequency calculations. The C_{2h} and C_{2v} **b** structures of H_2OMSPz were optimized at B3LYP/TZ2P level in in CH_2Cl_2 solution by constraining the C_{Me}–S–C_β–C_β torsion angles formed by the methylthio groups with the C_β–C_β bonds of the pyrroles (θ_1) and pyrrolenine rings (θ_2) to the values of 170° and 10°, respectively. The lowest singlet and triplet excited states of the **a** and **b** structures of the C_{2h} and C_{2v} conformers of H_2OMSPz were computed in CH_2Cl_2 solution at TDDFT/B3LYP/TZ2P level of theory using the ground state B3LYP geometries. Solvent effects on the ground state molecular and electronic structure and on the excited states were modeled through a dielectric continuum model, which was chosen to be the COSMO model.[14-17] The calculated excitation energies contain, apart from the altered “solvated” orbitals (slow term), also the contributions from the “fast” solvent response term.[18, 19]

Syntheses

TBDMS-*o*-carborane (2). This compound was prepared according to a slightly modified literature procedure.[20] A solution of 1,2-dicarba-*closo*-dodecaborane, **1**, (1.52 g, 10.5 mmol) in 20 mL of dry THF was cooled to 0 °C and a 1.6 M solution of *n*-BuLi in hexane (7.8 mL; 12.5 mmol, 20% excess) was added dropwise with stirring. The mixture was allowed to stir for 30 min while being warmed to ambient temperature. The solution was cooled to 0 °C and *terz*-butyldimethylsilyl chloride (1.76 g, 11.6 mmol, 10% excess), TBDMSCl, diluted in THF (3.0 mL) was added rapidly. The solution was refluxed at 70 °C for 8 h and then quenched with 40 mL of distilled water. The organic phase was extracted with diethyl ether (3 x 30 mL), dried over anhydrous Na_2SO_4 and concentrated in vacuo to give a pale orange oil. The crude product was purified by sublimation in vacuo (10 mmHg) at 84 °C and the residue was purified by silica-gel column chromatography to give a white solid. Yeld 94% (2.53 g, 9.8 mmol).^{1}H NMR ($CDCl_3$, 500 MHz): δ/ppm 3.46 (br s, 1H, C–H), 2.9-1.5 (br, 10H, B–H), 1.04 (s, 9H, $(CH_3)_3$–CSi-), 0.25 (s, 6H, $(CH_3)_2$–Si-). ^{13}C NMR ($CDCl_3$, 125 MHz) δ/ppm 66.3, 60.5, 27.2, 19.6,
–4.31. ^{11}B NMR ($CDCl_3$, 128 MHz) δ/ppm 0.3 (1B), –1.7 (1B), –7.0 (2B), -10.6 (2B), –12.2 (2B), –13.3 (2B). MS (EI): *m/z* calcd for $C_8H_{26}B_{10}Si$ 258.5; found 258 ([M^+]).

6-(TBDMS-*o*-carboranyl)-1-bromohexane (3). This compound was prepared according to a slightly modified literature procedure.[20]A solution of **2** (2.47 g, 9.6 mmol) in 25 mL of dry benzene/diethyl ether (2:1, v/v) was cooled to 0 °C and a 1.6 M solution of *n*-BuLi in hexane (7.4 mL, 11.8 mmol, 20% excess) was added dropwise with stirring. The mixture was allowed to stir for 30 min while being warmed to ambient temperature. The solution was cooled to 0 °C and 1,6-dibromohexane (5.2 mL, 35.7 mmol) was added dropwise with stirring. The solution was refluxed to 80 °C for 7 h and then quenched with 40 mL of water. The organic phase was extracted with diethyl ether (4 x 30 mL), dried over anhydrous Na_2SO_4 and concentrated in vacuo. Vacuum distillation of the crude product to remove excess 1,6-dibromohexane resulted in a crude residue that was purified by silica-gel column chromatography (pentane). Yield 44% (1.77 g, 4.2 mmol). ^{1}H NMR ($CDCl_3$, 500 MHz) δ/ppm 3.4 (t, 2H, *J* = 6.8 Hz, CH_2-Br), 2.2 (m, 2H), 1.85 (qt, 2H, *J* = 6.8 Hz), 1.54 (m, 2H), 1.45 (m, 2H), 1.27 (m, 2H), 1.1 (s, 9H, $(CH_3)_3$-CSi-), 0.3 (s, 6H, $(CH_3)_2$-Si-). ^{13}C NMR ($CDCl_3$, 125 MHz) δ/ppm 83.8, 76.6, 40.2, 30.1, 34.8, 32.4, 30.8, 30.2, 30.0, 22.8, 2.5. MS (EI): *m/z* calcd for $C_{14}H_{37}B_{10}SiBr$ 407; found 407 ($[M-15]^+$).

***cis*-2,3-bis[6-(1,2-*closo*-1-TBDMS-dodecarboran-2-yl)hexylthio]maleonitrile (4).** To a solution of **3** (619 mg, 1.5 mmol) in 14 mL of MeOH/THF (6:1, v/v) mixture dimercaptomaleonitrile disodium salt (290 mg, 1.6 mmol) was added at 0 °C. The mixture was stirred for 24 h at room temperature in the dark. The solution was concentrated in vacuo and the crude product was diluted with 80 mL and extracted with $CHCl_3$ (3 x 40 mL). The organic phase was dried over anhydrous Na_2SO_4, and concentrated in vacuo; the crude product was purified at first by column chromatography on silica gel (CH_2Cl_2/Hexane, 5:5) and the product was purified again by PLC (preparative layer chromatography, 2 mm) using a 65:35 v/v CH_2Cl_2/hexane mixture as eluant. (R_f = 0.71). Yield 12% (147 mg, 0.18 mmol). ^{1}H NMR ($CDCl_3$, 500 MHz) δ/ppm 3.12 (4H, t, *J*=7.5 Hz, CH_2S), 2.19 (4H, m), 1.72 (4H, m), 1.54 (4H, m), 1.43(4H, m), 1.28 (4H, m), 1.07 (18H, s, $(CH_3)_3CSi$-), 0.33 (12H, s, $(CH_3)_2Si$-). ^{13}C NMR ($CDCl_3$, 125 MHz) δ/ppm 121.1, 121.3, 81.6, 76.4, 38.0, 35.1, 30.3, 29.9, 28.8, 28.3, 27.84, 27.79, 20.6.

[MgHE(TBDMS)CSPz]: Mg(II) [2,3,7,8,12,13,17,18 - octakis - (1-TBDMS - 1,2 - dicarba - *closo* -dodecaboran - 2 - yl)hexylthio - 5,10,15,20 - porphyrazinate] (5). A dispersion of Mg (15 mg) and I_2 in catalytic amount in dry 1-propanol (5 mL) was refluxed at 130°C for 12 h under N_2. **4** was then added (147 mg, 0.18 mmol) and the solution was heated at reflux at 90-100°C for 24 h. The hot mixture was filtered and evaporated in vacuo. The crude product was purified twice by PLC (preparative layer chromatography, 2 mm) using a 95:5 v/v $CHCl_3$/MeOH mixture as eluant. (R_f = 0.55). The pure product was retrieved in 20% yield (50 mg, 0.01 mmol). ^{1}H NMR ($CDCl_3$, 400 MHz): δ/ppm 4.0 (br m, CH_2S), 3.2 (br s, 8H, C_{carb}–H), 2.07 (br, 16H), 1.80 (br, 16H), 1.58 (br, 16H), 1.42 (16H, br), 1.25 (br, 16H), 2.9-1.5 (br, 80H, B-H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ/ppm 157, 140, 77.6, 63.6, 40.2, 32.5, 32.2, 31.5, 30.8, 30.6. ^{11}B NMR ($CDCl_3$, 128 MHz) δ/ppm –2.6 (1B), –5.7 (1B), –9.3 (2B), –11.7 (6B). FT-IR: (film on KBr disk, cm^{-1}) 3062 (C_{carb}–H), 2931, 2588 (B–H). UV-Vis ($CHCl_3$/MeOH, 99:1, v:v): [λ_{max}/nm (log ε)] 676 (4.10), 513 (2.50), 377 (4.20). Anal. Calcd. for $C_{128}H_{304}B_{80}N_8S_8MgSi_8$: C, 46.22%; H, 9.21%; N, 3.37%; S, 7.71%. Found: C, 46.51%; H, 9.30%; N, 3.18%; S, 7.80%.

MgHEHCSPz: Mg(II) [2,3,7,8,12,13,17,18 - octakis - (1,2 - dicarba - *closo* - dodecaboran - 2 - yl) hexylsulfanyl - 5,10,15,20 - porphyrazinate] (6). This compound and the corresponding free base porphyrazine **7** were prepared according to a literature procedure.[21] A solution of **5** (25 mg, 0.008 mmol) in 2 mL of freshly distillated THF was cooled to -78°C and tetrabutylammonium fluoride (627 mg, 2.40 mmol) diluted in THF (2 mL) was added dropwise with stirring. The mixture was allowed to stir for 7 h while being warmed to room temperature, and then 15 mL of water was added. The solution was diluted with 15 mL of CH_2Cl_2 and transferred to a separatory funnel. The organic layer was separated and the aqueous layer was extracted with additional CH_2Cl_2 (3 x10 mL). The organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuo; the crude product was purified by semipreparative layer chromatography (0.5 mm) using a 95:5 v/v CH_2Cl_2/MeOH mixture as eluant. (R_f = 0.9). The pure product was retrieved in 37% yield (7 mg, 0.003 mmol). ^{1}H NMR ($CDCl_3$, 400 MHz) δ/ppm 4.0 (br m, SCH_2), 3.2 (br s, 8H, C_{carb}–H), 2.07 (br, 16H), 1.80 (br, 16H) , 1.58 (br, 16H), 1.42 (br, 16H), 1.25 (br, 16H), 2.9-1.5 (br, 80H, B-H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ/ppm 157, 140, 77.6, 63.6, 40.2, 32.5, 32.2, 31.5, 30.8, 30.6. ^{11}B NMR ($CDCl_3$, 128 MHz) δ/ppm –2.6 (1B), –5.7 (1B, br), –9.3 (2B), –11.7 (6B, br). FT-IR (film on KBr disk, cm^{-1}): 3062 (C_{carb}–H), 2931, 2588 (B–H). UV-Vis: ($CHCl_3$/MeOH, 99:1, v:v) [λ_{max} (log ε)] 676 (4.10), 513 (2.50), 377 (4.20). Anal. Calcd. for $C_{80}H_{184}B_{80}S_8N_8Mg$: C, 40.0%; H, 7.7%; N, 4.7%; S, 10.7%. Found: C, 40.8%; H, 7.9%; N, 4.5%; S, 10.8%.

H_2HEHCSPz: 2,3,7,8,12,13,17,18 – octakis - (1,2 - dicarba-*closo*-dodecaboran-2- yl) hexylthio-5,10,15,20 - (21*H*, 23*H*) porphyrazine (7). To a solution of **5** (20 mg, 0.008 mmol) in $CHCl_3$ (2 mL) TFA (1.5 mL) was added dropwise with stirring and a blue-green to violet color change was observed. The mixture was stirred for 15 min. at room temperature and then transferred on ice and neutralized with aqueous ammonia solution (30%). The organic phase was extracted with $CHCl_3$ (3 x 10 mL), dried over anhydrous Na_2SO_4 and concentrated under vacuum. The crude product was purified by PLC (20 x 20 x 0.5 mm, $CHCl_3$/hexane 6:4, v/v) to give a violet solid. Yield 25% (5 mg, 0.002 mmol). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 4.03 (t, 16H, J = 7.0 Hz, S-CH_2), 3.22 (s, 8H, C_{carb}–H), 1.91(m, 16H) 1.78 (m, 16H), 1.53 (m, 16H), 1.21 (m, 32H), 2.9-1.5 (br, 80H, B–H), –1.18 (s, 2H, N_p–H). ^{11}B NMR($CDCl_3$, 128 MHz) δ/ppm –2.6 (1B), –5.7 (1B, br), –9.3 (2B), –11.7 (6B, br). ^{13}C NMR ($CDCl_3$, 100 MHz) δ/ppm 157, 140, 77.4, 63.1, 40.0, 32.5, 32.2, 31.3, 30.8, 30.4. FT-IR: (film on KBr disk, cm^{-1}) 3289 (N_p–H), 3062 (C_{carb}–H), 2588 (B–H). MALDI-ToF: *m/z* calcd. for $C_{80}H_{187}B_{80}N_8S_8$: 2383.290; found: 2383.029 ($[M+H]^+$). Anal. Calcd. for $C_{80}H_{186}B_{80}N_8S_8$: C, 40.34%; H, 7.87%; N, 4.70%; S, 10.77%. Found C, 40.58%; H, 7.75%; N, 4.47%; S, 10.52%

H_2OMSPz: 2,3,7,8,12,13,17,18-Octakis(methylthio)-5,10,15,20-porphyrazine. This free-base porphyrazine was prepared according to a literature method.[22] This method involved the synthesis of *cis*-1,2-dicyano-1,2-bis(methylthio)-ethylene by reaction of disodium *cis*-1,2-dicyano-1,2-ethylenedithiolate with iodomethane in MeOH and its subsequent template condensation in a suspension of magnesium isopropoxide to form MgOMSPz. Dissolution of the Mg(II) derivative in cold, concentrated CF_3COOH followed by careful neutralization produced H_2OMSPz in high yield. Specifically, MgOMSPz was dissolved in a small amount of concentrated CF_3COOH and carefully transferred on iced water. The solution was then washed with a NH_3 solution (30%) until the washing water was fully neutralized. The dark product was collected with $CHCl_3$ using a separating funnel, dried over sodium sulfate, and filtered. After removal of the solvent, the crude product was carefully purified by flash chromatography on silica gel (first band) using (7:3) (v/v) CH_2Cl_2/*n*-hexane as eluant. The free-base porphyrazine was obtained in a yield of ca. 65% with respect to MgOMSPz. ^{1}H NMR ($CDCl_3$, 500 MHz), δ/ppm: 3.42 (s, 24 H, S–CH_3), -3.26 (s, 2H). UV-vis UV-Vis ($CHCl_3$/MeOH, 99:1, v:v): [λ_{max}/nm (log ε)]: 361 (4.50), 504 (4.16), 635 (4.24), 708 (4.34). Anal. Calcd. for $C_{24}H_{26}N_8S_8$: C, 42.20%; H, 3.84%; N, 16.41%; S, 37.55%. Found: C, 42.15%; H, 3.70%; N, 16.25%; S, 37.80%.

H_2OESPz: 2,3,7,8,12,13,17,18-Octakis(ethylthio)-5,10,15,20-porphyrazine. The free base porphyrazine was prepared according to a slightly modified literature method.[23] This method involved the synthesis of *cis*-1,2-dicyano-1,2-bis(ethylthio)- ethylene by reaction of disodium *cis*-1,2-dicyano-1,2-ethylenedithiolate with bromoethane in MeOH and its subsequent template condensation in a suspension of magnesium isopropoxide to form MgOESPz. Dissolution of the Mg(II) derivative in cold, concentrated CF_3COOH followed by careful neutralization produced H_2OESPz in high yield. Tipically, MgOESPz was dissolved in a small amount of concentrated CF_3COOH and carefully transferred on ice water. The solution was then washed with a NH_3 solution (30%) until the washing water was fully neutralized. The dark product was collected with $CHCl_3$ using a separating funnel, dried over sodium sulfate, and filtered. After removal of the solvent, the crude product was carefully purified by flash chromatography on silica gel (first band) using (7:3) (v/v) CH_2Cl_2/*n*-hexane as eluant. The free-base porphyrazine was obtained in a yield of ca. 65% with respect to MgOESPz. ^{1}H NMR ($CDCl_3$, 500 MHz), δ/ppm: –0.95 (s, 2H), 1.52 (t, 24 H, S–CH_2–CH_3), 4.25 (q, 16 H, S–CH_2–). UV–vis ($CHCl_3$), λ_{max}/nm (log ε): 360 (4.67); 490 (4.17), 655 (4.60), 715 (4.18). MALDI-ToF: *m/z* calcd. for $C_{32}H_{42}N_8S_8$: 794; found 794 ([M^+]). Anal. Calcd. for $C_{32}H_{42}N_8S_8$: C, 48.35%; H, 5.30%; N, 14.01%; S, 32.25%. Found: C, 48.25%; H, 5.25%; N, 14.00%; S, 32.15%.

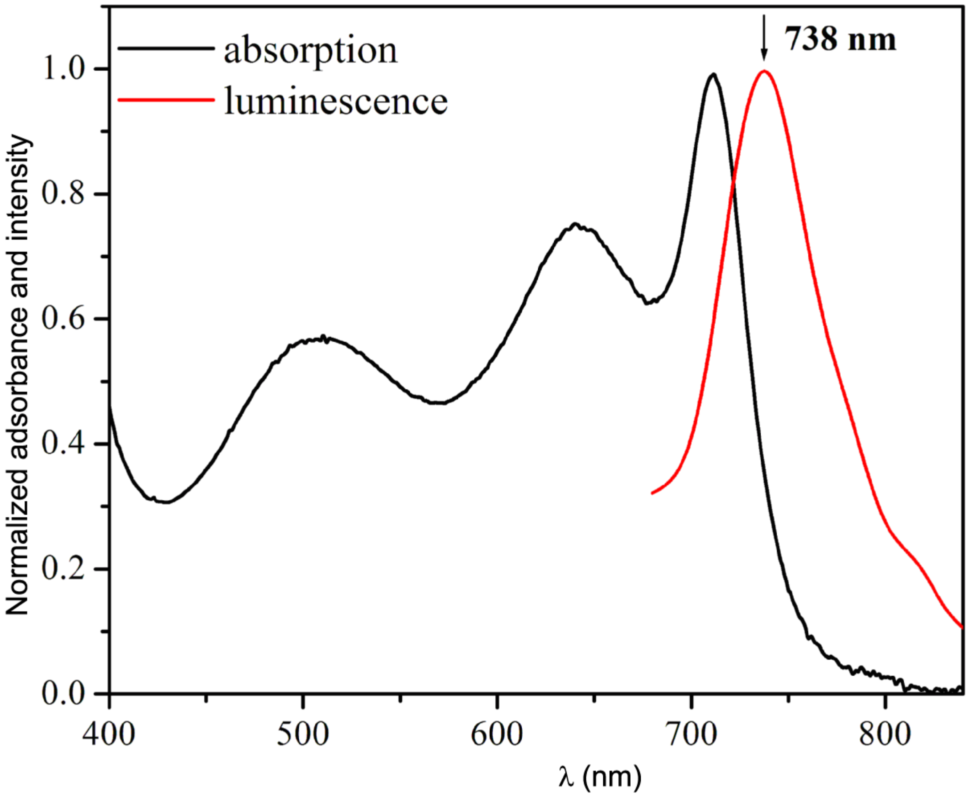

Figure S1. Normalized electronic absorption and emission spectra of H_2HEHCSPz in CH_2Cl_2.

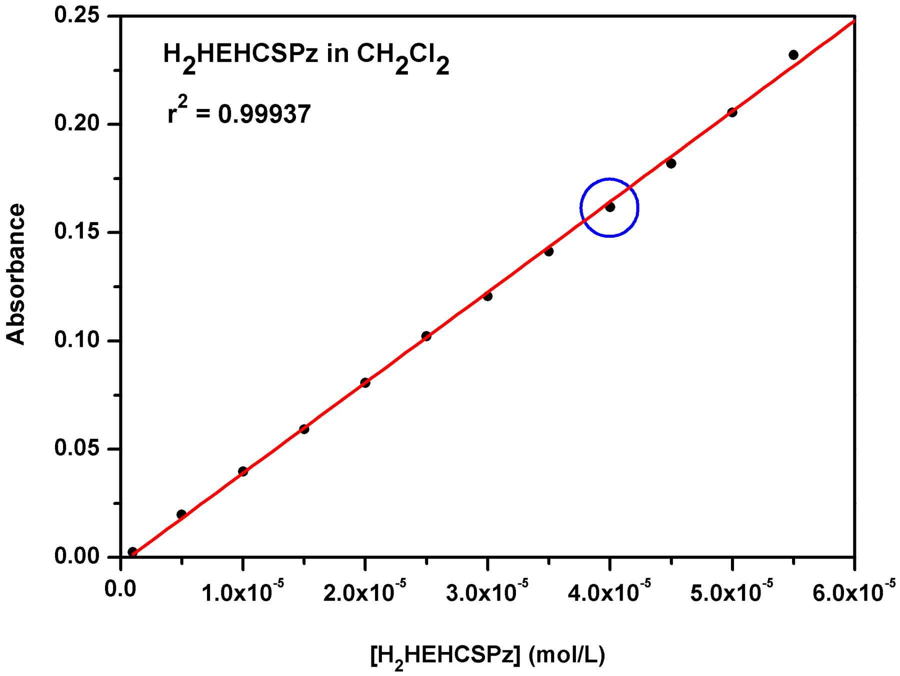

Figure S2. Lambert-Beer plot for $H_2HEHCSPz$ in CH_2Cl_2. The circled dot refers to the porphyrazine concentration used in the photophysical experiments.

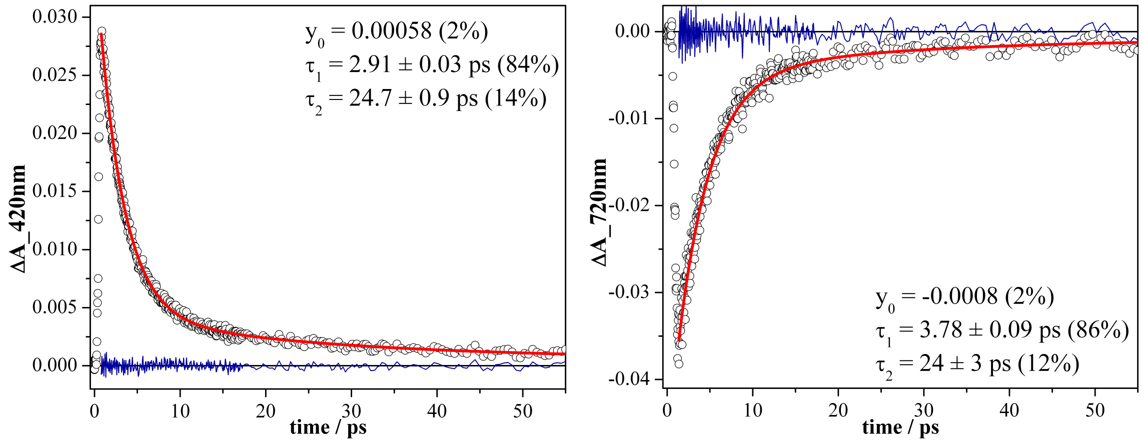

Figure S3. Kinetics profiles of the transient absorption signals of 40 *μ*M H_2HEHCSPz in CH_2Cl_2 after 340 nm excitation taken at 420 nm and 720 nm probe wavelengths. Solid red lines are fits to the experimental points, blue lines are residues of the fit.

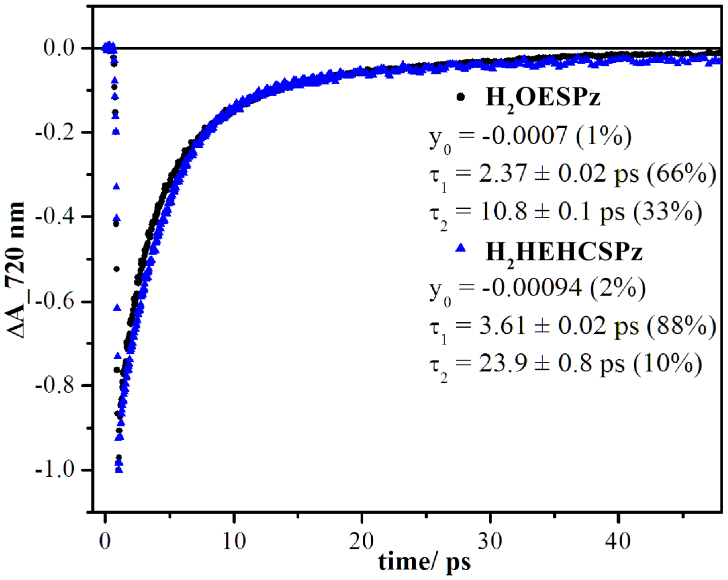

Figure S4. Normalized transient absorption temporal profiles for H_2OESPz and H_2HEHCSPz in CH_2Cl_2 after 640 nm excitation taken at 720 nm probe wavelength together with the fitting results.

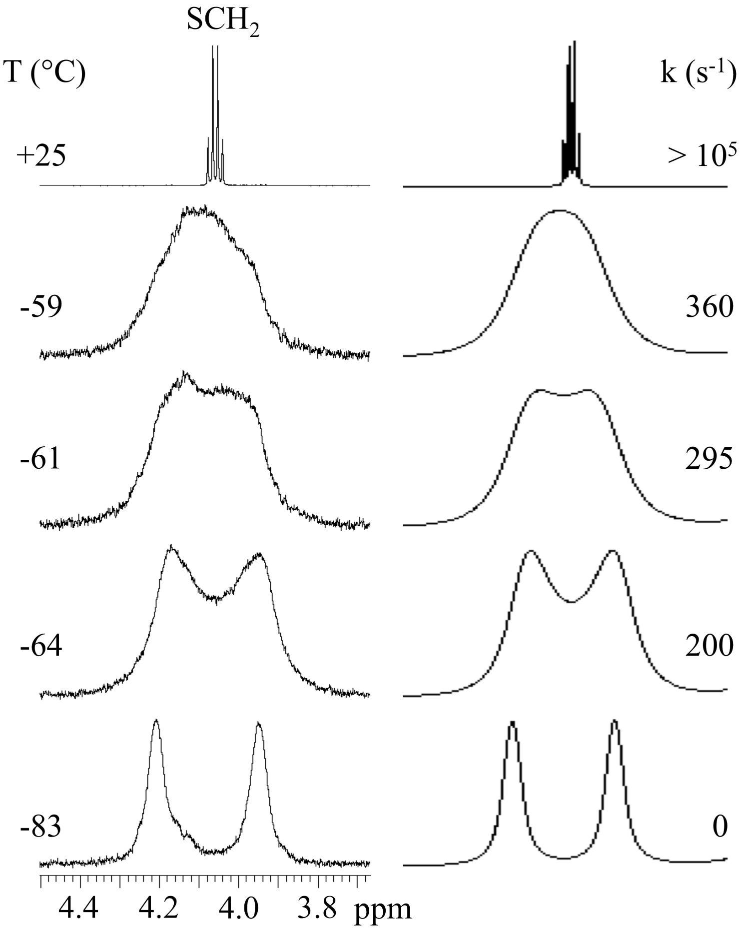

Figure S5. ^{1}H NMR experimental traces for H_2OESPz showing the temperature dependence of the SCH_2 signal at 4.10 ppm (left). Simulated traces and computed rate constants (right).

Table S1. Vertical Excitation Energies, E_{va} (eV/nm), Composition, Character, and Oscillator Strengths (f) of the Lowest Excited States of the H_2OMSPz C_{2h} Conformer in the Equilibrium **a** Structure

state	composition (%)	character	E_{va}	f	exp.[a]
1^1A_u	$43a_u \rightarrow 48a_g$ (82)	π, π*	1.841/673	0.5513	1.950/635 (Q_y)
1^1B_u $S_1(\pi,\pi^*)]$	$43a_u \rightarrow 42b_g$ (84)	π, π*	1.792/692	0.5235	1.750/708 (Q_x)
2^3A_u	$45b_u \rightarrow 42b_g$ (49) $46b_u \rightarrow 42b_g$ (42)	C_β-$2p_z/S_{\mathrm{l.p.}}$, π*	1.737/714		
2^3B_u	$46b_u \rightarrow 48a_g$ (83)	C_β-$2p_z/S_{\mathrm{l.p.}}$, π*	1.665/745		
1^3B_g	$41b_g \rightarrow 48a_g$ (90)	C_β-$2p_z/S_{\mathrm{l.p.}}$, π*	1.657/748		
1^3B_u	$43a_u \rightarrow 42b_g$ (95)	π, π*	1.253/990		
1^3A_u [$T_1(\pi,\pi^*)$]	$43a_u \rightarrow 48a_g$ (90)	π, π*	1.206/1028		

[a] CH_2Cl_2 solution spectrum, this work.

Table S2. Vertical Excitation Energies, E_{va} (eV/nm), Composition, Character, and Oscillator Strengths (f) of the Lowest Excited States of of the H_2OMSPz C_{2h} Conformer in the **b** Structure

state	composition (%)	character	E_{va}	f	exp.
3^1A_u	$43a_u \rightarrow 48a_g$ (66)	π, π^*	2.083/595	0.9435	1.950/635
	$45b_u \rightarrow 42b_g$ (15)	C_β-2p_z/$S_{\text{l.p.}}, \pi^*$			(Q_y)
2^1B_g	$47a_g \rightarrow 42b_g$ (92)		2.030/611	0.0000	
2^1A_u	$45b_u \rightarrow 42b_g$ (76)	C_β-2p_z/$S_{\text{l.p.}}, \pi^*$	1.903/652	$0.5379\text{x}10^{-3}$	
	$43a_u \rightarrow 48a_g$ (19)	π, π^*			
2^1B_u	$43a_u \rightarrow 42b_g$ (70)	π, π^*	1.835/676	0.3243	1.750/708
	$45b_u \rightarrow 48a_g$ (23)	C_β-2p_z/$S_{\text{l.p.}}, \pi^*$			(Q_x)
1^1B_u	$46b_u \rightarrow 48a_g$ (90)	C_β-2p_z/$S_{\text{l.p.}}, \pi^*$	1.792/692	$0.1135\text{x}10^{-1}$	
1^1B_g	$41b_g \rightarrow 48a_g$ (92)	C_β-2p_z/$S_{\text{l.p.}}, \pi^*$	1.780/697	0.0000	
1^1A_u	$46b_u \rightarrow 42b_g$ (98)	C_β-2p_z/$S_{\text{l.p.}}, \pi^*$	1.659/747	$0.2061\text{x}10^{-1}$	
2^1A_g	$41b_g \rightarrow 42b_g$ (97)	C_β-2p_z/$S_{\text{l.p.}}, \pi^*$	1.652/751	0.0000	
2^3B_g	$47a_g \rightarrow 42b_g$ (93)	C_β-2p_z/$S_{\text{l.p.}}, \pi^*$	1.664/745		
3^3A_u	$46b_u \rightarrow 42b_g$ (71)	C_β-2p_z/$S_{\text{l.p.}}, \pi^*$	1.586/782		
	$45b_u \rightarrow 42b_g$ (26)				
1^3A_g	$43a_u \rightarrow 48a_g$ (26)	π, π^*	1.551/799		
	$45b_u \rightarrow 42b_g$ (55)	C_β-2p_z/$S_{\text{l.p.}}, \pi^*$			
2^3A_u	$45b_u \rightarrow 42b_g$ (54)	C_β-2p_z/$S_{\text{l.p.}}, \pi^*$	1.534/808		
	$46b_u \rightarrow 42b_g$ (23)				
	$43a_u \rightarrow 48a_g$ (20)				
2^3B_u	$46b_u \rightarrow 48a_g$ (89)	C_β-2p_z/$S_{\text{l.p.}}, \pi^*$	1.449/856		
1^3B_g	$41b_g \rightarrow 48a_g$ (91)	C_β-2p_z/$S_{\text{l.p.}}, \pi^*$	1.436/863		
1^3A_u	$43a_u \rightarrow 48a_g$ (73)	π, π^*	1.297/956		
	$45b_u \rightarrow 42b_g$ (18)				
1^3B_u	$43a_u \rightarrow 42b_g$ (95)	π, π^*	1.255/988		

[a] CH_2Cl_2 solution spectrum, this work.

Table S3. Vertical Excitation Energies, E_{va} (eV/nm), Composition, Character, and Oscillator Strengths (*f*) of the Lowest Excited States of the H_2OMSPz C_{2v} Conformer in the Equilibrium **a** Structure

state	composition (%)	character	E_{va}	*f*	exp.[a]
1^1B_2	$40a_2 \rightarrow 45b_1$ (82)	π, π^*	1.833/676	0.4748	1.950/635 (Q_y)
1^1B_1 [$S_1(\pi,\pi^*)$]	$40a_2 \rightarrow 45b_2$ (85)	π, π^*	1.789/693	0.5229	1.750/708 (Q_x)
2^3B_2	$48a_1 \rightarrow 45b_2$ (54) $49a_1 \rightarrow 45b_2$ (37)	C_β-$2p_z$/$S_{\mathrm{l.p.}}$, π^*	1.766/702		
2^3B_1	$49a_1 \rightarrow 45b_1$ (88)	C_β-$2p_z$/$S_{\mathrm{l.p.}}$, π^*	1.673/741		
1^3A_2	$44b_2 \rightarrow 45b_1$ (91)	C_β-$2p_z$/$S_{\mathrm{l.p.}}$, π^*	1.664/745		
1^3B_1	$40a_2 \rightarrow 45b_2$ (94)	π, π^*	1.252/990		
1^3B_2 [$T_1(\pi,\pi^*)$]	$40a_2 \rightarrow 45b_1$ (89)	π, π^*	1.201/1032		

[a] CH_2Cl_2 solution spectrum, this work.

Table S4. Vertical Excitation Energies, E_{va}(eV/nm), Composition, Character, and Oscillator Strengths (f) of the Lowest Excited States of the H_2OMSPz C_{2v} Conformer in the **b** Structure

state	composition (%)	character	E_{va}	f	exp.^{b}
3^1B_2	$48a_1 \rightarrow 45b_2$ (76)	π, π^*	2.118/585	0.7955	1.950/635 (Q_y)
	$40a_2 \rightarrow 45b_1$ (11)				
2^1A_2	$44b_2 \rightarrow 45b_1$ (92)	C_β-$2p_z$/$S_{l.p.}$, π^*	2.070/599	0.0000	
3^1B_1	$48a_1 \rightarrow 45b_1$ (54)	C_β-$2p_z$/$S_{l.p.}$, π^*	2.053/604	0.6889	1.750/708
	$40a_2 \rightarrow 45b_2$ (26)	π, π^*			(Q_x)
2^3A_1	$44b_2 \rightarrow 45b_2$ (98)	C_β-$2p_z$/$S_{l.p.}$, π^*	2.013/616	0.0000	
3^3B_2	$48a_1 \rightarrow 45b_2$ (98)	C_β-$2p_z$/$S_{l.p.}$, π^*	1.908/650		
2^1B_1	$40a_2 \rightarrow 45b_2$ (55)	π, π^*	1.901/652	0.1741	
	$48a_1 \rightarrow 45b_1$ (36)	C_β-$2p_z$/$S_{l.p.}$, π^*			
2^1B_2	$40a_2 \rightarrow 45b_1$ (65)	π, π^*	1.821/681	0.3372	
	$48a_1 \rightarrow 45b_2$ (21)	C_β-$2p_z$/$S_{l.p.}$, π^*			
1^1B_2	$49a_1 \rightarrow 45b_2$ (76)	C_β-$2p_z$/$S_{l.p.}$, π^*	1.771/700	0.1949×10^{-2}	
1^1A_2	$44b_1 \rightarrow 45b_2$ (92)	C_β-$2p_z$/$S_{l.p.}$, π^*	1.765/702	0.0000	
2^1A_1	$44b_1 \rightarrow 45b_1$ (96)	C_β-$2p_z$/$S_{l.p.}$, π^*	1.753/707	0.8151×10^{-2}	
1^1B_1	$49a_1 \rightarrow 45b_1$ (95)	C_β-$2p_z$/$S_{l.p.}$, π^*	1.738/714	0.3601×10^{-1}	
2^3A_2	$44b_2 \rightarrow 45b_1$ (92)	C_β-$2p_z$/$S_{l.p.}$, π^*	1.689/734		
3^3B_1	$49a_1 \rightarrow 45b_1$ (98)	C_β-$2p_z$/$S_{l.p.}$, π^*	1.629/761		
1^3A_1	$44b_1 \rightarrow 45b_1$ (98)	C_β-$2p_z$/$S_{l.p.}$, π^*	1.613/769		
2^3B_1	$48a_1 \rightarrow 45b_1$ (87)	C_β-$2p_z$/$S_{l.p.}$, π^*	1.579/785		
2^3B_2	$49a_1 \rightarrow 45b_1$ (87)	C_β-$2p_z$/$S_{l.p.}$, π^*	1.426/869		
1^3A_2	$44b_1 \rightarrow 45b_2$ (91)	C_β-$2p_z$/$S_{l.p.}$, π^*	1.419/874		
1^3B_1	$40a_2 \rightarrow 45b_2$ (85)	π, π^*	1.235/1004		
1^3B_2	$40a_2 \rightarrow 45b_1$ (92)	π, π^*	1.231/1007		

[a] CH_2Cl_2 solution spectrum, this work.

References

1. QCPE Program n. 633; Indiana University: Bloomington, USA.
2. B. D. Rihter, M. E. Kenney, W. E. Ford and M. A. J. Rodgers, *J. Am. Chem. Soc.*, 1990, **112**, 8064.
3. A. P. Pelliccioli, K. Henbest, G. Kwag, T. R. Carvagno, M. E. Kenney and M. A. J. Rodgers, *J. Phys. Chem. A*, 2001, **105**, 1757.
4. A. V. Nikolaitchik, O. Korth and M. A. J. Rodgers, *J. Phys. Chem. A*, 1999, **103**, 7587.
5. ADF2013, SCM, Theoretical Chemistry, Vrije Universiteit, Amsterdam, The Netherlands, http://www.scm.com.
6. E. J. Baerends, D. E. Ellis and P. Ros, *Chem. Phys.*, 1973, **2**, 41.
7. C. Fonseca Guerra, J. G. Snijders, G. te Velde and E. J. Baerends, *Theor. Chem. Acc.*, 1998, **99**, 391.
8. G. te Velde, F. M. Bickelhaupt, E. J. Baerends, C. Fonseca Guerra, S. J. A. van Gisbergen, J. G. Snijders and T. Ziegler, *J. Comput. Chem.*, 2001, **22**, 931.
9. A. D. Becke, *Phys. Rev. A*, 1988, **38**, 3098.
10. J. P. Perdew, *Phys. Rev. B*, 1986, **33**, 8822
11. A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648.
12. C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785.
13. P. J. Stephens, F. J. Devlin, C. F. Chabalowski and M. J. Frisch, *J. Phys. Chem.*, 1994, **98**, 11623.
14. A. Klamt and G. Schürmann, *J. Chem. Soc., Perkin Trans.*, 1993, **2**, 799.
15. A. Klamt, *J. Phys. Chem.*, 1995, **99**, 2224.
16. A. Klamt and V. Jonas, *J. Chem. Phys.*, 1996, **105**, 9972.
17. C. C. Pye and T. Ziegler, *Theor. Chem. Acc.*, 1999, **101**, 396.
18. A. Klamt, *J. Phys. Chem.*, 1996, **100**, 3349–3353.
19. G. Scalmani, M. J. Frisch, B. Mennucci, J. Tomasi, R. Cammi and V. Barone, *J. Chem. Phys.*, 2006, **124**, 094107-094121.
20. F. A. Gomes and M. F. Hawthorne, *J. Org. Chem.*, 1997, **52**, 1384-1390.
21. G. Ricciardi, S. Ristori, A. Rosa and D. Pietrangeli, *J. Porphyrins Phthalocyanines*, 2010, **14**, 678-688.
22. G. Ricciardi, S. Belviso, G. Giancane, R. Tafuro, T. Wagner and L. Valli, *J. Phys. Chem. B*, 2004, **108**, 7854-7861.

23. G. Ricciardi, A. Rosa, I. Ciofini and A. Bencini, *Inorg. Chem.*, 1999, **38**, 1422-1431.

Cartesian Coordinates (Å) of the H_2OMSPz C_{2h} conformer optimized at DFT/BP86/COSMO/TZ2P level of theory in CH_2Cl_2 solution.

Atom	X	Y	Z
1.N	0.000000	0.000000	1.917725
2.N	0.000000	0.000000	-1.917725
3.N	-2.019448	-0.012272	0.000000
4.N	2.019448	0.012272	0.000000
5.C	-1.087129	0.035306	2.741403
6.C	-1.087129	0.035306	-2.741403
7.C	1.087129	-0.035306	2.741403
8.C	1.087129	-0.035306	-2.741403
9.C	-2.792617	0.071807	-1.135747
10.C	-2.792617	0.071807	1.135747
11.C	2.792617	-0.071807	-1.135747
12.C	2.792617	-0.071807	1.135747
13.C	-0.690099	0.007773	4.161121
14.C	-0.690099	0.007773	-4.161121
15.C	0.690099	-0.007773	4.161121
16.C	0.690099	-0.007773	-4.161121
17.C	-4.176318	0.164438	-0.697548
18.C	-4.176318	0.164438	0.697548
19.C	4.176318	-0.164438	-0.697548
20.C	4.176318	-0.164438	0.697548
21.S	-1.852549	-0.070566	5.458128
22.S	-1.852549	-0.070566	-5.458128
23.S	1.852549	0.070566	5.458128
24.S	1.852549	0.070566	-5.458128
25.S	-5.607607	0.404809	-1.660486
26.S	-5.607607	0.404809	1.660486
27.S	5.607607	-0.404809	-1.660486
28.S	5.607607	-0.404809	1.660486
29.C	-1.177756	-1.373269	6.540566
30.C	-1.177756	-1.373269	-6.540566
31.C	1.177756	1.373269	6.540566
32.C	1.177756	1.373269	-6.540566
33.C	-5.342051	-0.591682	-3.166132
34.C	-5.342051	-0.591682	3.166132
35.C	5.342051	0.591682	-3.166132
36.C	5.342051	0.591682	3.166132
37.N	-2.375698	0.076860	2.388582
38.N	-2.375698	0.076860	-2.388582
39.N	2.375698	-0.076860	2.388582
40.N	2.375698	-0.076860	-2.388582
41.H	-6.250135	-0.430609	3.758299
42.H	-6.250135	-0.430609	-3.758299
43.H	6.250135	0.430609	3.758299
44.H	6.250135	0.430609	-3.758299
45.H	-4.459180	-0.251279	3.710519
46.H	-4.459180	-0.251279	-3.710519

47.H	4.459180	0.251279	3.710519
48.H	4.459180	0.251279	-3.710519
49.H	-5.254215	-1.650753	2.903636
50.H	-5.254215	-1.650753	-2.903636
51.H	5.254215	1.650753	2.903636
52.H	5.254215	1.650753	-2.903636
53.H	-1.880066	-1.435949	-7.379223
54.H	-1.880066	-1.435949	7.379223
55.H	1.880066	1.435949	-7.379223
56.H	1.880066	1.435949	7.379223
57.H	-1.151996	-2.326295	-6.002892
58.H	-1.151996	-2.326295	6.002892
59.H	1.151996	2.326295	-6.002892
60.H	1.151996	2.326295	6.002892
61.H	-0.177304	-1.124239	-6.912107
62.H	-0.177304	-1.124239	6.912107
63.H	0.177304	1.124239	-6.912107
64.H	0.177304	1.124239	6.912107
65.H	-1.003947	-0.113603	0.000000
66.H	1.003947	0.113603	0.000000

Cartesian Coordinates (Å) of the H_2OMSPz C_{2h} conformer optimized at DFT/B3LYP/COSMO/TZ2P level of theory in CH_2Cl_2 solution.

1.N	0.000000	0.000000	1.909602
2.N	0.000000	0.000000	-1.909602
3.N	-2.015990	0.003771	0.000000
4.N	2.015990	-0.003771	0.000000
5.C	-1.078982	0.048162	2.723639
6.C	-1.078982	0.048162	-2.723639
7.C	1.078982	-0.048162	2.723639
8.C	1.078982	-0.048162	-2.723639
9.C	-2.779050	0.098289	-1.126804
10.C	-2.779050	0.098289	1.126804
11.C	2.779050	-0.098289	-1.126804
12.C	2.779050	-0.098289	1.126804
13.C	-0.684448	0.019962	4.143085
14.C	-0.684448	0.019962	-4.143085
15.C	0.684448	-0.019962	4.143085
16.C	0.684448	-0.019962	-4.143085
17.C	-4.161711	0.206139	-0.691299
18.C	-4.161711	0.206139	0.691299
19.C	4.161711	-0.206139	-0.691299
20.C	4.161711	-0.206139	0.691299
21.S	-1.866213	-0.017364	5.428710
22.S	-1.866213	-0.017364	-5.428710
23.S	1.866213	0.017364	5.428710
24.S	1.866213	0.017364	-5.428710
25.S	-5.570622	0.436843	-1.698238
26.S	-5.570622	0.436843	1.698238
27.S	5.570622	-0.436843	-1.698238
28.S	5.570622	-0.436843	1.698238
29.C	-1.242967	-1.342117	6.512731
30.C	-1.242967	-1.342117	-6.512731
31.C	1.242967	1.342117	6.512731
32.C	1.242967	1.342117	-6.512731
33.C	-5.348136	-0.779059	-3.042648
34.C	-5.348136	-0.779059	3.042648
35.C	5.348136	0.779059	-3.042648
36.C	5.348136	0.779059	3.042648
37.N	-2.356789	0.103227	2.367630
38.N	-2.356789	0.103227	-2.367630
39.N	2.356789	-0.103227	2.367630
40.N	2.356789	-0.103227	-2.367630
41.H	-6.269337	-0.721849	3.618598
42.H	-6.269337	-0.721849	-3.618598
43.H	6.269337	0.721849	3.618598
44.H	6.269337	0.721849	-3.618598
45.H	-4.496246	-0.526341	3.662976
46.H	-4.496246	-0.526341	-3.662976
47.H	4.496246	0.526341	3.662976

48.H	4.496246	0.526341	-3.662976
49.H	-5.240934	-1.777015	2.624442
50.H	-5.240934	-1.777015	-2.624442
51.H	5.240934	1.777015	2.624442
52.H	5.240934	1.777015	-2.624442
53.H	-1.987467	-1.434318	-7.300604
54.H	-1.987467	-1.434318	7.300604
55.H	1.987467	1.434318	-7.300604
56.H	1.987467	1.434318	7.300604
57.H	-1.177730	-2.273641	-5.955880
58.H	-1.177730	-2.273641	5.955880
59.H	1.177730	2.273641	-5.955880
60.H	1.177730	2.273641	5.955880
61.H	-0.276688	-1.099943	-6.948079
62.H	-0.276688	-1.099943	6.948079
63.H	0.276688	1.099943	-6.948079
64.H	0.276688	1.099943	6.948079
65.H	-1.012851	-0.102336	0.000000
66.H	1.012851	0.102336	0.000000

List of all frequencies of the H_2OMSPz C_{2h} conformer optimized at DFT/BP86/ COSMO/TZ2P level of theory in CH_2Cl_2 solution.

```
 Frequency      Dipole Strength     Absorption Intensity (degeneracy not counted)
   cm-1          1e-40 esu2 cm2        km/mole
----------     ----------        ----------
  5.543293        0.000000          0.000000
 18.132077        0.000000          0.000000
 21.257763        0.000007          0.000000
 27.233300     1002.798819          6.845295
 30.919909      999.901220          7.749495
 32.014797        0.000001          0.000000
 34.618956        0.000006          0.000000
 44.551657     1790.638584         19.996310
 46.177336        0.000001          0.000000
 48.177243      274.946949          3.320236
 52.500678        0.000000          0.000000
 59.540675      288.692832          4.308517
 67.910938        0.000058          0.000001
 68.782749        0.000000          0.000000
 84.805786      348.831617          7.415141
 87.923642        0.000000          0.000000
 93.663764        0.446257          0.010477
102.084183        0.000000          0.000000
108.554621        4.978767          0.135472
117.177689        0.000000          0.000000
117.332902      460.854442         13.553818
122.236629      158.835465          4.866614
123.413159        0.000010          0.000000
126.767632        0.000001          0.000000
127.436007       18.013515          0.575398
134.043403        0.000000          0.000000
135.362609        0.000100          0.000003
136.131504        0.000000          0.000000
141.444232      898.116020         31.841664
142.090529       43.346222          1.543812
142.344509        0.000000          0.000000
146.575260      123.984873          4.555200
154.650176        0.000000          0.000000
156.787760      117.036823          4.599523
171.045277      103.269315          4.427519
175.218447        0.000002          0.000000
186.783030      163.539198          7.656625
189.601072        0.000003          0.000000
190.880870       84.103853          4.023985
201.744228        0.000004          0.000000
207.174860        0.000001          0.000000
208.273232       14.052774          0.733624
229.716910        0.000036          0.000002
233.122679        0.000009          0.000001
```

248.502489	122.977061	7.660073
253.814752	45.816201	2.914835
267.551099	0.000021	0.000001
271.952635	104.229642	7.104976
293.238773	0.000003	0.000000
294.067389	51.077724	3.764926
306.742450	0.000000	0.000000
315.640064	89.608463	7.089559
318.370373	0.000000	0.000000
354.909081	66.319618	5.899799
368.391973	0.000010	0.000001
398.109715	183.751383	18.336290
405.105991	20.533912	2.085059
423.968461	0.000010	0.000001
446.896734	403.236203	45.169446
493.471767	0.000019	0.000002
505.169745	297.070184	37.616161
520.807483	0.000001	0.000000
523.673659	0.000036	0.000005
540.626251	862.628227	116.895789
552.416437	0.000004	0.000001
562.875875	13.874005	1.957458
576.742500	223.993451	32.381380
577.300592	0.000052	0.000007
579.299274	0.000584	0.000085
591.701427	56.759894	8.418259
636.074896	1239.947595	197.692256
663.391877	0.000000	0.000000
673.199653	0.000000	0.000000
673.956721	169.653344	28.659757
674.016829	0.077153	0.013035
675.863636	6.784629	1.149379
676.073648	0.000000	0.000000
677.506179	0.000000	0.000000
678.578968	94.163476	16.016254
693.799467	0.000003	0.000001
694.712471	88.930848	15.485870
699.298810	0.000000	0.000000
706.251194	0.000000	0.000000
711.629692	1.643857	0.293222
716.973242	0.000001	0.000000
723.798965	0.000002	0.000000
734.783482	1.446366	0.266389
737.003283	0.000000	0.000000
737.174161	418.289761	77.290374
740.282255	0.000000	0.000000
772.808291	1232.790134	238.802568
777.175900	621.262430	121.024274
831.908536	0.000010	0.000002
839.080240	22.847500	4.805297

874.260260	231.542339	50.739855
900.929819	0.000001	0.000000
931.050678	0.000000	0.000000
931.315148	221.094291	51.612188
933.930197	26.877661	6.291931
935.410830	0.000000	0.000000
937.176774	0.000000	0.000000
937.960545	443.068054	104.167701
938.573999	201.000918	47.287312
939.465136	0.000000	0.000000
948.865284	907.328824	215.797960
950.214737	0.984470	0.234478
950.864287	0.000000	0.000000
953.186611	0.000000	0.000000
955.530904	0.000000	0.000000
956.904520	5.022939	1.204771
958.269420	53.013866	12.733716
960.047782	0.000002	0.000001
998.048075	2549.615173	637.828861
1003.815400	0.000001	0.000000
1038.272981	0.000019	0.000005
1043.152329	1908.776954	499.092433
1044.470048	178.000461	46.600995
1072.137571	0.000002	0.000001
1076.212462	50.868012	13.722109
1089.153342	0.000001	0.000000
1180.090288	0.000024	0.000007
1180.616129	844.211878	249.826349
1200.140182	0.000012	0.000004
1202.945003	558.810874	168.495649
1250.194583	0.000009	0.000003
1251.265538	1418.746396	444.971633
1261.412032	0.000001	0.000000
1270.643506	978.937110	311.785981
1279.016902	321.034402	102.921458
1289.507306	7.410453	2.395227
1289.614187	0.000000	0.000000
1290.117094	0.000000	0.000000
1290.504471	94.699860	30.632816
1295.942690	0.000000	0.000000
1295.981290	73.315496	23.816206
1296.590963	108.062437	35.120106
1296.966663	0.000001	0.000000
1343.948895	0.000001	0.000000
1379.424257	401.383181	138.782626
1389.100071	0.000000	0.000000
1389.117768	37.096197	12.916550
1390.470788	0.000000	0.000000
1391.039584	0.000000	0.000000
1391.408072	227.702660	79.414662

1392.433533	323.404123	112.875087
1392.491931	0.000000	0.000000
1393.266032	76.795007	26.819156
1403.554105	0.000000	0.000000
1408.774491	0.000000	0.000000
1409.149854	44.850529	15.841738
1413.155529	0.000005	0.000002
1417.407074	864.888638	307.278984
1422.125938	0.000000	0.000000
1422.547059	7.429637	2.649185
1424.284031	309.165565	110.373748
1424.540499	0.000000	0.000000
1425.165588	0.000000	0.000000
1425.291116	183.431214	65.532221
1437.436362	0.000000	0.000000
1441.915025	333.618095	120.577794
1470.096866	208.782360	76.933914
1474.214987	0.000000	0.000000
1491.959833	579.678788	216.781696
1506.468358	0.000006	0.000002
1516.896414	78.613770	29.890462
1547.422391	0.000000	0.000000
2970.956609	96.263801	71.686502
2970.963913	0.000000	0.000000
2972.420194	0.000000	0.000000
2972.421821	54.967164	40.953577
2983.264804	0.000000	0.000000
2983.280217	70.340660	52.599130
2983.330176	133.642361	99.936361
2983.399904	0.000000	0.000000
3059.477425	2.356537	1.807172
3059.521968	0.000000	0.000000
3060.382343	0.000000	0.000000
3060.383834	7.217798	5.536798
3073.672438	0.056301	0.043377
3073.673031	0.000000	0.000000
3073.680210	26.711958	20.579863
3073.682150	0.000000	0.000000
3075.997746	0.000000	0.000000
3075.998727	15.732675	12.130167
3076.080629	0.924949	0.713171
3076.080992	0.000000	0.000000
3101.187144	48.253425	37.508888
3101.198029	0.288895	0.224568
3101.198033	0.000000	0.000000
3101.228620	0.000000	0.000000
3400.109512	592.123258	504.641655
3447.191797	0.000249	0.000215

Cartesian Coordinates (Å) of the H_2OMSPz C_{2v} conformer optimized at DFT/BP86/ COSMO/TZ2P level of theory in CH_2Cl_2 solution.

1.N	0.000000	-1.900890	-0.043636
2.N	0.000000	1.900890	-0.043636
3.N	1.992452	0.000000	0.107504
4.N	-1.992452	0.000000	0.107504
5.C	1.089750	-2.708108	-0.199711
6.C	-1.089750	-2.708108	-0.199711
7.C	-1.089750	2.708108	-0.199711
8.C	1.089750	2.708108	-0.199711
9.C	2.753205	1.133997	0.254605
10.C	-2.753205	1.133997	0.254605
11.C	-2.753205	-1.133997	0.254605
12.C	2.753205	-1.133997	0.254605
13.C	0.689897	-4.068607	-0.597808
14.C	-0.689897	-4.068607	-0.597808
15.C	-0.689897	4.068607	-0.597808
16.C	0.689897	4.068607	-0.597808
17.C	4.087843	0.697433	0.632069
18.C	-4.087843	0.697433	0.632069
19.C	-4.087843	-0.697433	0.632069
20.C	4.087843	-0.697433	0.632069
21.N	2.364896	-2.378728	0.033884
22.N	-2.364896	-2.378728	0.033884
23.N	-2.364896	2.378728	0.033884
24.N	2.364896	2.378728	0.033884
25.S	5.493337	1.686246	0.918178
26.S	-5.493337	1.686246	0.918178
27.S	-5.493337	-1.686246	0.918178
28.S	5.493337	-1.686246	0.918178
29.S	-1.704097	5.459799	-0.876469
30.S	1.704097	5.459799	-0.876469
31.S	1.704097	-5.459799	-0.876469
32.S	-1.704097	-5.459799	-0.876469
33.C	4.859103	-3.106953	1.876271
34.C	-4.859103	-3.106953	1.876271
35.C	-4.859103	3.106953	1.876271
36.C	4.859103	3.106953	1.876271
37.C	3.064262	4.818384	-1.916041
38.C	-3.064262	4.818384	-1.916041
39.C	-3.064262	-4.818384	-1.916041
40.C	3.064262	-4.818384	-1.916041
41.H	-0.987771	0.000000	-0.067293
42.H	0.987771	0.000000	-0.067293
43.H	5.747532	3.712981	2.086752
44.H	-5.747532	3.712981	2.086752
45.H	-5.747532	-3.712981	2.086752
46.H	5.747532	-3.712981	2.086752
47.H	4.136251	3.680207	1.292920

48.H	-4.136251	3.680207	1.292920
49.H	-4.136251	-3.680207	1.292920
50.H	4.136251	-3.680207	1.292920
51.H	4.418705	2.758116	2.815614
52.H	-4.418705	2.758116	2.815614
53.H	-4.418705	-2.758116	2.815614
54.H	4.418705	-2.758116	2.815614
55.H	3.706193	-5.686838	-2.102311
56.H	-3.706193	-5.686838	-2.102311
57.H	-3.706193	5.686838	-2.102311
58.H	3.706193	5.686838	-2.102311
59.H	2.667349	-4.443306	-2.864816
60.H	-2.667349	-4.443306	-2.864816
61.H	-2.667349	4.443306	-2.864816
62.H	2.667349	4.443306	-2.864816
63.H	3.622129	-4.041362	-1.389412
64.H	-3.622129	-4.041362	-1.389412
65.H	-3.622129	4.041362	-1.389412
66.H	3.622129	4.041362	-1.389412

Cartesian Coordinates (Å) of the H_2OMSPz C_{2v} conformer optimized at DFT/B3LYP/COSMO/TZ2P level of theory in CH_2Cl_2 solution.

1.N	0.000000	-1.925141	0.017475
2.N	0.000000	1.925141	0.017475
3.N	2.009889	0.000000	0.081503
4.N	-2.009889	0.000000	0.081503
5.C	1.082665	-2.736333	0.038451
6.C	-1.082665	-2.736333	0.038451
7.C	-1.082665	2.736333	0.038451
8.C	1.082665	2.736333	0.038451
9.C	2.776188	1.127509	0.039886
10.C	-2.776188	1.127509	0.039886
11.C	-2.776188	-1.127509	0.039886
12.C	2.776188	-1.127509	0.039886
13.C	0.682368	-4.156912	0.054809
14.C	-0.682368	-4.156912	0.054809
15.C	-0.682368	4.156912	0.054809
16.C	0.682368	4.156912	0.054809
17.C	4.162771	0.690680	0.000256
18.C	-4.162771	0.690680	0.000256
19.C	-4.162771	-0.690680	0.000256
20.C	4.162771	-0.690680	0.000256
21.N	2.359328	-2.371482	0.036285
22.N	-2.359328	-2.371482	0.036285
23.N	-2.359328	2.371482	0.036285
24.N	2.359328	2.371482	0.036285
25.S	5.577751	1.702907	-0.175054
26.S	-5.577751	1.702907	-0.175054
27.S	-5.577751	-1.702907	-0.175054
28.S	5.577751	-1.702907	-0.175054
29.S	-1.728427	5.552712	0.206114
30.S	1.728427	5.552712	0.206114
31.S	1.728427	-5.552712	0.206114
32.S	-1.728427	-5.552712	0.206114
33.C	5.362325	-2.968039	1.123917
34.C	-5.362325	-2.968039	1.123917
35.C	-5.362325	2.968039	1.123917
36.C	5.362325	2.968039	1.123917
37.C	2.878769	5.360678	-1.199667
38.C	-2.878769	5.360678	-1.199667
39.C	-2.878769	-5.360678	-1.199667
40.C	2.878769	-5.360678	-1.199667
41.H	-1.002301	0.000000	0.111627
42.H	1.002301	0.000000	0.111627
43.H	6.254907	3.586622	1.056374
44.H	-6.254907	3.586622	1.056374
45.H	-6.254907	-3.586622	1.056374
46.H	6.254907	-3.586622	1.056374

47.H	4.476100	3.566682	0.947870
48.H	-4.476100	3.566682	0.947870
49.H	-4.476100	-3.566682	0.947870
50.H	4.476100	-3.566682	0.947870
51.H	5.319210	2.492487	2.100389
52.H	-5.319210	2.492487	2.100389
53.H	-5.319210	-2.492487	2.100389
54.H	5.319210	-2.492487	2.100389
55.H	3.541080	-6.222000	-1.142417
56.H	-3.541080	-6.222000	-1.142417
57.H	-3.541080	6.222000	-1.142417
58.H	3.541080	6.222000	-1.142417
59.H	2.327946	-5.384726	-2.136561
60.H	-2.327946	-5.384726	-2.136561
61.H	-2.327946	5.384726	-2.136561
62.H	2.327946	5.384726	-2.136561
63.H	3.450682	-4.443307	-1.114245
64.H	-3.450682	-4.443307	-1.114245
65.H	-3.450682	4.443307	-1.114245
66.H	3.450682	4.443307	-1.114245

List of all frequencies of the H_2OMSPz C_{2v} conformer optimized at DFT/BP86/COSMO/TZ2P level of theory in CH_2Cl_2 solution.

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 Frequency      Dipole Strength      Absorption Intensity (degeneracy not counted)
   cm-1          1e-40 esu2 cm2              km/mole
----------       ----------        ----------
 13.316000         0.000000          0.000000
 21.425403         0.000001          0.000000
 25.606815         5.601664          0.035954
 30.123866       595.844642            4.499060
 30.839139        57.030860           0.440849
 36.110148         0.000007          0.000000
 39.909977       257.410674            2.575053
 41.170284        16.859780           0.173986
 42.362775         0.000027          0.000000
 48.142903       800.276131            9.657177
 55.079927         0.676828          0.009344
 62.350853       109.886469            1.717373
 63.052432         0.000006          0.000000
 65.239952      2108.637157           34.482088
 66.814105       923.534045           15.466753
 67.899094        20.204744           0.343871
 70.183802         0.000160          0.000003
 96.034998        42.951929           1.033928
 96.930549        48.241554           1.172088
100.411723          0.000040          0.000001
104.260475          1.571397          0.041066
113.030324          1.238907          0.035100
117.396023          5.644868          0.166106
120.768387        257.716617           7.801422
121.280378          1.578758          0.047994
126.429736          0.120340          0.003814
127.907478        105.094668           3.369416
127.991728        139.380517           4.471591
131.038239          0.000000          0.000000
134.407517        528.259054          17.797073
135.383123          0.000006          0.000000
138.227535        213.296794           7.390213
147.489893          0.308094          0.011390
148.228813          0.000235          0.000009
157.223724         24.369343           0.960373
191.689134        242.274505          11.640812
193.261475        423.265328          20.503880
196.494962          9.421480          0.464033
199.533026         12.723885           0.636374
202.789818          0.000005          0.000000
204.697074         11.018418           0.565339
208.093968         82.562391           4.306454
209.120883          0.000099          0.000005
```

230.871450	24.386914	1.411254
240.625490	26.807560	1.616877
253.076927	55.716811	3.534410
262.770053	0.000091	0.000006
273.606947	11.054563	0.758135
276.203912	246.429278	17.060832
278.924089	197.502116	13.808161
313.126281	55.710333	4.372536
318.109012	32.561613	2.596330
319.745619	0.208277	0.016693
364.094723	25.595082	2.335872
373.270103	0.000078	0.000007
410.499888	0.000024	0.000002
412.305543	0.617951	0.063863
413.134935	0.020200	0.002092
440.065562	0.000000	0.000000
504.329994	525.250223	66.398629
514.844035	230.940531	29.802584
521.140241	58.025858	7.579739
523.855853	0.952704	0.125097
533.628497	876.514806	117.240143
554.388926	0.428307	0.059518
559.469811	2.262726	0.317312
565.087002	0.000043	0.000006
582.149515	124.504466	18.167599
582.874127	0.000122	0.000018
585.347351	62.463706	9.164726
644.754111	1077.172264	174.083397
650.951431	0.000003	0.000001
668.781092	2.713961	0.454952
670.058009	75.616967	12.700176
670.422784	0.000000	0.000000
670.547800	95.376678	16.030608
671.160945	0.554574	0.093296
671.340116	5.138972	0.864763
671.783474	18.182306	3.061656
694.982671	30.337913	5.284912
696.218478	0.000003	0.000001
696.645033	8.383379	1.463891
705.859932	0.927666	0.164130
714.471813	0.000002	0.000000
721.055608	17.941453	3.242683
722.653281	88.428057	16.017625
734.144186	128.884983	23.717109
734.353808	0.000001	0.000000
737.739651	8.498548	1.571542
737.921617	447.931914	82.851487
773.926993	1375.771704	266.885167
775.116347	924.816221	179.680276
831.950769	0.000046	0.000010

839.076323	4.495753	0.945544
865.772129	198.853199	43.153324
893.957164	0.000008	0.000002
927.250737	11.684305	2.715677
927.459667	0.000000	0.000000
930.351032	157.300653	36.682206
932.022875	0.000000	0.000000
932.356083	250.207865	58.473735
933.250794	414.881816	97.051184
935.745847	439.132853	102.998739
936.318788	59.074114	13.864334
946.025006	836.987491	198.472186
947.200591	12.702844	3.015928
949.476706	609.312781	145.011576
951.243877	7.429541	1.771462
954.370429	0.000005	0.000001
954.732247	103.046797	24.660062
956.487211	0.000001	0.000000
957.102889	15.713277	3.769671
1017.818177	1650.865406	421.172435
1021.159055	33.778156	8.645844
1039.836233	1776.722009	463.086903
1043.018312	0.000001	0.000000
1051.813642	251.725309	66.365711
1073.707912	94.136944	25.335199
1080.886119	210.882685	57.134566
1094.637464	0.000274	0.000075
1183.278378	1376.313612	408.208839
1185.468038	0.000005	0.000001
1198.433081	0.000056	0.000017
1202.528069	601.322403	181.251111
1254.160123	1069.172177	336.107890
1255.263632	0.000000	0.000000
1263.181799	229.877538	72.784762
1274.449078	572.969272	183.034050
1278.763624	396.265870	127.015000
1283.811775	17.126169	5.511117
1284.076981	23.959723	7.711714
1284.753647	149.703177	48.209091
1285.322394	0.000000	0.000000
1288.628526	6.088358	1.966554
1289.904826	0.953132	0.308169
1295.244552	151.691700	49.248348
1296.417251	0.000000	0.000000
1346.097841	4.859541	1.639646
1383.609982	392.584533	136.152288
1392.510851	84.153585	29.373066
1393.237794	0.000001	0.000000
1393.530359	144.522215	50.481135
1393.678084	1.368951	0.478221

1394.961525	0.000001	0.000000
1395.643816	159.194261	55.690366
1395.739703	30.084639	10.525126
1398.561492	73.534453	25.778076
1408.087808	28.159619	9.938815
1413.316174	0.000010	0.000004
1418.781834	472.952180	168.194163
1422.179428	0.629774	0.224500
1422.343232	0.000000	0.000000
1422.622767	50.928155	18.160415
1423.574406	106.523120	38.010372
1427.400589	403.993890	144.543557
1427.558930	0.000000	0.000000
1427.814057	0.677754	0.242562
1427.990101	220.531035	78.935613
1447.072626	0.400114	0.145128
1451.125163	340.635989	123.900618
1473.001189	100.057886	36.943028
1475.461051	0.474926	0.175643
1487.082444	498.412280	185.781237
1503.518345	0.000008	0.000003
1512.081391	87.160065	33.034732
1540.619415	24.862503	9.601040
2982.893730	96.470055	72.128745
2982.896957	0.000000	0.000000
2983.024486	25.065057	18.741467
2983.092149	86.735283	64.854564
2985.293844	0.000000	0.000000
2985.298836	90.254636	67.536010
2985.376101	48.671937	36.421326
2985.467778	45.450180	34.011522
3073.382095	11.059943	8.520156
3073.388667	12.604907	9.710357
3073.390333	0.000000	0.000000
3073.392542	0.416468	0.320832
3075.835866	9.765457	7.528939
3075.836630	0.000000	0.000000
3075.838929	0.013515	0.010420
3075.842170	9.112519	7.025554
3095.982592	7.966657	6.182337
3095.995778	2.062214	1.600340
3095.998506	0.082851	0.064295
3096.043520	0.000000	0.000000
3101.138105	11.710950	9.103141
3101.146805	6.731533	5.232562
3101.166730	1.182258	0.919000
3101.166812	0.000000	0.000000
3403.891600	544.314343	464.412146
3455.564829	32.064776	27.773162