

Supporting Information

for

Transforming hemithioindigo from a two-way to a one-way molecular photoswitch by isolation in the gas phase

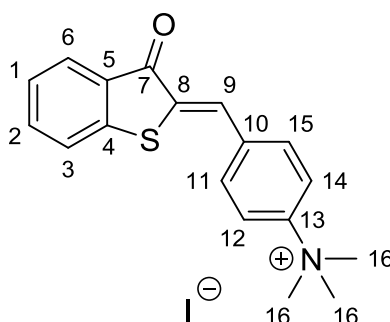
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Synthesis and characterization of HTI



2-[4-(Dimethylamino)benzylidene]-1-benzothiophen-3(2H)-one (73 mg, 0.3 mmol) was dissolved in acetonitrile (2 mL) and iodomethane (5.0 eq, 80 μ L, 1.3 mmol) was added. The solution was stirred for 48 h at 50 $^{\circ}$ C. The precipitated product filtered off and washed with CH_2Cl_2 to afford the HTI (93 mg, 85% yield) as yellow solid.

M.p.: 163 $^{\circ}$ C (decomposition);

^1H NMR (800 MHz, CD_3OD) δ = 8.10 – 8.06 (m, 2H, H-C(12), H-C(14)), 8.03 – 8.00 (m, 2H, (H-C(11), H-C(15))), 7.97 (s, 1H, H-C(9)), 7.93 (ddd, $^3J(\text{H,H})=7.6$ Hz, $^4J(\text{H,H})=1.3$ Hz, $^5J(\text{H,H})=0.7$ Hz, 1H, H-C(6)), 7.72 (ddd, $^3J(\text{H,H})=8.4$, 7.2 Hz, $^4J(\text{H,H})=1.3$ Hz, 1H, H-C(2)), 7.67 (dt, $^3J(\text{H,H})=7.9$ Hz, $^4J(\text{H,H})=0.8$ Hz, 1H, H-C(3)), 7.42 (ddd, $^3J(\text{H,H})=7.9$, 7.1 Hz, $^4J(\text{H,H})=0.9$ Hz, 1H, H-C(1)), 3.73 ppm (s, 9H; H-C(16));

^{13}C NMR (201 MHz, CD_3OD) δ = 189.6 (C(7)), 148.7 (C(13)), 146.9 (C(2)), 138.0 (C(10)), 137.4 (C(4)), 134.6 (C(8)), 133.5 (C(11), C(15)), 131.0 (C(5)), 130.9 (C(9)), 128.0 (C(6)), 127.5 (C(1)), 125.5 (C(3)), 122.1 (C(12), C(14)), 57.7 ppm (C(16));

IR (ATR): $\tilde{\nu}$ = 3060w, 3033w, 3004w, 2229w, 1934w, 1817w, 1695w, 1677vs, 1592m, 1583m, 1569m, 1509m, 1490m, 1466m, 1448s, 1418m, 1346w, 1312w, 1281s, 1233m, 1212m, 1154w, 1122w, 1110w, 1066s, 1053s, 1014m, 975w, 954m, 945m, 931m, 913m, 869w, 849m, 830m, 804w, 783m, 740vs, 727m, 686w, 676m;

HR-ESI-MS calc. [$\text{C}_{18}\text{H}_{18}\text{NOS}^+$]: 296.1104, found: 296.1108; calc. [I⁻]: 126.9050, found: 126.9049.

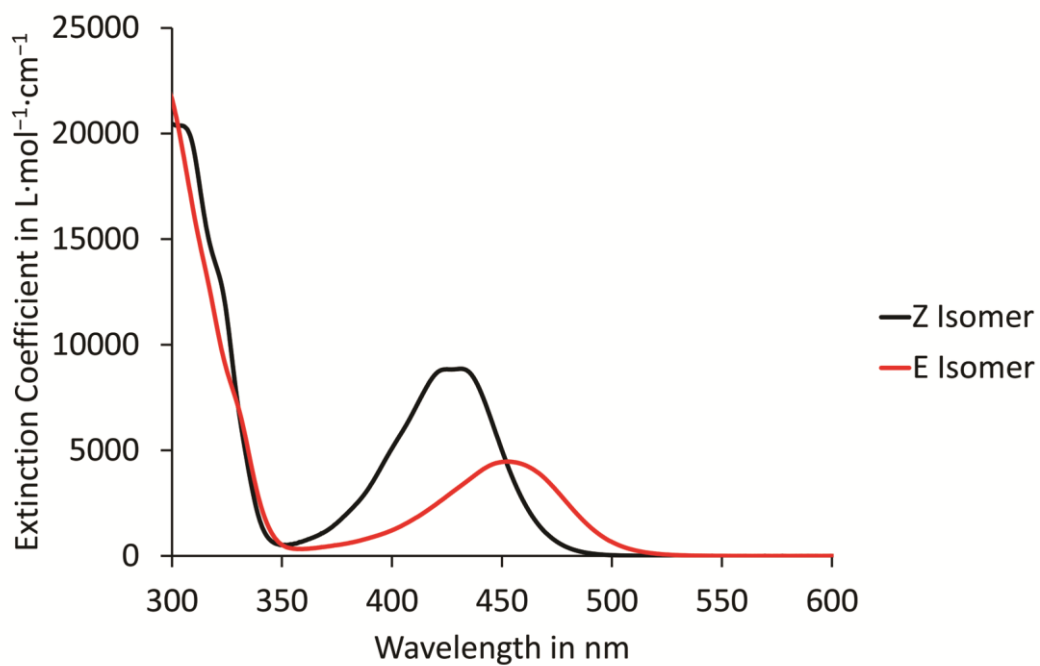


Figure S1. Molar extinction coefficients of the pure *Z*-HTI (black) and *E*-HTI (red) in methanol solution.

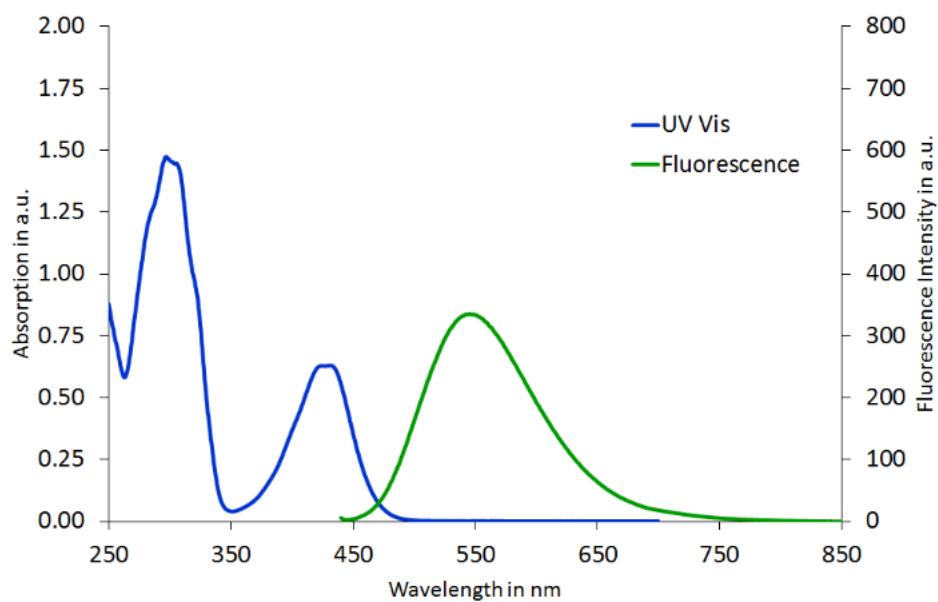


Figure S2. UV/vis absorption and fluorescence spectra (424 nm excitation) of Z-HTI in methanol.

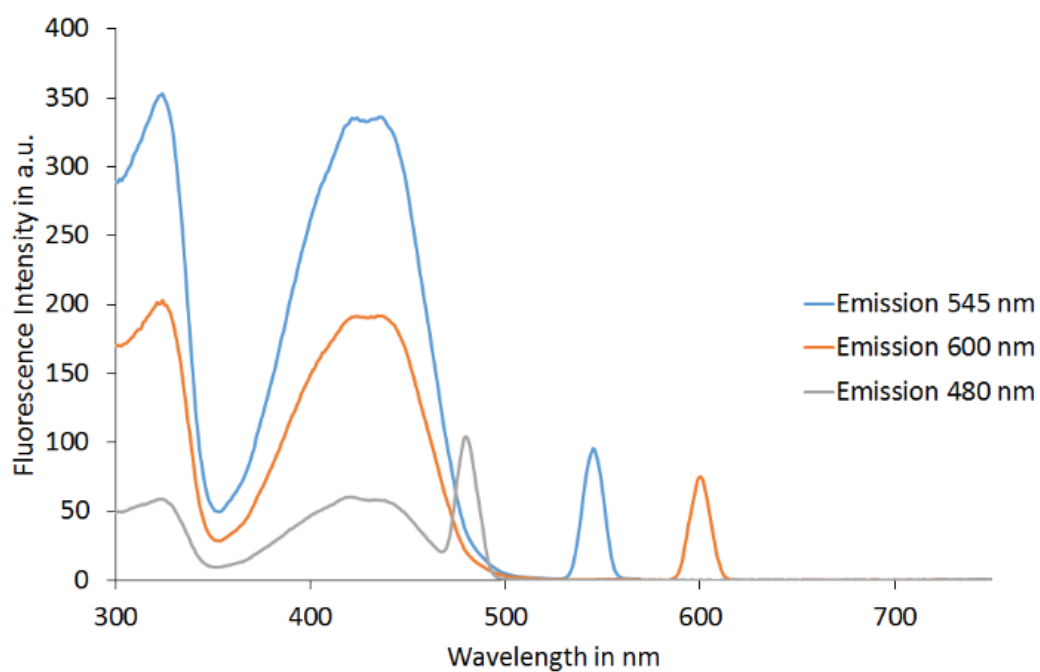


Figure S3. Excitation spectra for Z-HTI in methanol acquired at different emission wavelengths (color-coded).

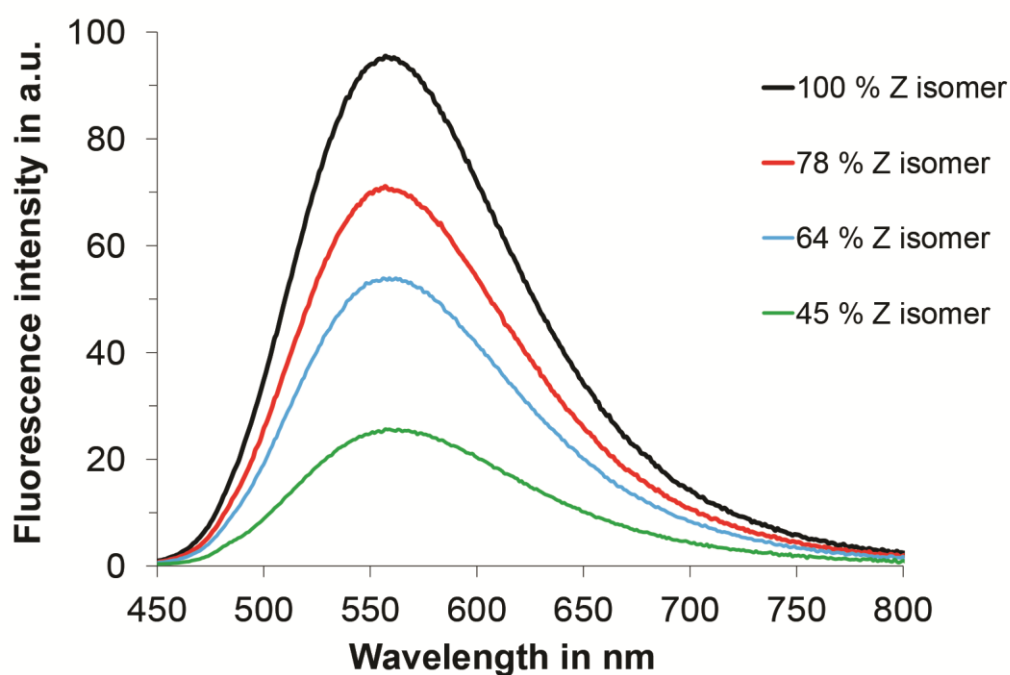


Figure S4. Fluorescence intensity changes (424 nm excitation wavelength) upon Z → E photoisomerization of HTI in methanol. The percentage of remaining fluorescent Z isomer is given in colour code.

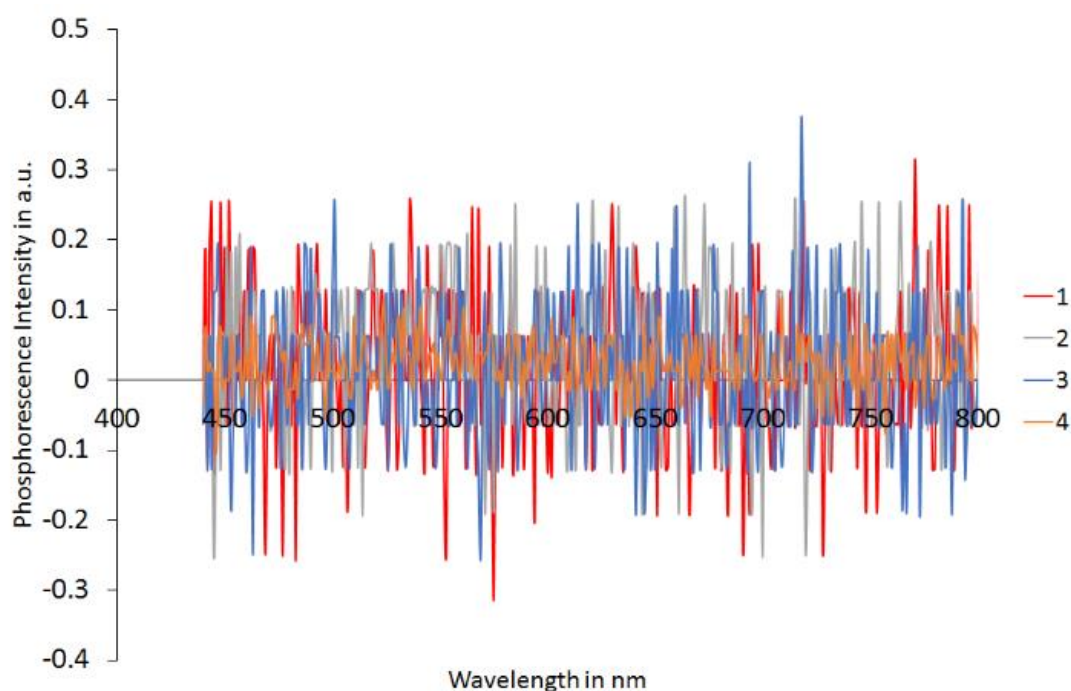


Figure S5. Phosphorescence of the Z isomer in methanol (excitation wavelength 431 nm). Color-code: 1 – Total decay time 0.02 s, No. of flashes 1, delay time 0.2 ms, gate time 5 ms; 2 – Total decay time 0.02 s, No. of flashes 5, delay time 0.2 ms, gate time 5 ms; 3 – Total decay time 0.05 s, No. of flashes 1, delay time 0.1 ms, gate time 5 ms; 4 – Total decay time 0.005 s, No. of flashes 1, delay time 0.1 ms, gate time 1 ms.

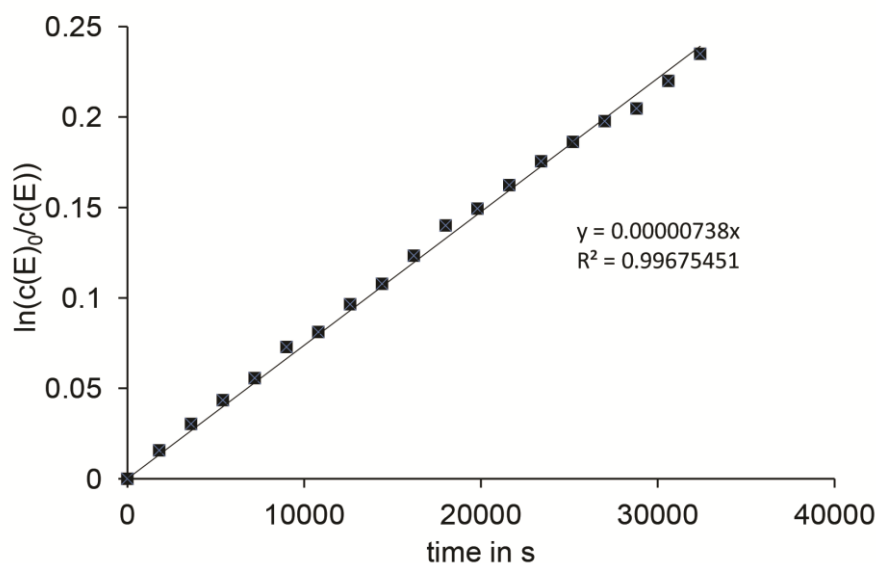


Figure S6. First order kinetic analysis of the thermal $E \rightarrow Z$ isomerization of HTI in methanol in the absence of light at 23 °C. A barrier of $\Delta G^* = 24.3 \text{ kcal mol}^{-1}$ was determined for this process.

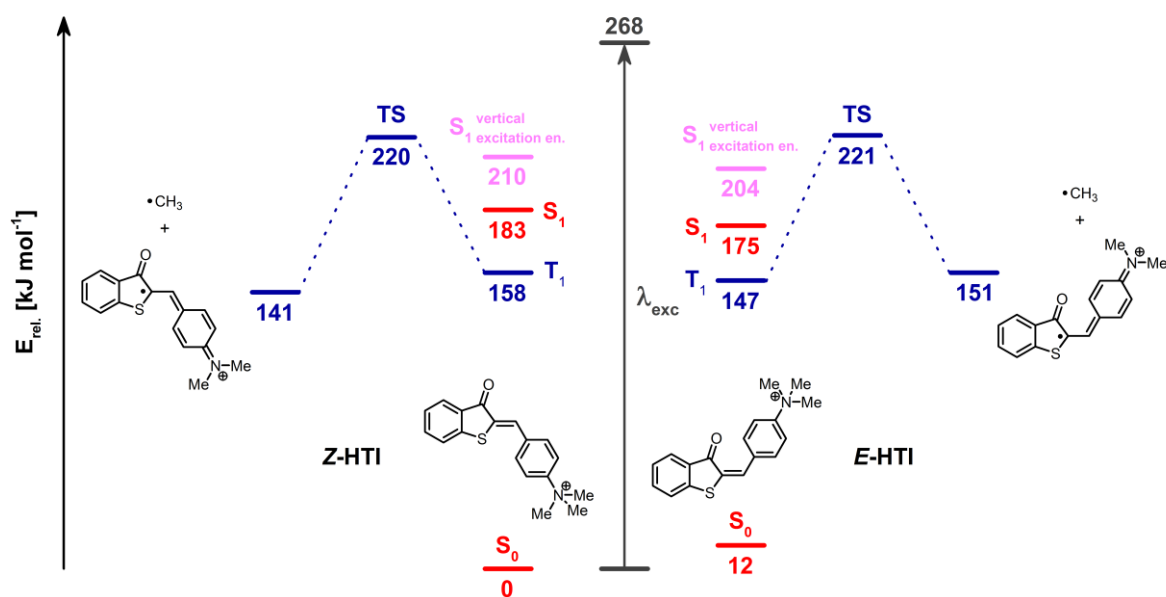


Figure S7. Calculated relative energies (including the zero-point energy correction) of HTI isomers at M06L/def2TZVP level of theory. Fragmentation observed in the visPD experiments to the CH_3 radical and fragment m/z 281 is also included. The optimized geometries of the singlet excited state S_1 were obtained by the broken-symmetry approach. The grey arrow indicates the energy of the 0–0 transition of Z-HTI ($\lambda_{\text{exc}} = 446 \text{ nm}$). S_0 , S_1 and T_1 denote singlet and triplet states, respectively. Both fragments have doublet multiplicity.

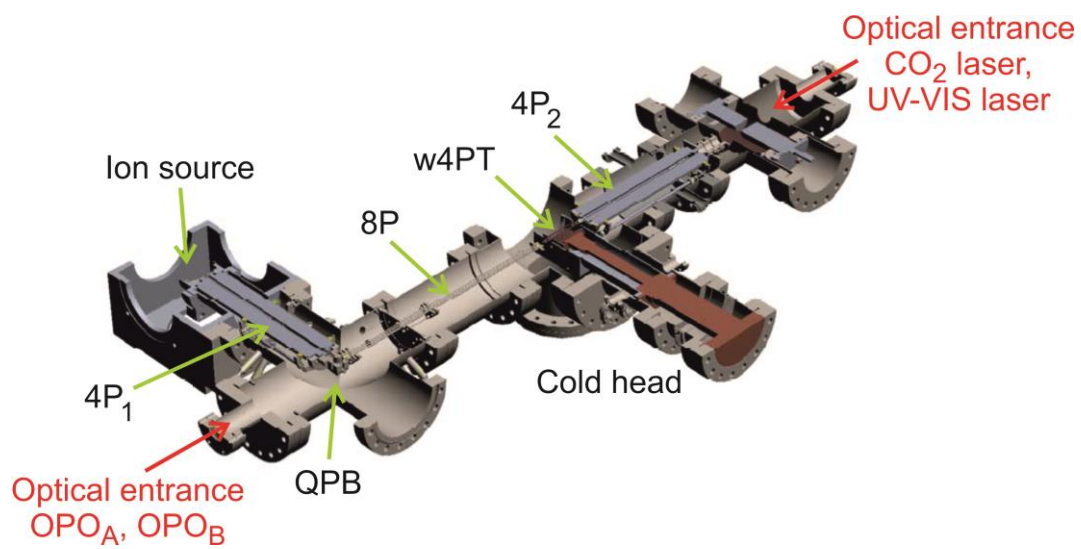


Figure S8. ISORI instrument.

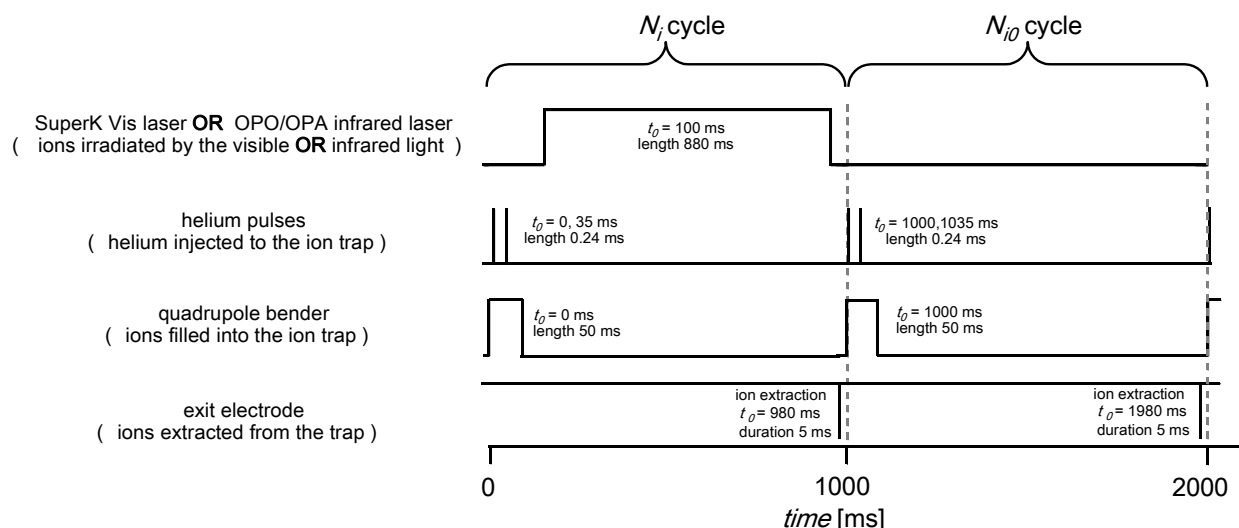


Figure S9a. Typical timing sequence used for the acquisition of the He-visPD and VisPD spectra (Figure 3) or the He-IRPD spectra (Figure 2).

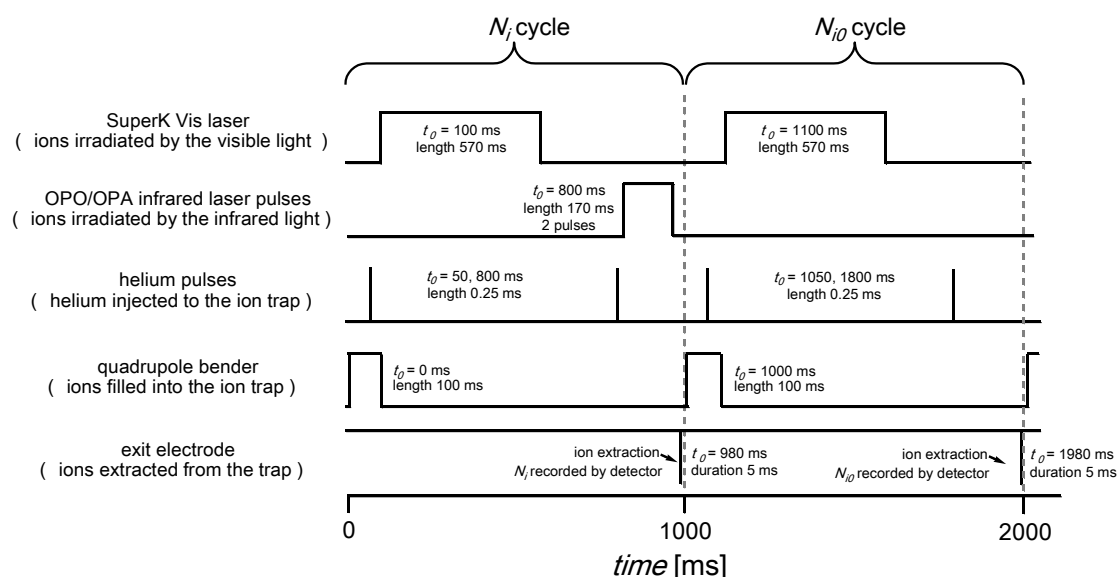


Figure S9b. Timing sequence used for the $Z \rightarrow E$ and $E \rightarrow Z$ photoisomerization and the subsequent acquisition of He-IRPD spectra at 3 Kelvin (Figure 4 and Figure S10, red trace).

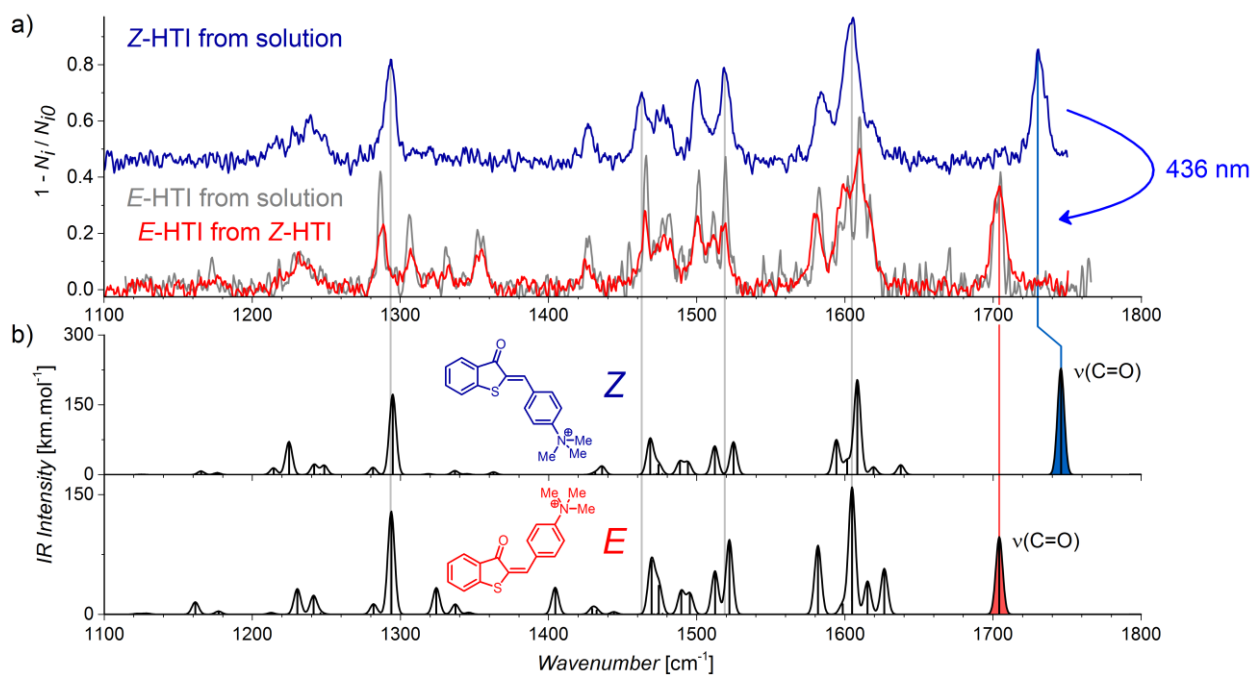


Figure S10. (a) The $Z \rightarrow E$ photoswitching processes of HTI isomers. Blue trace is the spectrum of Z-HTI transferred from HTI solution that was irradiated by 525 nm LEDs. Red trace corresponds to E-HTI ions formed upon irradiation of Z-HTI ions with 436 nm light in the ion trap at 3 K. Gray trace is the spectrum of E-HTI transferred from HTI solution that was irradiated by 400 nm LEDs. (b) Theoretical spectra calculated at B3LYP-GD3BJ/6-311++G** level of theory (frequencies scaled by 0.99).

Betaine complexes

Upon mixing of equimolar quantities of HTI and betaine in methanol, the $[\text{HTI.betaine}]^+$ complexes are readily formed and observed in the mass spectrum. We again irradiated the syringe with HTI and betaine methanolic solution with 400 or 525 nm LEDs prior to ESI to selectively transfer $[\text{E-HTI.betaine}]^+$ or $[\text{Z-HTI.betaine}]^+$ ions to the gas phase. First, we measured He-visPD and visPD spectra of these isomeric complexes. In case of visPD, the spectra were obtained by monitoring fragmentation of $[\text{HTI.betaine}]^+$ complexes. Figure S11b presents spectra of $[\text{Z-HTI.betaine}]^+$ ions at 3 K. Comparison with the spectra of bare Z-HTI shows a decrease of the He-visPD signal. The visPD spectrum has also changed intensity of several bands. Moreover, both spectra are blue-shifted by a few nanometers compared to the spectrum of bare Z-HTI ions (*cf.* Figure 3). This suggests that transitions of bare Z-HTI possess some charge transfer character. The betaine's carboxylate moiety most likely binds to the positively charged trimethylammonium group of HTI. This causes the positive charge to move away from the central C=C bond towards the stilbene part bearing the positively charged trimethylammonium group. Resulting changes in the electron density eventually lead to the blue-shift in the spectra.

Figure S11a presents the visPD and He-visPD spectra of $[\text{E-HTI.betaine}]^+$ ions. The spectra feature only small shifts of band position compared to bare E-HTI ions (*cf.* Figure 3). The biggest difference is the increased absorption evidenced by the increased He-visPD signal. Differences in intensity between the visPD and He-visPD spectra remain unclear thus far.

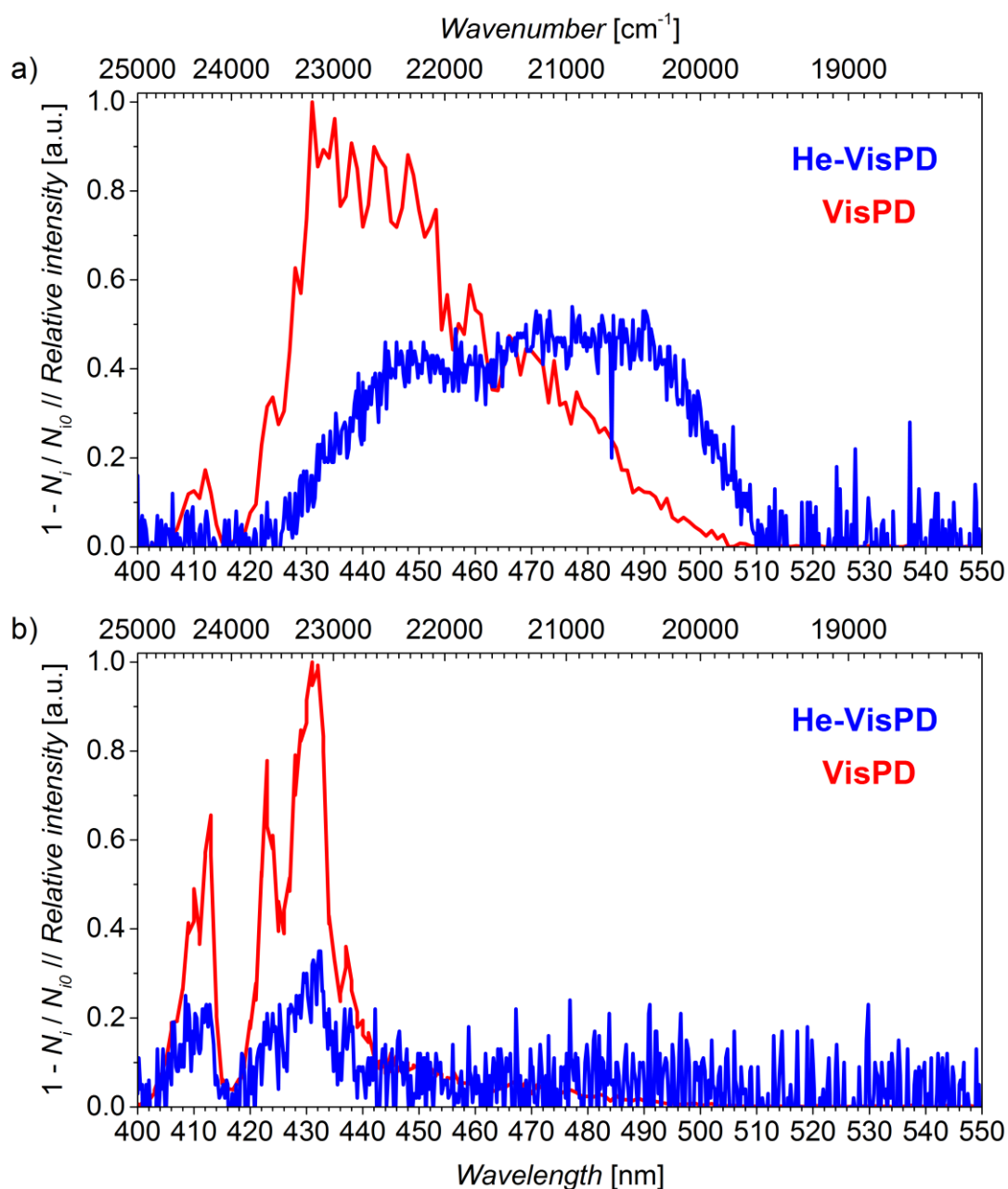


Figure S11. Visible absorption spectra of (a) $[E\text{-HTI.betaine}]^+$ and (b) $[Z\text{-HTI.betaine.He}]^+$ ions measured by the He-visPD (blue traces, loss of the He tag was monitored) and the visPD (red traces, loss of betaine molecule monitored) techniques at 3 K. For the timing of the experiment see Figure S9a. The syringe containing a solution of HTI and betaine in MeOH was irradiated with 400 or 525 nm LEDs prior to ESI in order to obtain $[E\text{-HTI.betaine}]^+$ or $[Z\text{-HTI.betaine}]^+$ ions, respectively (their identity confirmed by IRPD).

We then studied the $E \rightarrow Z$ photoswitching of betaine complexes. Figure 12a depicts the He-IRPD spectra of the Z (blue trace) and E betaine complexes (red trace). The Z betaine complex features two strong bands at 1666 and 1713 cm^{-1} . According to DFT calculations,

both bands correspond to the carbonyl stretches of the betaine and HTI moiety, respectively. The spectrum of *E* isomer has an intense band at 1662 cm⁻¹ and virtually no absorption at 1713 cm⁻¹. Two carbonyl stretches of the *E* complex should lie close to each other according to DFT, and this is the reason why these bands overlap in the experiment. We note that during the course of our calculations, we considered only the betaine complex in which is the betaines' carboxylate group coordinated to the positively charged trimethylammonium group of HTI.

Unfortunately, we did not see any *E* → *Z* photoswitching to occur when we irradiated [E-HTI.betaine]⁺ complexes in the ion trap at 3 K with 490 nm light. We chose this wavelength, because it is an absorption maximum (see He-visPD spectrum in Figure S11) and the other isomer does not absorb in this region. The IRPD spectrum of ions subjected to 490 nm light is almost the same as the spectrum of non-irradiated ions (Figure S12, black vs. red trace), with no increased absorption at 1713 cm⁻¹.

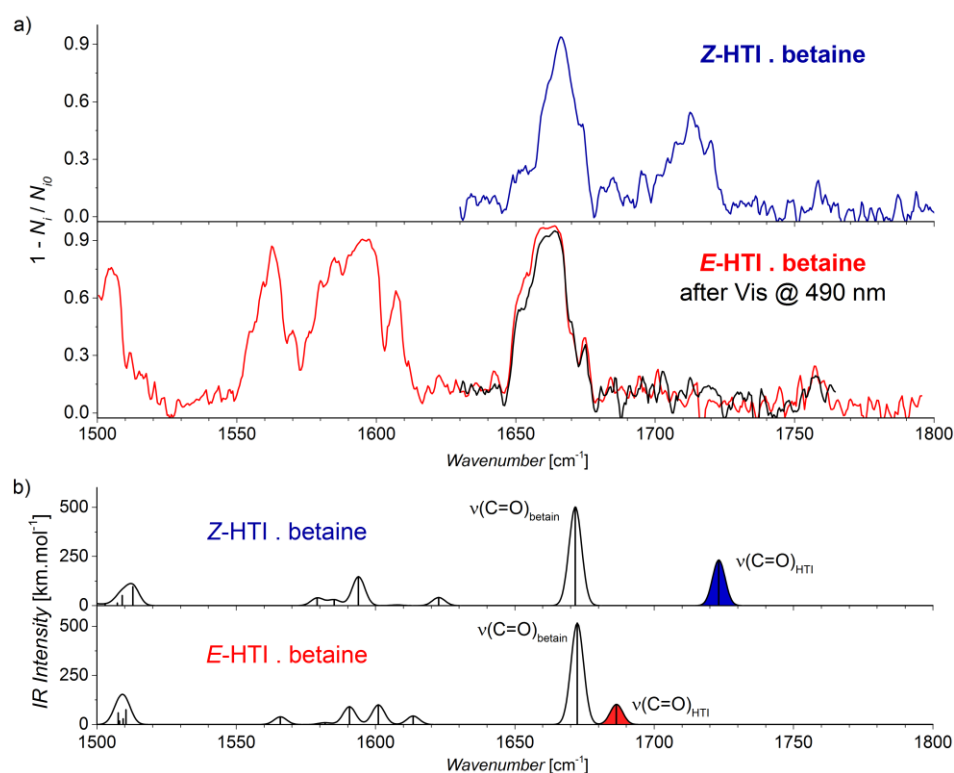


Figure S12. (a) Infrared spectra of [Z-HTI.betaine]⁺ (blue trace) and [E-HTI.betaine]⁺ complexes (red trace) measured by the He-IRPD technique at 3 K. Fragmentation of [HTI.betaine.He]⁺ complexes (loss of the helium tag) was monitored in both cases. The syringe with HTI solution was irradiated with 400 or 525 nm LEDs prior to ESI in order to obtain desired isomer (*E* or *Z*). Black trace corresponds to the IRPD spectrum of attempted isomerization; trapped [E-HTI.betaine]⁺ ions were first irradiated by a 490 nm light in the ion trap at 3 K and then the IRPD spectrum of product ions was measured. For the detailed timing sequences see Figure S9a and S13. (b) Theoretical spectra calculated at B3LYP-GD3BJ/6-311++G** level of theory, frequency scaling factor 0.99 was used. Betaine zwitterion was

considered to be coordinated by the carboxylate group to the positively charged trimethylammonium group of HTI.

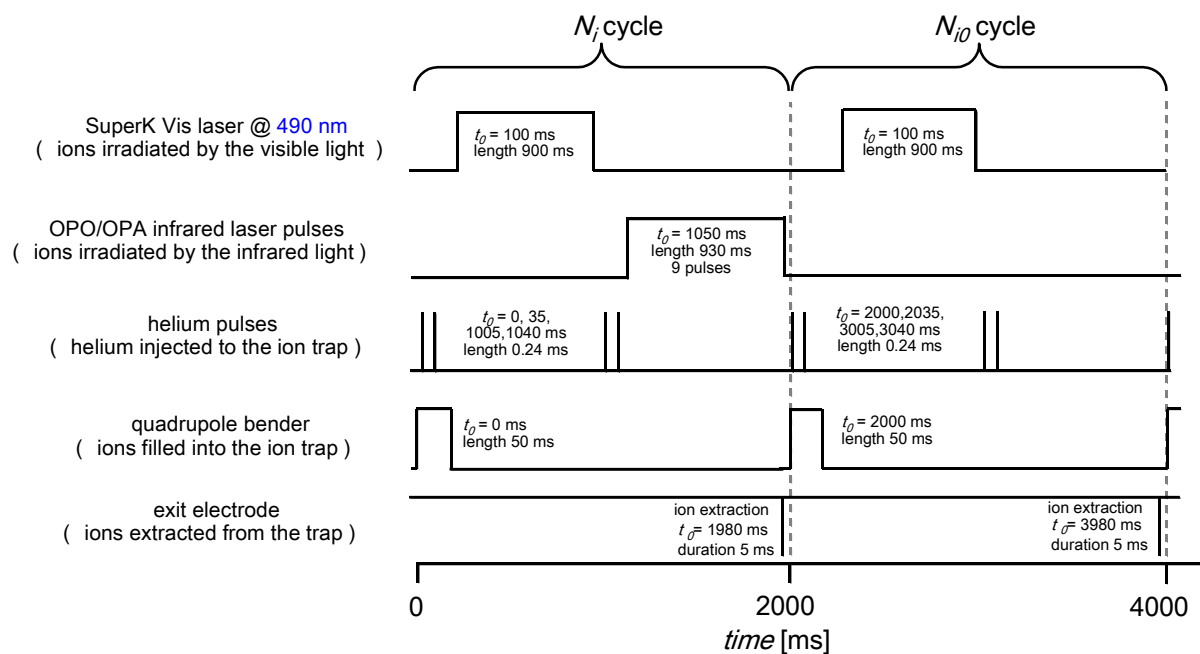
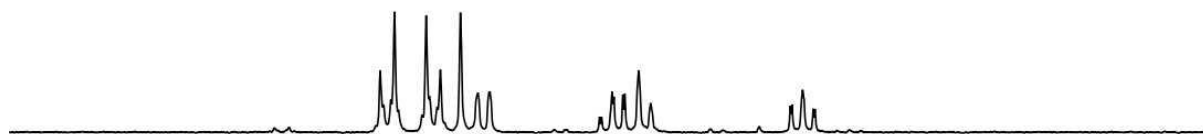


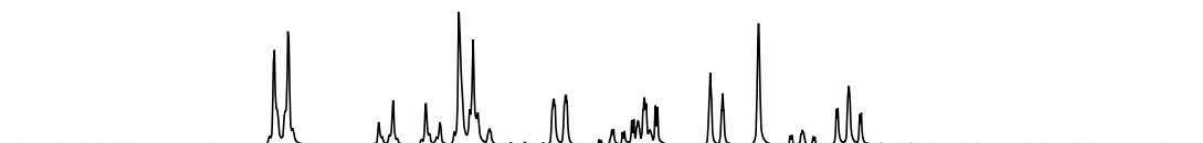
Figure S13. Timing sequence used for attempted $E \rightarrow Z$ isomerization of $[E\text{-HTI.betaine}]^+$ ions at 3 K (Figure S12a, black trace).

NMR data

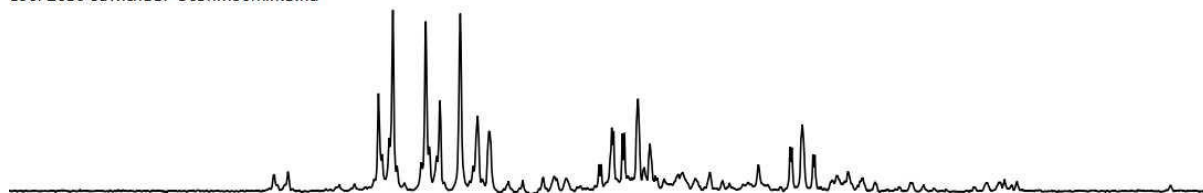
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18072016-sawich117-505nm80min.1.fid



8.6 8.4 8.2 8.0 7.8 7.6 7.4 7.2 7.0 6.8
 δ (ppm)

Figure S14. Investigation of HTI photoisomerization by NMR. ^1H NMR (400 MHz, CD_3OD) spectrum of (a) *Z*-HTI iodide salt; (b) the spectrum of *E*-HTI iodide salt obtained by the irradiation (420 nm, 30 min) of solution from (a); (c) the spectrum of *Z*-HTI iodide salt obtained by the irradiation (505 nm, 80 min) of solution from (b). Note that the spectrum in (c) contains signals of decomposed HTI which formed during $E \rightarrow Z$ photoisomerization.

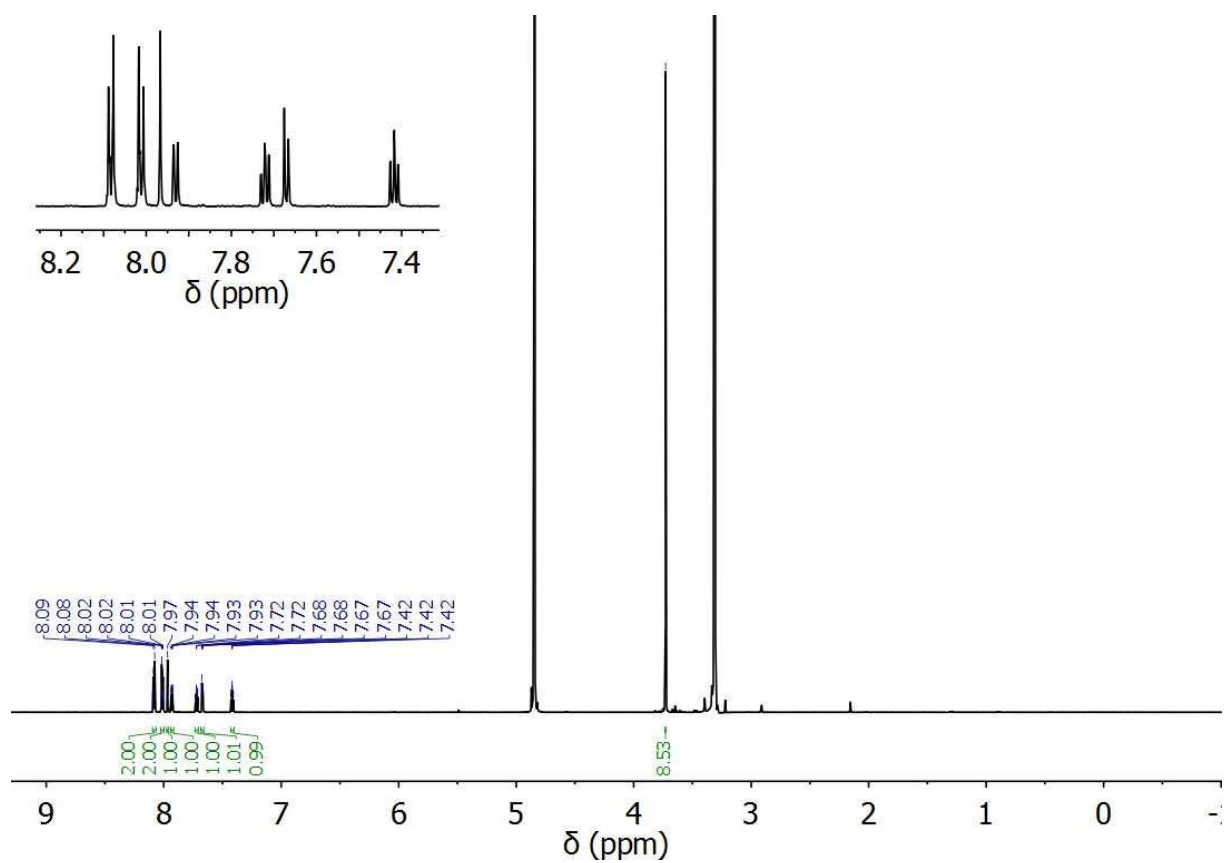


Figure S15. ^1H NMR (800 MHz, CD_3OD) spectrum of Z-HTI.

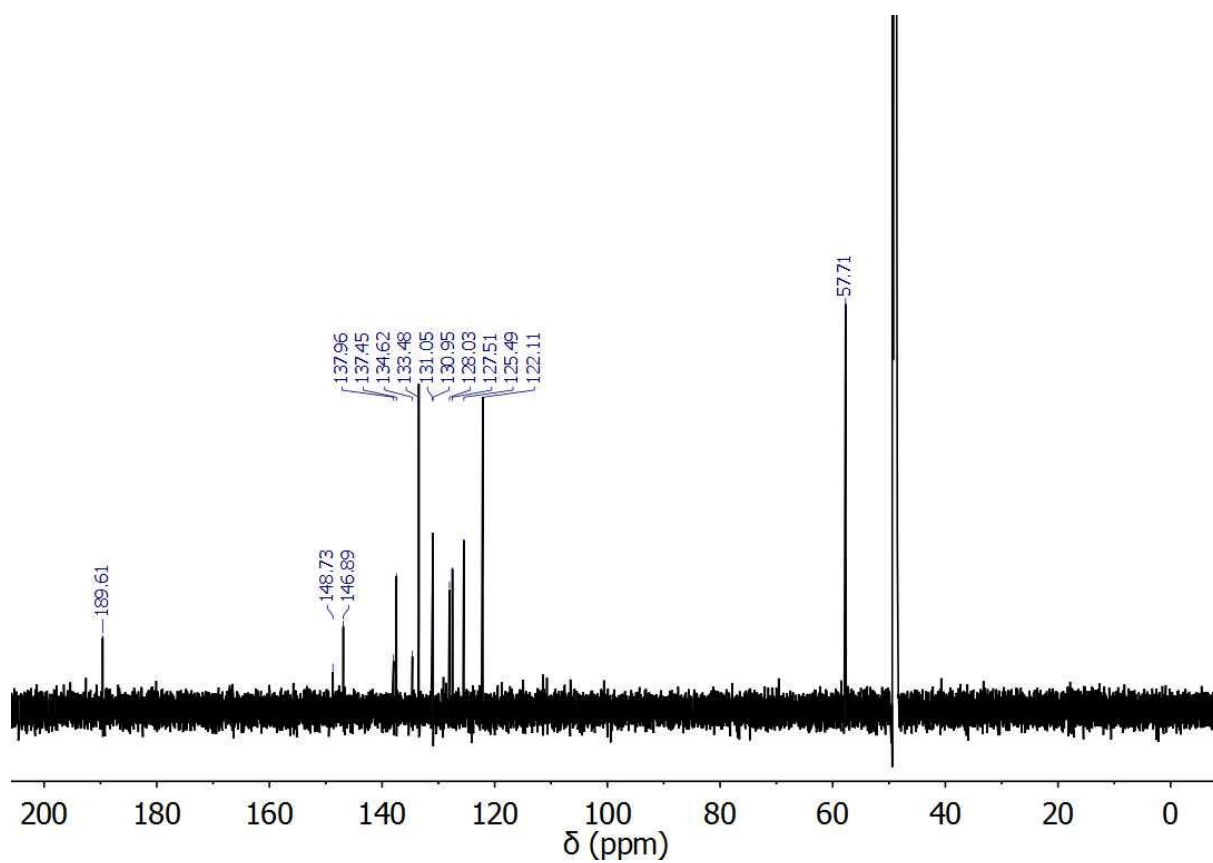


Figure S16. ^{13}C NMR (201 MHz, CD_3OD) spectrum of Z-HTI.

Note on the selection of the theoretical methods.

Typically, B3LYP functional provides very good IR spectra for optimized ions/molecules and therefore it is the most often used functional in this field. Nevertheless, in the case of HTI compounds, the optimization using the B3LYP often did not fully converge to minima (one small imaginary frequency was still present). Hence, the geometries and energies of the ground/excited state could be wrong. Therefore, we used the M06L functional, which in our experience also provides good results. We did not encounter any convergence issues using this functional. Further, for optimization of excited states we used a broken-symmetry approach to get the geometries of excited states, because the alternative TD-DFT method often provides unreliable optimized geometries of the excited states.

XYZ Coordinates of Calculated Structures

The format of individual records is following:

number_of_atoms

NAME method/basis_set charge multiplicity electronic_energy(Hartree) ZPE_correction
(Hartree) number_of_imaginary_frequencies

atom1 x y z

atom2 x y z

...

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39
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39

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S -3.0096171381 1.8335837087 -0.4032592406
H -3.3346959736 -2.7492941705 0.7073664868
H -5.9606080815 1.2724462713 -0.6227235984
H -7.09690224 -0.8910791284 -0.2301342722
H -5.8026231564 -2.8840215807 0.417788763
O -0.9806513726 -1.2343241184 0.6642360441
C -0.3508771858 1.6917438143 0.1044741887
H -0.4077817775 2.7465943157 0.3541197067
C 0.9386327114 1.1476915682 -0.0078998073
C 1.2105032411 -0.1204065852 -0.5921454154
C 2.0545480643 1.8848411735 0.464407081
C 2.4826831816 -0.6346866309 -0.6083416968
C 3.328245321 1.3708230176 0.4507878587
C 3.539992931 0.0946937486 -0.0692712642
H 0.4153444401 -0.6797919968 -1.0560513433
H 1.8912803153 2.8702704251 0.8812976012
H 2.6433546981 -1.6073238816 -1.0560512059
H 4.1331187564 1.9689799946 0.8504011202
N 4.9022937602 -0.5370676732 -0.0749031593
C 5.9486776525 0.3458108986 0.5236978802
C 5.3181631021 -0.8483373153 -1.4859660562
H 4.6008273249 -1.5310876538 -1.9266616354
H 5.3385223441 0.0789359495 -2.050155322
H 6.3043137322 -1.3057413845 -1.4679483268
H 6.0236631483 1.2602557604 -0.0558019634
H 6.8940433934 -0.1874413426 0.4932410479
H 5.6854031146 0.5704078688 1.552165515
C 4.8671485228 -1.8125801911 0.7220209074
H 4.1464792494 -2.4895624101 0.277702785
H 5.8580094539 -2.2599978049 0.7107407848
H 4.5675549685 -1.5735402752 1.737701938

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Z_T1 UM06L-D3/def2TZVP 1 3 -1224.8097236
0.3188982 0

C 5.3102411714 0.8545045329 -0.0694716435
C 3.9723902582 0.4880141822 -0.0385195059
C 3.6354677941 -0.8702460812 -0.0879562714

C 4.5950371351 -1.8718939391 -0.1673766648
C 5.922701145 -1.4856247837 -0.1980718368
C 6.2767813727 -0.1350570552 -0.1496533353
C 2.8062688677 1.3608987766 0.0451072387
C 1.5875574899 0.5700060875 0.0429378607
S 1.913683219 -1.1005585711 -0.0326685829
H 5.5735312454 1.9037651569 -0.0297582428
H 4.3157311805 -2.9163535967 -0.2041157835
H 6.6950082954 -2.2402938046 -0.2607485234
H 7.3231220011 0.1388075797 -0.1733777289
O 2.8105307755 2.5948489289 0.1122903807
C 0.3211727389 1.2183190636 0.1279612626
H 0.4497050052 2.2916387683 0.2468267724
C -0.9933099418 0.7449064797 0.0717466006
C -2.0515298757 1.6873918522 0.2156747428
C -1.3808879845 -0.6089916312 -0.122987719
C -3.3669180466 1.3157538511 0.1778201575
C -2.7030455797 -0.9876165683 -0.1612515135
C -3.7024232022 -0.0303066368 -0.0108862948
H -1.7992426102 2.7297206409 0.3626454435
H -0.6312071281 -1.3758112291 -0.2561766447
H -4.1302432677 2.074333569 0.2953061563
H -2.9327167402 -2.031397437 -0.3148420368
N -5.1571827164 -0.3915728466 -0.0533978781
C -5.3822287722 -1.8540425684 -0.2641832234
C -5.830968634 0.3418556784 -1.1810873329
H -5.7242935974 1.4095744615 -1.0264884809
H -5.3510616923 0.0547995722 -2.1117360543
H -6.8835156875 0.0714548282 -1.1949607025
H -4.9459818453 -2.1531121256 -1.2118215543
H -6.4538759786 -2.0278831722 -0.2815828758
H -4.9326790423 -2.4098889197 0.5522653715
C -5.8139364622 -0.009216272 1.2449675885
H -5.7132573725 1.0599887911 1.3929826411
H -6.8653481514 -0.2811792665 1.198933969
H -5.317289366 -0.5415132962 2.0500872446

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E_T1 UM06L-D3/def2TZVP 1 3 -1224.8137062
0.31878 0
C -3.9413285963 -1.7828491017 -0.5806412778
C -3.2652195801 -0.6148214387 -0.2578877085
C -3.9513543417 0.4226352701 0.3770347135
C -5.292599835 0.3212837388 0.7136401091
C -5.9501775469 -0.8550087688 0.3903698713
C -5.2820398617 -1.8969781641 -0.2500528351
C -1.862472353 -0.2991482821 -0.5285250564
C -1.5625605737 1.0443136545 -0.0534058338
S -2.916119448 1.7980248755 0.6585836822
H -3.4092487791 -2.5833054537 -1.0788140006
H -5.8119349968 1.1331743699 1.2046019319
H -6.9976501961 -0.9617968836 0.6391634239
H -5.8186849445 -2.8060827139 -0.4870609221
O -1.0416786571 -1.041693544 -1.0787291141
C -0.3183264763 1.747786808 -0.178397518
H -0.3676042642 2.796784062 -0.4548593053
C 0.9601436705 1.1888611072 -0.0405082723
C 1.1903625698 -0.1196666824 0.4627317201
C 2.1008835533 1.9441449666 -0.409270137

C 2.4578207203 -0.6386990494 0.531418066
C 3.3720532069 1.4232472531 -0.3476085424
C 3.5490478561 0.1210133733 0.1113552729
H 0.3581573158 -0.716341439 0.8011771185
H 1.9643035591 2.9542201241 -0.7740881253
H 2.5899757917 -1.6419189599 0.9164403517
H 4.2007582126 2.0395852892 -0.6609504345
N 4.9093615808 -0.513675398 0.1728698996
C 5.9904621065 0.3917090717 -0.3225489568
C 4.9254705274 -1.7541959787 -0.6778239426
H 4.18208425 -2.4508210546 -0.3074178837
H 4.6878905888 -1.4729660923 -1.6990370681
H 5.9152425444 -2.200325748 -0.6246663047
H 5.7888051711 0.6624932673 -1.3538413553
H 6.9315972304 -0.1461554887 -0.2600459902
H 6.0332159463 1.2788557034 0.3007598046
C 5.2349014759 -0.8836645467 1.5933007319
H 4.4930183894 -1.5847036381 1.958488862
H 6.2214217708 -1.3397081717 1.6182634446
H 5.2173734125 0.0190206636 2.195963581

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Z_TS UM06L-D3/def2TZVP 1 3 -1224.7813501
0.3144501 1 (610i)
C -5.3064852991 0.8186384803 0.1773818494
C -3.9664411161 0.4727565573 0.1049428493
C -3.6104941477 -0.8205503688 -0.2856951315
C -4.556767619 -1.7825482351 -0.6095336246
C -5.8915865043 -1.4193780578 -0.5317827044
C -6.2639826722 -0.1334089258 -0.1419025121
C -2.8107241916 1.3181471016 0.3987724992
C -1.5649711002 0.5508955798 0.2018976845
S -1.8803155563 -1.0456021981 -0.3005693551
H -5.5814491066 1.8206420844 0.4811173506
H -4.2663873618 -2.779979622 -0.9107493523
H -6.6538494811 -2.1468375299 -0.7769930128
H -7.3135067869 0.1225478285 -0.0887877419
O -2.8228567333 2.4875111415 0.756157657
C -0.3282606258 1.1744792019 0.4336070091
H -0.4729560806 2.2084748289 0.741779203
C 0.9912503309 0.7331128698 0.3459834289
C 2.0300090076 1.6560466222 0.6587018495
C 1.4039900875 -0.5742498244 -0.03353086
C 3.3492494437 1.3132771956 0.6095847415
C 2.7211061398 -0.9242714244 -0.0806703018
C 3.7356690805 0.0025012622 0.256316381
H 1.7533001016 2.6611714633 0.9506582755
H 0.6671763856 -1.322962264 -0.2909793654
H 4.0883492752 2.0568719369 0.8663078636
H 2.9763088606 -1.9314875081 -0.3737877887
N 5.087663159 -0.3396467363 0.1191803886
C 5.4195158293 -1.7674344926 0.2913553147
C 6.049964221 0.5178779577 0.8366949376
H 6.0043765703 1.5366219256 0.4674505357
H 5.8448139867 0.5083595675 1.9070887897
H 7.049648889 0.1351659113 0.6588146591
H 5.1393783771 -2.1034726207 1.2892712434
H 6.489564522 -1.8892478378 0.1571051919
H 4.9133356811 -2.374181983 -0.4504638067

C 5.6550732925 -0.0292555655 -1.8222759705
H 5.4276968356 1.0230925511 -1.919948648
H 6.702754911 -0.297294187 -1.8246277651
H 4.9845888993 -0.7081671782 -2.3304170734

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E_TS UM06L-D3/def2TZVP 1 3 -1224.7801566
0.3135578 1 (585i)

C -3.9893750939 -1.9018943125 -0.0252209904
C -3.3088452032 -0.6945246852 -0.0538394093
C -4.0199114664 0.5021438536 0.0609216568
C -5.3973138454 0.5263461505 0.2220151332
C -6.0611856454 -0.6902219723 0.2573651339
C -5.3665026947 -1.8920699298 0.1354553694
C -1.8671794682 -0.5017411653 -0.2109384084
C -1.5575677192 0.9377705436 -0.1925109254
S -2.9682377648 1.8880480519 -0.0240996821
H -3.4349116562 -2.8269430519 -0.1204888252
H -5.9380994833 1.4593968149 0.3077757672
H -7.1359828745 -0.702797871 0.3787136537
H -5.9102228456 -2.8265591717 0.1719830237
O -1.0394030844 -1.3906600276 -0.3843431238
C -0.3096674796 1.5612348649 -0.4088949056
H -0.3444294374 2.5514760386 -0.8553015482
C 0.9668557057 1.0576593995 -0.1600586933
C 1.2451827474 -0.0810837472 0.6484107523
C 2.089486299 1.7339802306 -0.7161350995
C 2.5204929303 -0.530645858 0.8281464628
C 3.362524427 1.275481659 -0.5545640727
C 3.6156297328 0.1220901375 0.22317623
H 0.4374063042 -0.5845879326 1.1545459228
H 1.9175014307 2.6252876257 -1.3068671668
H 2.6772245537 -1.3877445494 1.4654023873
H 4.173446549 1.8171613255 -1.0175796244
N 4.9033469837 -0.4114831877 0.3136206463
C 6.0224093721 0.5142217643 0.0642883214
C 5.1617685411 -1.7609232492 -1.2658965792
H 4.35964459 -2.4498656134 -1.0427187097
H 5.0029592601 -1.0918005357 -2.0993692764
H 6.1703383246 -2.1193154615 -1.1130966196
H 5.9754191375 0.9116333343 -0.9436539576
H 6.9526733729 -0.0346242551 0.1692039583
H 6.0057680617 1.3358595421 0.7804448971
C 5.1746544251 -1.2922665287 1.4639881064
H 4.5292620292 -2.1632944059 1.4422297625
H 6.2041320494 -1.630191985 1.4026931887
H 5.0267789352 -0.7538558395 2.4002472441

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Z_fragment UM06L-D3/def2TZVP 1 2 -
1184.9618987 0.2802062 0

C -5.2872821636 0.8856363557 0.0752609274
C -3.9496240096 0.5195495971 0.0665616549
C -3.598568566 -0.8213879812 -0.0656801753
C -4.5500056223 -1.8174979668 -0.1906609353
C -5.8859170898 -1.4362217969 -0.1803370542
C -6.2540139304 -0.1009239845 -0.0490662387
C -2.793577949 1.4056665766 0.1845675422
C -1.5227671545 0.5903789714 0.1274862587

S -1.8563912765 -1.0752880745 -0.053762818
H -5.551729175 1.930474531 0.178501456
H -4.2701215761 -2.8571524524 -0.2930175113
H -6.6509590627 -2.1954745831 -0.2764817642
H -7.3014674432 0.1670094568 -0.0442114471
O -2.7896964067 2.6086821029 0.310261979
C -0.3196966091 1.2441336137 0.2221984417
H -0.4578412476 2.3185211462 0.3312130091
C 1.0126925774 0.7893352258 0.2040675204
C 2.0471998015 1.753950111 0.3271444361
C 1.4114210483 -0.5644530939 0.0719218614
C 3.3644706927 1.4115607339 0.32025309
C 2.7247099046 -0.9249605011 0.0631026636
C 3.7522888209 0.0518019103 0.1871447779
H 1.7690583116 2.7952080213 0.4295140393
H 0.666934511 -1.3427790568 -0.0252407826
H 4.1141191795 2.1826485326 0.4169689698
H 2.9836516101 -1.9679735133 -0.0397030949
N 5.0502904125 -0.3044739808 0.1783006208
C 5.4423682916 -1.6985966076 0.0419390446
C 6.0968194587 0.6975260603 0.3054186857
H 6.0116847672 1.2357499446 1.2497826335
H 6.0497013272 1.4193245301 -0.5103586788
H 7.06279884 0.2078443699 0.2751879413
H 5.0471919321 -2.2999045798 0.8613168656
H 6.5234469405 -1.7655969079 0.0583077243
H 5.0852231757 -2.1169523357 -0.8996165858

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E_fragment UM06L-D3/def2TZVP 1 2 -
1184.957846 0.279883 0

C -4.3145391522 -1.8449650985 0.1689051577
C -3.5181736797 -0.7148257214 0.0616723831
C -4.1059848593 0.5424836558 -0.0628728507
C -5.4814186451 0.7046968564 -0.0835732265
C -6.2657025041 -0.4359360947 0.0247184693
C -5.6926058618 -1.6986481366 0.1497434367
C -2.0568389075 -0.6879506118 0.0642421396
C -1.5795357964 0.7290974879 -0.0720892911
S -2.9166967062 1.8155418295 -0.1826255172
H -3.8457397708 -2.8164929078 0.2651979817
H -5.9331309372 1.6829319196 -0.1804519461
H -7.3430533375 -0.3370695967 0.011248014
H -6.3295002089 -2.5684966179 0.2321888074
O -1.3394564787 -1.6636744142 0.1618420854
C -0.3148562903 1.2857824648 -0.1217844675
H -0.3304091404 2.3680385672 -0.2270850034
C 1.0009848478 0.7786653971 -0.0678883832
C 1.3896720296 -0.5807859332 0.0655154147
C 2.0467996112 1.740395568 -0.1576771905
C 2.7029962129 -0.9385102378 0.1048223617
C 3.3612107078 1.3951532682 -0.11955921
C 3.7389967554 0.0314371957 0.0142240687
H 0.621188307 -1.3360977328 0.1362237069
H 1.7800544106 2.7850696318 -0.2600893693
H 2.9548213448 -1.9835914846 0.2071659132
H 4.1153702958 2.1645649461 -0.1916670918
N 5.0341278983 -0.3289498853 0.0537307147
C 6.0883737003 0.6686868369 -0.0397008946

H 6.0304301047 1.2137625233 -0.9821541592
H 7.0509298657 0.1740529094 0.0117562387
H 6.0243495592 1.3851656957 0.7795880265
C 5.4165349165 -1.7261029983 0.1908111637
H 5.0390641255 -2.3198476991 -0.6421691893
H 6.4974193289 -1.7977374566 0.2018830511
H 5.0323777884 -2.148786887 1.1195817664

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CH3 radical UM06L-D3/def2TZVP 0 2 -
39.8446496 0.0292223 0
C -5.42886192 2.1228891958 -0.0075326147
H -4.8970356264 2.2185566233 0.924787492
H -6.4904878142 1.937247135 -0.0073736817
H -4.8983486394 2.2120840459 -0.9413341956

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Z_IR B3LYP RB3LYP-D3BJ/6-311+G** 1 1 -
1225.0027451 0.3192522 1 (21i)
C -1.3088096488 0.0499193965 -6.1586746444
C -0.8835825706 -0.2941644271 -4.8752703687
C 0.3184827804 0.2090897851 -4.3742582291
C 1.1181982469 1.0565233929 -5.1270089466
C 0.6834479933 1.3945253735 -6.4099403258
C -0.5184983726 0.8981777575 -6.9254407288
C -1.5914097926 -1.1738204419 -3.9344114257
C -0.7935226418 -1.293046839 -2.6415501258
S 0.6859262108 -0.3476621177 -2.7156091273
H -2.2442805849 -0.349882715 -6.5312764294
H 2.0505556521 1.4469329744 -4.7385542087
H 1.2925951963 2.0551354812 -7.0153312108
H -0.8308522817 1.1771587371 -7.9237456092
O -2.6478593159 -1.7402205622 -4.1117777874
C -1.2755024479 -2.0608627964 -1.6438606629
H -2.2252548076 -2.5314334888 -1.8858248927
C -0.7414683705 -2.3535133733 -0.3282978216
C -1.4850774267 -3.209671932 0.5096056248
C 0.4666910684 -1.8473513993 0.1799927471
C -1.0515440876 -3.5433602267 1.7802508399
C 0.9123032488 -2.1761907107 1.4563045944
C 0.1532303812 -3.0232975547 2.2543909965
H -2.4214431446 -3.617803274 0.1494611186
H 1.0822571946 -1.1863126895 -0.4119090209
H -1.6630317837 -4.2049765592 2.3796094413
H 1.848660932 -1.755353373 1.7899661249
N 0.5970063468 -3.4058737146 3.6419222403
C 1.909318785 -2.7771784948 4.0261381837
C 0.7671283428 -4.9067644127 3.7252811186
H -0.1830350821 -5.3878409021 3.515142761
H 1.505285652 -5.2063134667 2.9848348142
H 1.1023074382 -5.1621602301 4.7292683517
H 2.6817719332 -3.1069789697 3.3364598771
H 2.1507672573 -3.1054510084 5.0344780455
H 1.809710007 -1.6951736615 4.0049684286
C -0.4382480136 -2.9552964999 4.648783722
H -1.3835698418 -3.444108162 4.434680898
H -0.0934240718 -3.226703552 5.6452805675
H -0.5508766844 -1.8771574759 4.5604601822

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E_IR B3LYP RB3LYP-D3BJ/6-311+G** 1 1 -
1224.998821 0.3193278 1 (9i)
C 0.1809095101 0.5343483007 -5.9266384231
C -0.3335745938 -0.1595702934 -4.828073983
C -0.6591182922 0.5213482177 -3.6510420658
C -0.4810833625 1.8955129513 -3.5431462491
C 0.0327609347 2.5766913434 -4.6454423702
C 0.363079084 1.9065888127 -5.8308563965
C -0.5820590413 -1.6019029795 -4.7739625964
C -1.1412603388 -1.9813316195 -3.4186629394
S -1.2939701387 -0.5412360433 -2.3843560275
H 0.4266305458 -0.0121554282 -6.829115047
H -0.7322364409 2.4255069464 -2.6330118474
H 0.1786076744 3.6484310437 -4.5803036467
H 0.7602698985 2.463582651 -6.6698466222
O -0.3691257391 -2.3826783683 -5.6883339375
C -1.5205620617 -3.1774287437 -2.9034510161
H -1.8882171922 -3.1215848306 -1.8813291006
C -1.5509130342 -4.5445440973 -3.4083668621
C -1.1476862832 -4.9735423188 -4.6882710992
C -2.0325760999 -5.5263611372 -2.5217140902
C -1.2262823558 -6.3094795698 -5.0485583787
C -2.1145820391 -6.8675373895 -2.8750308737
C -1.7080429251 -7.2557029423 -4.1461993419
H -0.773243876 -4.246343576 -5.3930920469
H -2.3524308049 -5.2361979216 -1.5282050062
H -0.9034553167 -6.5859889583 -6.044277916
H -2.4935727838 -7.5683482846 -2.1467251441
N -1.7728160243 -8.6949495516 -4.587650807
C -2.3109067277 -9.6070428786 -3.519141004
C -0.3849494635 -9.1774700613 -4.9461655567
H 0.0063628463 -8.5732816112 -5.7585279144
O 0.2485174294 -9.0712636932 -4.068473189
H -0.4487380001 -10.2207696721 -5.251302433
H -1.6609462519 -9.5636439302 -2.6492441739
H -2.3225194806 -10.6175619869 -3.9212761834
H -3.3212804241 -9.3010029239 -3.2611866872
C -2.6796060708 -8.8148877804 -5.7921563498
H -2.2820631363 -8.2116891737 -6.6022186053
H -2.7236210232 -9.8612894797 -6.0900777679
H -3.6660835905 -8.4528103404 -5.5116825319

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Z_betaine RB3LYP-D3BJ/6-311+G** 1 1 -
1627.5311691 0.486101 2 (19i, 15i)
C 5.5795813713 -0.6733212277 -0.2310506259
C 4.2227224714 -0.3650523749 -0.1311234697
C 3.81619123 0.8665987279 0.3864911391
C 4.7407211415 1.8107305733 0.8124856211
C 6.0952614581 1.492424702 0.7081229467
C 6.5165288964 0.2621005765 0.1914435312
C 3.1049223044 -1.2341877502 -0.5299591157
C 1.7858704725 -0.5306632446 -0.260466301
S 2.0434573635 1.0699857426 0.4303930248
H 5.8746206567 -1.6342260386 -0.6354327254
H 4.4267033617 2.7661677986 1.2141404184
H 6.8330687193 2.2156874005 1.0349400412
H 7.5743755234 0.0421753783 0.1220191322

O 3.1804417234 -2.3479865175 -1.0048717643
C 0.6308449173 -1.1553074216 -0.5619567668
H 0.7782201706 -2.1441402122 -0.9894824005
C -0.7493203267 -0.7297385543 -0.417123451
C -1.7588852438 -1.5990154836 -0.8757514174
C -1.1583938321 0.4874857522 0.1499278135
C -3.0999483997 -1.270742761 -0.7806731076
C -2.5047784517 0.8246934144 0.2503221586
C -3.4762836986 -0.0514128679 -0.2171248662
H -1.4777962444 -2.5482758909 -1.3156824721
H -0.4336333536 1.1929792789 0.5287304425
H -3.8368986427 -1.9722218131 -1.1479234114
H -2.7620245862 1.7732978645 0.6957275193
N -4.9356056163 0.273416284 -0.1287700811
C -5.2064548785 1.6319879208 0.4650360865
C -5.6380214193 -0.7490939257 0.7409445306
H -5.5095104818 -1.7320004561 0.2961861231
H -5.1673014779 -0.7271815964 1.7220188692
H -6.6985680468 -0.4936928956 0.8038007216
H -4.8339924716 1.6530219816 1.4864160897
H -6.285812413 1.7766503985 0.4337507662
H -4.7112910197 2.3869725122 -0.1412588483
C -5.5541574619 0.2649518605 -1.511905008
H -5.4750005187 -0.7349920327 -1.9283066273
H -6.594998548 0.5700787988 -1.4042909741
H -4.9992545 0.9686474634 -2.1291686269
C -9.0361937883 0.8024757926 0.2573778944
O -8.8008773111 -0.201050324 0.9634061734
O -8.2463032887 1.5123086991 -0.3941172768
C -10.5039664991 1.3032674899 0.1202527048
H -10.5565194046 2.3340891677 0.4704366895
N -11.5774875426 0.5279425144 0.8740604134
H -10.7841077814 1.2849674193 -0.9329377988
C -12.9037334436 1.1743484423 0.6054140071
H -13.1008042276 1.1480828249 -0.4647357518
H -13.678876998 0.6271210889 1.1399805984
H -12.8714517567 2.2061344403 0.9505355856
C -11.6219223079 -0.9001435118 0.4003559611
H -10.6533872909 -1.3461021515 0.6069186852
H -12.4208340294 -1.4145393879 0.9321637363
H -11.8259382292 -0.8994115682 -0.6693174062
C -11.3050185991 0.5616940215 2.3538742571
H -12.1100152376 0.0353294007 2.8644187904
H -10.3449258795 0.0832963459 2.5239099309
H -11.2788936355 1.6025078131 2.6729211065

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E_betaine RB3LYP-D3BJ/6-311++G** 1 1 -
1627.5261381 0.486199 2 (13i, 2i)
C -4.406641851 2.0372888895 -0.071463753
C -3.6918657575 0.8396884801 0.0116692263
C -4.366247305 -0.3817631553 0.1025366694
C -5.7562506474 -0.4347872683 0.1125494154
C -6.4580484129 0.7657925958 0.0286820467

C -5.7935912816 1.9963752553 -0.0630913984
C -2.2300152479 0.7206796696 0.0155676001
C -1.8296047768 -0.7320974626 0.1113463096
S -3.2776945892 -1.7726274482 0.1980346314
H -3.8631938017 2.9719125301 -0.1409052074
H -6.2815512009 -1.379027365 0.1830534333
H -7.5414895422 0.7438209131 0.034809092
H -6.3665621321 2.9127649354 -0.1271524968
O -1.4559812581 1.6632376021 -0.049779053
C -0.6151196373 -1.3343306078 0.1320887575
H -0.6620008453 -2.419119615 0.1999894823
C 0.7639616559 -0.8633623934 0.0796383494
C 1.1883432525 0.4776910811 0.0133272864
C 1.7621083609 -1.854793521 0.1002678119
C 2.5368939135 0.7940348767 -0.0311581805
C 3.1154992525 -1.5423405763 0.0534118655
C 3.5036937117 -0.2096728754 -0.0136182884
H 0.4497918724 1.2644839801 -0.0049131609
H 1.4750429482 -2.8983867696 0.1530314583
H 2.8142477391 1.8387668073 -0.0797554244
H 3.832803242 -2.3480274258 0.0702506739
N 4.9482253981 0.1870385297 -0.0618502339
C 5.8856731337 -0.9925801896 -0.0633289473
C 5.2896107544 1.0372088304 1.1446152175
H 4.646249803 1.9122558618 1.151058071
H 5.1089540031 0.439095844 2.0353746627
H 6.3337294693 1.3335595429 1.047931572
H 5.7401316288 -1.5578065704 0.8543375545
H 6.909632235 -0.6188622803 -0.1185378675
H 5.6684083138 -1.6117624633 -0.9307666309
C 5.2275138474 0.9836109795 -1.3194748248
H 4.586881079 1.8601713652 -1.3327360915
H 6.2749515126 1.2814415193 -1.2873708169
H 5.0033395766 0.3484057388 -2.1739036363
C 9.0087080988 1.05830378 -0.2401671471
O 8.0498555668 1.8490661875 -0.1542854235
O 9.0026283964 -0.1898241362 -0.2947794489
C 10.3709547293 1.8111656735 -0.2789255595
H 10.3686276286 2.4961773707 -1.1265638952
N 11.6314410759 0.964191804 -0.403215796
H 10.4743497217 2.3965912868 0.6346090723
C 12.8174094633 1.8814180124 -0.4291096889
H 12.8418221609 2.4552240165 0.4954023572
H 13.7239141329 1.2848557156 -0.5212043726
H 12.7264731575 2.5536391141 -1.2802041201
C 11.7562057797 0.0340934231 0.7739047991
H 10.8913454248 -0.6228519716 0.7695520245
H 12.6846585278 -0.5259102682 0.6730995116
H 11.7794505402 0.6340209529 1.6824699894
C 11.5998742375 0.1651305536 -1.6782346355
H 12.5286425594 -0.3981271348 -1.7550573343
H 10.736795882 -0.4927518768 -1.6339367278
H 11.5139963157 0.8581504835 -2.5138835727