|  |
| --- |
| **Table S1: Vibrational frequency assignments of OTTHPYHCT****Supplementary Table file:** |
| Mode No | Un-scaled | Scaled  | IRValue (Cm-1) | RamanValue (Cm-1) | IR intensity | Raman intensity | PED> 10**%** |
| 54 | 3711 | 3570 | 3720 |  | 12.4 | 1.6 | νN15H18 (71) + νN15H19 (29) |
| 53 | 3611 | 3474 |  |  | 16.8 | 1.9 | νN1H9 (83) |
| 52 | 3572 | 3437 |  |  | 12.2 | 7.3 | νN15H18 (27) +ν N15H19(64) |
| 51 | 3563 | 3428 |  |  | 7.1 | 2.1 | νN14 H17(92) |
| 50 | 3510 | 3377 |  | 3255 | 51.2 | 4.8 | νN2H8(96) |
| 49 | 3164 | 3044 |  | 3180 | 0.0 | 3.3 | νC5H11 (96) |
| 48 | 3042 | 2927 | 2954 |  | 0.4 | 4.3 | νC5H10 (95) |
| 47 | 1833 | 1763 | 1834 |  | 100.0 | 7.4 | νO12C4(86) |
| 46 | 1729 | 1663 | 1639 | 1604 | 70.7 | 28.7 | νN13C6 (70) |
| 45 | 1645 | 1583 | 1537 | 1517 | 37.7 | 0.9 | βH19N15H18 (86) |
| 44 | 1561 | 1502 |  |  | 68.5 | 1.4 | βH8N2C3 (24) +β H17N14N13 (40) |
| 43 | 1534 | 1476 |  | 1457 | 53.8 | 8.7 | βH9N1C3 (16) + βH8N2C3 (15) + βH17N14N13(35) |
| 42 | 1455 | 1399 | 1392 | 1367 | 5.1 | 4.0 | βH11C5H10 (87) |
| 41 | 1436 | 1381 |  |  | 91.8 | 6.3 | νN14C16 (27) +ν H8N2C3 (18) + βH18N1C16 (13) |
| 40 | 1417 | 1363 |  |  | 40.8 | 1.7 | νN2C3 (34)+ νN1C3 (21) |
| 39 | 1390 | 1337 |  |  | 19.1 | 0.8 | νN14C16 (13) + βH9N1C3 (28) + βH8N2C3 (20) + βH18N15C16 (12) |
| 38 | 1360 | 1308 | 1294 |  | 51.3 | 1.0 | νN2C6 (18) +ν C5C6 (15) + βH9N1C3 (11) |
| 37 | 1334 | 1283 |  | 1301 | 43.9 | 0.7 | νN15C16 (37) + βH17N14N13 (14) |
| 36 | 1308 | 1258 |  |  | 18.4 | 0.5 | νC4C5 (11) + βH10C5C6 (22) +τH11C5C6N2 (14) |
| 35 | 1268 | 1220 |  |  | 23.7 | 2.6 | νN2C6(15) + νN1C4 (33) + νC4C5 (10) + τH11C5C6N2 (13) |
| 34 | 1200 | 1154 |  | 1173 | 1.1 | 3.1 | βH10C5C6 (57) + τH11C5C6N2 (18) |
| 33 | 1172 | 1127 | 1165 | 1049 | 32.8 | 5.1 | νN1C3 (11) + νN14N13 (12) + νS7C3 (10) + βH9N1C3 (11) |
| 32 | 1137 | 1094 |  |  | 16.1 | 3.7 | νN14C16 (14) + νN14N13 (19) + νS7C3 (10) + βH18N15C16 (17) |
| 31 | 1044 | 1004 | 997 | 1009 | 0.4 | 0.5 | νN14N13 (15) + βH18N15C16 (35) |
| 30 | 1002 | 964 |  |  | 3.8 | 3.2 | ГC5C4C6H10 (50) + ГO12C5N1C4 (18) |
| 29 | 967 | 930 |  |  | 1.5 | 2.0 | νN1C4 (15) + νC4C5 (23) + νS7C3 (10) + βN2C6N13 (12) |
| 28 | 920 | 885 |  |  | 1.9 | 4.0 | νN2C6 (19) + νC5C6 (23) |
| 27 | 893 | 859 |  | 831 | 0.8 | 1.3 | βN2C6N13 (16) + βC4C5C6 (19) |
| 26 | 782 | 752 | 796 | 728 | 21.1 | 0.9 | βN14N13C6 (17) + τH9N1C3N2 (12) + ГN14C16N13H17 (13) |
| 25 | 732 | 704 |  |  | 3.5 | 5.5 | νN14C16 (11) + νS20C16 (59) |
| 24 | 716 | 689 |  |  | 20.4 | 0.4 | τH9N1C3N2 (66) |
| 23 | 649 | 624 |  |  | 24.9 | 1.6 | τH8N2C3S7 (27) + ГS20N14N15C16(14) |
| 22 | 636 | 612 | 644 | 647 | 2.7 | 3.8 | τS20N14N15C16 (16) + τS7N1N2C3 (66) |
| 21 | 616 | 593 |  |  | 1.7 | 8.1 | τO12C5N1C4 (10) + τS20N14N15C16 (19) + τS7N1N2C3 (14) |
| 20 | 613 | 590 |  |  | 0.9 | 3.5 | νC4C5 (10) + βN1C4O12 (13) + τH8N2C3S7 (31) |
| 19 | 570 | 548 | 557 | 534 | 5.8 | 2.8 | τH8N2C3S7 (18) + ГN14C16N13H7(13) + ГS20N14N15C16 (35) |
| 18 | 567 | 545 |  |  | 5.9 | 13.2 | βN1C4O12 (10) |
| 17 | 544 | 523 |  |  | 2.5 | 2.9 | τH18N1C16N14 (13) + ГO12C5N1C4 (21) |
| 16 | 516 | 497 |  | 505 | 8.7 | 1.9 | βN1C4O12 (13) + τH18N15C16N14 (22) + ГO12C5N1C4 (14) |
| 15 | 490 | 471 |  | 472 | 5.6 | 4.4 | βN1C4O12 (15) + ГN14C16N13H17 (11) + τH18N15C16N14 (16) |
| 14 | 470 | 452 |  | 448 | 50.8 | 9.3 | νS7C3 (10) + βC6N2C3 (22) + τH18N15C16N14 (14) |
| 13 | 462 | 444 |  |  | 10.0 | 6.9 | βC6N2C3 (14) + βN14C16S20 (12) + τH18N15C16N14 (11) |
| 12 | 426 | 409 |  | 405 | 2.3 | 7.1 | βN15C16N14 (44) + βN1C3S7 (12) |
| 11 | 358 | 345 |  |  | 33.1 | 4.7 | ГN15H18C16H19 (61) |
| 10 | 314 | 302 |  |  | 0.5 | 12.3 | βN1C3S7 (18) |
| 9 | 294 | 283 |  |  | 2.8 | 3.1 | βN14C16S20 (30) + τC5C6N13N14 (27) |
| 8 | 281 | 271 |  |  | 3.7 | 7.0 | βN2C6N13 (18) + τN15C16N14N13 (17) + τC16N14N13C6 (23) |
| 7 | 181 | 174 |  |  | 3.3 | 25.8 | βN1C3S7 (11) + τC16N14N13C6 (11) + ГN2C3C6C5 (33) |
| 6 | 146 | 141 |  |  | 3.7 | 3.7 | τN1C4C3N2 (54) + τC5C6C4N1 (16) |
| 5 | 123 | 118 |  |  | 0.9 | 2.3 | τN15C16N14N13 (18) + τC5C6C4N1 (27) |
| 4 | 120 | 116 |  |  | 0.5 | 9.7 | τN15C16N14N13 (37) + τC5C6N13N14 (13) |
| 3 | 73 | 70 |  |  | 0.1 | 20.6 | τC16N14N13C6 (20) + τC4C5C6N13 (47) |
| 2 | 57 | 55 |  |  | 1.5 | 60.9 | βC16N14N13 (14) + τC16N14N13C6 (16) + τC5C6C4N1 (13) + τC5C6N13N14 (23) |
| 1 | 32 | 31 |  |  | 1.0 | 100.0 | νN1C3 (10) + βC3N1C4 (47) |

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| **Table S2: Bond parameters of OTTHPYHCT** |
| **Bond Length** | **( Å)** | N1-C4-O12 | 121.36 | H8-N2-C3-N1 | -174.04 |
| N1-C3 | 1.38 | C5-C4-O12 | 124.03 | H8-N2-C3-S7 | 7.64 |
| N1-C4 | 1.39 | C4-C5-C6 | 113.96 | C3-N2-C6-C5 | -21.06 |
| N1-H9 | 1.01 | C4-C5-H10 | 106.59 | C3-N2-C6-N13 | 159.44 |
| N2-C3 | 1.37 | C4-C5-H11 | 109.53 | H8-N2-C6-C5 | 153.38 |
| N2-C6 | 1.38 | C6-C5-H10 | 108.67 | H8-N2-C6-N13 | -26.10 |
| N2-H8 | 1.01 | C6-C5-H11 | 110.42 | N1-C4-C5-C6 | -24.57 |
| C3-S7 | 1.65 | H10-C5-H11 | 107.36 | N1-C4-C5-H10 | 95.30 |
| C4-C5 | 1.51 | N2-C6-C5 | 115.78 | N1-C4-C5-H11 | -148.83 |
| C4-O12 | 1.21 | N2-C6-N13 | 127.28 | O12-C4-C5-C6 | 158.43 |
| C5-C6 | 1.50 | C5-C6-N13 | 116.93 | O12-C4-C5-H10 | -81.68 |
| C5-H10 | 1.09 | C6-N13-N14 | 118.89 | O12-C4-C5-11 | 34.17 |
| C5-H11 | 1.08 | N13-N14-16 | 126.15 | C4-C5-C6-N2 | 32.22 |
| C6-N13 | 1.28 | N13-N14-H17 | 107.53 | C4-C5-C6-N13 | -148.23 |
| N13-N14 | 1.40 | C16-N14-H17 | 113.77 | H10-C5-C6-N2 | -86.47 |
| N14-C16 | 1.37 | C16-N15-H18 | 115.35 | H10-C5-C6-N13 | 93.06 |
| N14-H17 | 1.01 | C16-N15-H19 | 120.32 | H11-C5-C6-N2 | 156.00 |
| N15-C16 | 1.36 | H18-N15-H19 | 116.27 | H11-C5-C6-N13 | -24.45 |
| N15-H18 | 1.00 | N14-C16-N15 | 112.72 | N2-C6-N13-N14 | -2.63 |
| N15-H19 | 1.01 | N14-C16-S20 | 125.54 | C5-C6-N13-N14 | 177.88 |
| C16-S20 | 1.67 | N15-C16-S20 | 121.72 | C6-N13-N14-C16 | 72.53 |
| **Bond Angle** | **( °)** | **Dihedral Angle** | **( ° )** | C6-N13-N14-H17 | -148.48 |
| C3-N1-C4 | 127.54 | C4-N1-C3-N2 | 8.20 | N13-N14-C16-N15 | 160.34 |
| C3-N1-H9 | 115.92 | C4-N1-C3-S7 | -173.46 | N13-N14-C16-S20 | -19.26 |
| C4-N1-H9 | 116.49 | H9-N1-C3-N2 | -173.94 | H17-N14-C16-N15 | 23.48 |
| C3-N2-C6 | 125.28 | H9-N1-C3-S7 |  4.38 | H17-N14-C16-S20 | -156.12 |
| C3-N2-H8 | 116.10 | C3-N1-C4-C5 | 4.90 | H18-N15-C16-N14 | 169.45 |
| C6-N2-H8 | 118.39 | C3-N1-C4-O12 | -178.02 | H18-N15-C16-S20 | -10.91 |
| N1-C3-N2 | 115.24 | H9-N1-C4-C5 | -172.93 | H19-N15-C16-N14 | 21.80 |
| N1-C3-S7 | 121.94 | H9-N1-C4-O12 | 4.14 | H19-N15-C16-S20 | -158.57 |
| N2-C3-S7 | 122.78 | C6-N2-C3-N1 | 0.51 |  |  |
| N1-C4-C5 | 114.53 | C6-N2-C3-S7 | -177.79 |  |  |

**TABLE S3: FMO’s OF OTTHPYHCT**

|  |  |  |
| --- | --- | --- |
| orbital | a.u | eV |
| 52 (A)--O | -0.27035 | -7.3568 |
| 53 (A)--O | -0.24776 | -6.7420 |
| 54 (A)--O | -0.24124 | -6. 5646 |
| 55 (A)--O | -0.23259 | -6.3292 |
| 56 (A)--O | -0.22837 | -6.2143 |
| 57 (A)--V | -0.07451 | -2.0275 |
| 58 (A)--V | -0.02827 | -0.7692 |
| 59 (A)--V | -0.00855 | -0.2326 |
| 60 (A)--V | 0.01965 | 0.5347 |
| 61 (A)--V | 0.03914 | 1.0650 |

|  |
| --- |
| **TABLE S4: NBO TABLE OF OTTHPYHCT** |
| **Type** | **Donor(i)** | **ED/e** | **Acceptor(j)** | **ED/e** | **E(2)****KJ/ mol.** | **E(j)−E(i) a. u** | **F( i, j) a. u** |
| n -π\* | LP ( 1) N 1 | 1.63092 | BD\*( 2) C 3 - S 7 | 0.41588 | 269.37 | 0.21 | 0.105 |
|  |  |  | BD\*( 2) C 4 - O 12 | 0.22219 | 207.32 | 0.29 | 0.11 |
| n -π\* | LP ( 1) N 2 | 1.62646 | BD\*( 2) C 3 - S 7 | 0.41588 | 292.42 | 0.21 | 0.109 |
|  |  |  | BD\*( 1) C 5 - C 6 | 0.02936 | 7.45 | 0.66 | 0.034 |
|  |  |  | BD\*( 1) C 6 - N 13 | 0.01655 | 4.69 | 0.86 | 0.031 |
|  |  |  | BD\*( 2) C 6 - N 13 | 0.23576 | 174.64 | 0.28 | 0.1 |
| n -π\* | LP ( 1) N 14 | 1.72592 | BD\*( 2) C 6 - N 13 | 0.23576 | 39.25 | 0.32 | 0.049 |
|  |  |  | BD\*( 2) C 16 - S 20 | 0.47855 | 213.76 | 0.26 | 0.108 |
| n -σ\* | LP ( 1) N 15 | 1.76031 | BD\*( 1) C 16 - S 20 | 0.04547 | 11 | 0.56 | 0.036 |
|  |  |  | BD\*( 2) C 16 - S 20 | 0.47855 | 195.77 | 0.24 | 0.101 |
| n -σ\* | LP ( 2) O 12 | 1.85531 | BD\*( 1) N 1 - C 4 | 0.09199 | 121.5 | 0.67 | 0.126 |
|  |  |  | BD\*( 1) C 4 - C 5 | 0.06488 | 88.74 | 0.63 | 0.105 |
| n -σ\* | LP ( 1) N 13 | 1.91415 | BD\*( 1) N 2 - C 6 | 0.0588 | 68.16 | 0.81 | 0.104 |
|  |  |  | BD\*( 1) C 5 - C 6 | 0.02936 | 6.44 | 0.78 | 0.031 |
|  |  |  | BD\*( 1) N 14 - C 16 | 0.07051 | 18.41 | 0.81 | 0.053 |
| n -σ\* | LP ( 2) S 7 | 1.88135 | BD\*( 1) N 1 - C 3 | 0.06379 | 49.58 | 0.61 | 0.077 |
|  |  |  | BD\*( 1) N 2 - C 3 | 0.06117 | 49.37 | 0.62 | 0.078 |
| n -σ\* | LP ( 2) S 20 | 1.87737 | BD\*( 1) N 2 - H 8 | 0.04233 | 6.23 | 0.63 | 0.028 |
|  |  |  | BD\*( 1) N 14 - C 16 | 0.07051 | 48.37 | 0.61 | 0.076 |
|  |  |  | BD\*( 1) N 15 - C 16 | 0.0483 | 43.14 | 0.63 | 0.073 |
| n -σ\* | LP ( 1) S 7 | 1.98627 | BD\*( 1) N 1 - C 3 | 0.06379 | 12.76 | 1.11 | 0.053 |
|  |  |  | BD\*( 1) N 2 - C 3 | 0.06117 | 13.35 | 1.13 | 0.054 |
| π -σ\* | BD ( 2) C 16 - S 20 | 1.96469 | BD\*( 1) N 2 - H 8 | 0.04233 | 13.64 | 0.73 | 0.044 |
|  |  |  | BD\*( 1) N 15 - H 19 | 0.01585 | 4.27 | 0.74 | 0.025 |
|  |  |  | BD\*( 1) C 16 - S 20 | 0.04547 | 7.36 | 0.56 | 0.028 |
|  |  |  | BD\*( 2) C 16 - S 20 | 0.47855 | 31.71 | 0.24 | 0.043 |

E(2) means energy of hyper conjugative interaction (stabilization energy).

**E(j)−E(i) -** Energy difference between donor(i) and acceptor(j) NBO orbitals.

F(i, j) - is the fork matrix element between i and j NBO orbitals

**TABLE S5: NLO PARAMETERS OF OTTHPYHCT**

|  |  |
| --- | --- |
| **Parameters** | **B3LYP/6-31G(d,p)** |
| *Dipole moment ( μ )* Debye |
| μx | 1.4064 |
| μy | -0.8975 |
| μz | -1.3616 |
| **μ** | **2.1175Debye** |
| *Polarizability (* α0 *)* x*10-30esu* |
| αxx | 162.54 |
| αxy | -1.94 |
| αyy | 145.97 |
| αxz | -6.25 |
| αyz | 5.13 |
| αzz | 86.81 |
| **α** | **2.915x*10-30esu*** |
| *Hyperpolarizability (* β0 ) x*10-30esu* |
| βxxx | -358.52 |
| βxxy | 329.78 |
| βxyy | 101.46 |
| βyyy | -390.10 |
| βxxz | 24.22 |
| βxyz | 46.62 |
| βyyz | 24.29 |
| βxzz | 42.93 |
| βyzz | -38.99 |
| βzzz | -71.69 |
| **β0** | **2.048x*10-30esu*** |

Standard value for urea (**μ**=1.3732 Debye, **β0**=0.3728x10-30esu): **esu**-electrostatic unit

**TABLE S6: THERMODYNAMIC PLOT OF OTTHPYHCT**

|  |  |  |  |
| --- | --- | --- | --- |
| T (K) | S0m(cal mol -1 K -1) | C 0pm(cal mol -1 K -1) | H 0mK cal mol -1 |
| 100 | 65.68 | 7.95 | 0.80 |
| 200 | 71.19 | 7.95 | 1.59 |
| 298.15 | 74.37 | 7.95 | 2.37 |
| 300 | 74.42 | 7.95 | 2.39 |
| 400 | 76.70 | 7.95 | 3.18 |
| 500 | 78.48 | 7.96 | 3.97 |
| 600 | 79.93 | 8.00 | 4.77 |
| 700 | 81.17 | 8.07 | 5.58 |
| 800 | 82.25 | 8.16 | 6.39 |
| 900 | 83.22 | 8.27 | 7.21 |
| 1000 | 84.10 | 8.41 | 8.04 |