|  |
| --- |
| **S Table 1** Selected optimized geometrical parameters of (**3a-c)**, calculated at B3LYP/6–31G(d,p): bond length (Å), bond angle (°) and dihedral angle (°) |
| Bond length (Å) | Bond angle (°) | Dihedral angle (°) |
| **(3a)** |
| R(1,2)  | 1.3824 | A(2,1,5)  | 109.7955 | D(5,1,2,6)  | 179.899 |
| R(1,5)  | 1.3648 | A(2,6,7)  | 130.3048 | D(2,1,5,15)  | 179.9436 |
| R(1,27)  | 1.014 | A(2,6,30)  | 115.1664 | D(6,2,3,4)  | -179.871 |
| R(2,3)  | 1.4064 | A(6,7,8)  | 122.3064 | D(1,2,6,30)  | 179.7413 |
| R(2,6)  | 1.4221 | A(6,7,10)  | 118.0456 | D(28,3,4,29)  | 0.048 |
| R(3,4)  | 1.3975 | A(7,10,11)  | 124.1293 | D(29,4,5,1)  | 179.992 |
| R(4,5)  | 1.4019 | A(7,10,12)  | 111.4906 | D(1,5,15,16)  | -0.4739 |
| R(5,15)  | 1.4412 | A(10,12,13)  | 116.0638 | D(2,6,7,10)  | 179.9632 |
| R(6,7)  | 1.3685 | A(12,13,14)  | 107.366 | D(6,7,10,12)  | -179.928 |
| R(6,30)  | 1.087 | A(14,13,31)  | 112.276 | D(7,10,12,13)  | 179.9475 |
| R(7,8)  | 1.4242 | A(14,13,32)  | 112.2728 | D(10,12,13,31)  | 58.5336 |
| R(7,10)  | 1.4886 | A(13,14,33)  | 110.927 | D(12,13,14,34)  | -60.2926 |
| R(8,9)  | 1.1661 | A(13,14,34)  | 110.9472 | D(5,15,16,17)  | 179.3568 |
| R(10,11) | 1.2164 | A(13,14,35)  | 109.7097 | D(15,16,17,18)  | 175.0475 |
| R(10,12) | 1.3452 | A(5,15,16)  | 120.5521 | D(37,17,18,19)  | 169.2787 |
| R(12,13) | 1.448 | A(5,15,36)  | 116.5791 | D(17,18,20,25)  | 168.0973 |
| R(13,14) | 1.5157 | A(15,16,17)  | 117.2202 | D(18,20,21,22)  | 178.1462 |
| R(15,16) | 1.2885 | A(16,17,18)  | 120.7319 | D(18,20,25,26)  | 2.3652 |
| R(16,17) | 1.3528 | A(18,17,37)  | 119.4765 | D(38,21,22,23)  | -177.699 |
| R(17,18) | 1.3844 | A(17,18,19)  | 120.7223 | D(39,22,23,40)  | 0.8029 |
| R(17,37) | 1.0152 | A(17,18,20)  | 116.6334 | D(22,23,24,25)  | -0.2948 |
| R(18,19) | 1.2357 | A(18,20,21)  | 123.9985 | D(41,24,25,20)  | 179.1692 |
| R(18,20) | 1.4803 | A(20,21,38)  | 120.0996 | D(24,25,26,42)  | -176.202 |
| R(19,42) | 1.6654 | A(22,21,38)  | 118.2779 |  |  |
| R(25,26) | 1.3381 | A(24,25,26)  | 117.8097 |  |  |
| R(26,42) | 0.9931 | A(25,26,42)  | 106.5932 |  |  |
| **(3b)** |
| R(1,2)  | 1.38 | A(2,1,26)  | 126.3 | D(26,1,2,6)  | –0.2 |
| R(1,5)  | 1.36 | A(1,5,15)  | 123.1 | D(26,1,5,15)  | –0.1 |
| R(2,3)  | 1.40 | A(2,6,7)  | 130.3 | D(3,2,6,7)  | 179.4 |
| R(3,4)  | 1.39 | A(6,7,8)  | 122.3 | D(3,4,5,15)  | –179.8 |
| R(4,5)  | 1.40 | A(6,7,10)  | 118.0 | D(4,5,15,16)  | 179.2 |
| R(1,26)  | 1.01 | A(8,7,10)  | 119.6 | D(2,6,7,8)  | –0.1 |
| R(2,6)  | 1.42 | A(7,10,11)  | 124.1 | D(2,6,7,10)  | –179.9 |
| R(5,15)  | 1.44 | A(7,10,12)  | 111.4 | D(6,7,10,12)  | 179.9 |
| R(6,7)  | 1.36 | A(11,10,12) | 124.3 | D(7,10,12,13)  | 179.9 |
| R(7,8)  | 1.42 | A(10,12,13) | 116.0 | D(10,12,13,14)  | 179.9 |
| R(7,10)  | 1.48 | A(12,13,14) | 107.3 | D(5,15,16,17)  | 179.3 |
| R(8,9)  | 1.16 | A(5,15,16)  | 120.6 | D(15,16,17,18)  | 173.7 |
| R(10,11)  | 1.21 | A(15,16,17) | 117.3 | D(16,17,18,19)  | –1.9 |
| R(10,12)  | 1.34 | A(16,17,18) | 120.6 | D(16,17,18,20)  | 178.8 |
| R(12,13)  | 1.44 | A(17,18,19) | 123.4 | D(17,18,20,21)  | –27.0 |
| R(13,14)  | 1.51 | A(17,18,20) | 114.0 |   |   |
| R(15,16)  | 1.28 | A(18,20,21) | 124.5 |   |   |
| R(16,17)  | 1.35 |  |  |  |  |
| R(17,18)  | 1.39 |  |  |  |  |
| R(17,36)  | 1.01 |   |   |  |  |
| R(18,19)  | 1.21 |  |  |  |  |
| R(18,20)  | 1.50 |  |  |  |  |
| **(3c)** |
| R(1,2)  | 1.38113 |  A(3,2,6)  | 126.1937 | D(20,1,2,6)  | -0.1823 |
| R(1,5)  | 1.36555 |  A(4,5,15)  | 128.8034 | D(20,1,5,15)  | -0.0769 |
|  R(1,20)  | 1.014 |  A(2,6,7)  | 130.218 | D(3,2,6,7)  | 179.262 |
| R(2,3)  | 1.40623 |  A(6,7,8)  | 122.2627 | D(4,5,15,16)  | 179.2094 |
| R(3,4)  | 1.39764 |  A(6,7,10)  | 118.0427 | D(2,6,7,8)  | -0.1884 |
|  R(2,6)  | 1.4237 |  A(8,7,10)  | 119.6944 | D(2,6,7,10)  | 179.9832 |
|  R(4,5)  | 1.4016 |  A(7,10,11)  | 124.0118 | D(6,7,10,11)  | -0.1078 |
|  R(5,15)  | 1.4403 |  A(7,10,12)  | 111.4622 | D(6,7,10,12)  | 179.8763 |
|  R(6,7)  | 1.3674 |  A(11,10,12)  | 124.526 | D(8,7,10,11)  | -179.9407 |
|  R(7,8)  | 1.4244 |  A(10,12,13)  | 116.0761 | D(8,7,10,12)  | 0.0434 |
|  R(7,10)  | 1.49 |  A(12,13,14)  | 107.3809 | D(7,10,12,13)  | -179.9663 |
|  R(8,9)  | 1.166 |  A(5,15,16)  | 120.7097 | D(10,12,13,14) | 179.8448 |
|  R(10,11)  | 1.216 |  A(15,16,17)  | 117.0052 | D(5,15,16,17)  | 179.1946 |
|  R(10,12)  | 1.3442 |  A(16,17,18)  | 120.3867 | D(15,16,17,18) | 173.9708 |
|  R(12,13)  | 1.4489 |  A(17,18,19)  | 123.9804 | D(16,17,18,19) | -2.6663 |
|  R(13,14)  | 1.5156 |  A(17,18,31)  | 114.4726 | D(17,18,31,32) | 157.4406 |
|  R(16,17)  | 1.3571 |  A(32,33,37)  | 119.025 | D(19,18,31,32) | -22.0131 |
|  R(17,18)  | 1.3851 |  A(34,35,40)  | 118.8008 | D(19,18,31,36) | 155.3457 |
|  R(17,30)  | 1.0169 |  A(33,37,38)  | 117.179 | D(32,33,37,38) | 179.3942 |
|  R(18,19)  | 1.2151 |  A(33,37,39)  | 117.3031 | D(34,35,40,41) | -179.3952 |
|  R(18,31)  | 1.5091 |  A(38,37,39)  | 125.5178 | D(34,35,40,42) | 0.3461 |
|  R(33,37)  | 1.4797 |  A(35,40,42)  | 117.4584 | D(36,35,40,41) | 0.8516 |
|  R(35,40)  | 1.477 |  A(41,40,42)  | 125.3155 | D(36,35,40,42) | -179.4071 |
|  R(37,38)  | 1.2284 |  |  |  |  |
|  R(37,39)  | 1.227 |  |  |  |  |
|  R(40,41)  | 1.23 |  |  |  |  |
|  R(40,42)  | 1.227 |  |  |  |  |

|  |
| --- |
| **S Table 2a** Second–order perturbation theory analysis of the Fock matrix in NBO basis for (**3a**): Selected donor (Lewis) and acceptor (non–Lewis) orbitals, percentage electron density over bonded atoms (ED**A**, EDB in%), NBO hybrid orbitals of bonded atoms and stabilization energy of various intramolecularinteractions(*E*(2)) |
| Donor (i)  | Acceptor (j) | *E*(2) (kJ/mol) |
| orbital / lp(occupancy) | EDA, %EDB, % | NBO hybridorbitals | orbital (occupancy) | EDA, %EDB, % | NBO hybridorbitals |
| π(C2–C3)(1.66648) | 52.1347.87 | 0.7220(sp1.00)C0.6919(sp1.00)C | π\*(C4–C5)(0.42196) | 48.5451.46 | 0.6967(sp1.00)C-0.7174(sp1.00)C | 83.68 |
|  |  |  | π\*(C6–C7)(0.25353) | 58.6841.32 | 0.7660(sp1.00)C-0.6428(sp1.00)C | 104.2 |
| π(C4–C5)(1.67634) | 51.4648.54 | 0.7174(sp1.00)C0.6967(sp1.00)C | π\*(C2–C3)(0.43340) | 47.8752.13 | 0.6919(sp1.00)C-0.7220(sp1.00)C | 95.60 |
|  |  |  | π\*(C15–N16)(0.23287) | 55.4844.52 | 0.7449(sp1.00)C-0.6672(sp1.00)N | 79.88 |
| π(C6–C7)(1.79042) | 41.3258.68 | 0.6428(sp1.00)C0.7660(sp1.00)C | π\*(C2–C3)(0.43340) | 47.8752.13 | 0.6919(sp1.00)C-0.7220(sp1.00)C | 51.41 |
|  |  |  | π2\*(C8–N9)(0.09631) | 54.7645.24 | 0.7400(sp1.00)C-0.6726(sp1.00)N | 87.86 |
| π(C15–N16)(1.91775) | 44.5255.48 | 0.6672(sp1.00)C0.7449(sp1.00)N | π\*(C4–C5)(0.42196) | 48.5451.46 | 0.6967(sp1.00)C-0.7174(sp1.00)C | 45.65 |
| π(C20–C25)(1.60421) | 59.3640.64 | 0.7705(sp1.00)C0.6375(sp1.00)C | π\*(C21–C22)(0.31606) | 51.8948.11 | 0.7204(sp1.00)C-0.6936(sp1.00)C | 98.44 |
|  |  |  | π\*(C23–C24)(0.29373) | 52.9447.06 | 0.7276(sp1.00)C-0.6860(sp1.00)C | 57.43 |
| π(C21–C22)(1.71913) | 48.1151.89 | 0.6936(sp1.00)C0.7204(sp1.00)C | π\*(C20–C25)(0.44107) | 40.6459.36 | 0.6375(sp1.00)C-0.7705(sp1.00)C | 60.44 |
|  |  |  | π\*(C23–C24)(0.29373) | 52.9447.06 | 0.7276(sp1.00)C-0.6860(sp1.00)C | 87.19 |
| π(C23–C24)(1.70330) | 47.0652.94 | 0.6860(sp1.00)C0.7276(sp1.00)C  | π\*(C20–C25)(0.44107) | 40.6459.36 | 0.6375(sp1.00)C-0.7705(sp1.00)C | 99.02 |
|  |  |  | π\*(C21–C22)(0.31606) | 51.8948.11 | 0.7204(sp1.00)C-0.6936(sp1.00)C | 70.02 |
| π1(C8–C9)(1.97837) | 45.9354.07 | 0.6777(sp99.99)C0.7353(sp99.99)C | σ\*(N1–H27)(0.02547) | 25.2574.75 | 0.5025(sp2.24)N-0.8646(sp0.00)H | 11.08 |
| σ(N1–C2)(1.98309) | 61.7238.28 | 0.7856(sp1.90)N0.6187(sp2.72)C | σ\*(C5–C15)(0.02588) | 48.9251.08 | 0.6995(sp1.78)C-0.7147(sp1.86)C | 16.51 |
| σ(N1–C5)(1.98329) | 61.5838.42 | 0.7847(sp1.89)N0.6199(sp2.63)C | σ\*(C2–C6)(0.02144) | 49.3750.63 | 0.7026(sp1.66)C-0.7116(sp1.84)C | 16.47 |
| σ(C2–C3)(1.97445) | 51.3648.64 | 0.7166(sp1.82)C0.6974(sp2.05)C | σ\*(C2–C6)(0.02144) | 49.3750.63 | 0.7026(sp1.66)C-0.7116(sp1.84)C | 15.22 |
| σ(C18–C20)(1.97486) | 48.6751.33 | 0.6976(sp1.60)C0.7165(sp2.26)C | σ\*(C20–C21)(0.02199) | 48.8151.19 | 0.6986(sp1.80)C-0.7155(sp1.89)C | 10.58 |
| σ(C21–C22)(1.97960) | 50.7449.26 | 0.7123(sp1.73)C0.7018(sp1.85)C | σ\*(C18–C20)(0.05197) | 51.3348.67 | 0.7165(sp1.60)C-0.6976(sp2.26)C | 13.75 |
| σ(C24–C25)(1.97745) | 49.4750.53 | 0.7033(sp1.96)C0.7109(sp1.72)C | σ\*(C18–C20)(0.05197) | 51.3348.67 | 0.7165(sp1.60)C-0.6976(sp2.26)C | 11.83 |
| σ(C23–C24)(1.97925) | 49.9150.09 | 0.7065(sp1.82)C0.7077(sp1.77)C | σ\*(C25–O26)(0.01784) | 65.9734.03 | 0.8122(sp2.82)C-0.5833(sp1.99)O | 13.33 |
| n1(N1)(1.55481) | – | (sp1.00) | π\*(C2–C3)(0.43340) | 47.8752.13 | 0.6919(sp1.00)C-0.7220(sp1.00)C | 164.5 |
|  |  |  | π\*(C4–C5)(0.42196) | 48.5451.46 | 0.6967(sp1.00)C-0.7174(sp1.00)C | 188.9 |
| n1(N9)(1.96718) | – | (sp0.84) | σ\*(C7–C8)(0.03364) | 49.2750.73 | 0.7019(sp2.24)C-0.7123(sp0.89)C | 53.21 |
| n2(O11)(1.83780) | – | (sp1.00) | σ\*(C10–O12)(0.09671) | 68.7431.26 | 0.8291(sp2.52)C-0.5591(sp2.07)O | 135.6 |
| n2(O12)(1.78646) | – | (sp1.00) | π\*(C10–O11)(0.28967) | 70.0429.96 | 0.8369(sp1.00)C-0.5474(sp1.00)O | 210.1 |
| n1(N17) (1.65131) | – | (sp99.99) | π\*(C15–N16)(0.23287) | 55.4844.52 | 0.7449(sp1.00)C-0.6672(sp1.00)N | 131.5 |
|  |  |  | π\*(C18–O19)(0.34752) | 71.1328.87 | 0.8434(sp99.99)C-0.5373(sp99.99)O | 250.71 |
| n2(O19)(1.84565) | – | (sp25.39) | σ\*(N17–C18)(0.07057) | 36.8363.17 | 0.6069(sp1.43)N-0.7948(sp2.31)C | 103.4 |
|  |  |  | σ\*(C18–C20)(0.05197) | 51.3348.67 | 0.7165(sp1.60)C-0.6976(sp2.26)C | 47.32 |
|  |  |  | σ\*(O26–H42)(0.06638) | 20.9879.02 | 0.4580(sp2.84)O-0.8889(sp0.00)H | 96.6 |

|  |
| --- |
| **S Table 2b** Second–order perturbation theory analysis of the Fock matrix in NBO basis for (**3b**): Selected donor (Lewis) and acceptor (non–Lewis) orbitals, percentage electron density over bonded atoms (ED**A**, EDB in%), NBO hybrid orbitals of bonded atoms and stabilization energy of various intramolecularinteractions(*E*(2)) |
| Donor (i)  | Acceptor (j) | *E*(2) (kJ/mol) |
| Orbital / lp(occupancy) | EDA, %EDB, % | NBO hybridorbitals | orbital (occupancy) | EDA, %EDB, % | NBO hybridorbitals |
| π(C2–C3)(1.668) | 52.1547.85 | 0.722(sp1.00)C0.691(sp1.00)C | π\*(C4–C5)(0.420) | 48.5851.42 | 0.697(sp1.00)C–0.717(sp1.00)C | 83.01 |
|  |  |  | π\*(C6–C7)(0.251) | 58.6041.40 | 0.765(sp1.00)C–0.643(sp1.00)C | 103.46 |
| π(C4–C5)(1.677)  | 51.42 48.58 | 0.717(sp1.00)C0.697(sp1.00)C | π\*(C2–C3)(0.430) | 47.8552.15 | 0.691(sp1.00)C–0.722(sp1.00)C | 95.34 |
|  |  |  | π\*(C15–N16)(0.228) | 55.2744.73 | 0.743(sp1.00)C–0.668(sp1.00)N | 81.67 |
| π(C6–C7)(1.792) | 41.4058.60 | 0.643(sp1.00)C0.765(sp1.00)C | π\*(C2–C3)(0.430) | 47.8552.15 | 0.691(sp1.00)C–0.722(sp1.00)C | 50.70 |
|  |  |  | π2\*(C8–N9)(0.095) | 54.7845.22 | 0.740(sp1.00)C–0.672(sp1.00)N | 87.52 |
| π(C15–N16)(1.917) | 44.7355.27 | 0.668(sp1.00)C0.743(sp1.00)N | π\*(C4–C5)(0.420) | 48.5851.42 | 0.697(sp1.00)C–0.717(sp1.00)C | 45.26 |
| π(C20–C21)(1.647) | 49.0550.95 | 0.700(sp99.99)C0.713(sp1.00)C | π\*(C22–N23)(0.363) | 57.6742.33 | 0.759(sp1.00)C–0.650(sp1.00)N | 110.52 |
|  |  |  | π\*(C24–C25)(0.276) | 51.4348.57 | 0.717(sp1.00)C–0.696(sp1.00)C | 69.63 |
| π(C22–N23)(1.704) | 42.3357.67 | 0.650(sp1.00)C0.759(sp1.00)N | π\*(C20–C21)(0.358) | 50.9549.05 | 0.713(sp99.99)C–0.700(sp1.00)C | 59.10 |
|  |  |  | π\*(C24–C25)(0.276) | 51.4348.57 | 0.717(sp1.00)C–0.696(sp1.00)C | 103.12 |
| π(C24–C25)(1.616) | 48.5751.43 | 0.696(sp1.00)C0.717(sp1.00)C | π\*(C20–C21)(0.358) | 50.9549.05 | 0.713(sp99.99)C–0.700(sp1.00)C | 96.34 |
|  |  |  | π\*(C22–N23)(0.363) | 57.6742.33 | 0.759(sp1.00)C–0.650(sp1.00)N | 76.57 |
| π1(C8–N9)(1.9788) | 45.9354.07 | 0.677(sp99.99)C 0.735(sp99.99)N | σ\*(N1–H26)(0.023) | 25.3874.62 |  0.503(sp2.26)N-0.863(sp0.00)H | 10.03 |
| σ(N1–C2)(1.983) | 61.7138.29 | 0.785(sp1.90)N0.618(sp2.71)C | σ\*(C5–C15)(0.026) | 48.8451.16 | 0.698(sp1.76)C–0.715(sp1.83)C | 16.38 |
| σ(N1–C5)(1.983) | 61.6038.40 | 0.784(sp1.88)N0.619(sp2.65)C | σ\*(C2–C6)(0.021) | 49.3750.63 | 0.702(sp1.66)C–0.711(sp1.85)C | 16.84 |
| σ(C2–C3)(1.974) | 51.3348.67 | 0.716(sp1.82)C0.697(sp2.05)C | σ\*(C2–C6)(0.021) | 49.3750.63 | 0.702(sp1.66)C–0.711(sp1.85)C | 14.96 |
| σ(C18–C20)(1.975) | 47.6152.39 | 0.690(sp1.75)C0.723(sp2.29)C | σ\*(C24–C25)(0.024) | 51.1048.90 | 0.714(sp1.62)C–0.699(sp1.87)C | 9.57 |
| σ(C24–C25)(1.985) | 48.9051.10 | 0.699(sp1.62)C0.714(sp1.87)C | σ\*(C18–C20)(0.071) | 52.3947.61 | 0.723(sp1.75)C–0.690(sp2.29)C | 13.54 |
| n1(N1)(1.557) | – | (sp1.00) | π\*(C2–C3)(0.430) | 47.8552.15 | 0.691(sp1.00)C–0.722(sp1.00)C | 163.23 |
|  |  |  | π\*(C4–C5)(0.420) | 48.5851.42 | 0.697(sp1.00)C–0.717(sp1.00)C | 186.89 |
| n1(N9) (1.967) | – | (sp0.84) | σ\*(C7–C8)(0.033) | 49.2650.74 | 0.701(sp2.24)C–0.712(sp0.89)C | 53.12 |
| n2(O11)(1.837) | – | (sp1.00) | σ\*(C10–O12)(0.096) | 68.7531.25 | 0.829(sp2.52)C–0.559(sp2.07)O | 135.26 |
| n2(O12)(1.785) | – | (sp1.00) | π\*(C10–O11)(0.289) | 70.0329.97 | 0.836(sp1.00)C–0.547(sp1.00)O | 211.26 |
| n1(N17)(1.662) | – | (sp99.99) | π\*(C15–N16)(0.2288) | 55.2744.73 | 0.743(sp1.00)C–0.668(sp1.00)N | 125.44 |
|  |  |  | π\*(C18–O19)(0.262) | 67.5132.49 | 0.821(sp99.99)C–0.570(sp99.99)O | 189.48 |
| n2(O19)(1.852) | – | (sp99.99) | σ\*(N17–C18)(0.087) | 36.7363.27 | 0.606(sp1.63)N–0.795(sp2.29)C | 126.28 |
|  |  |  | σ\*(C18–C20)(0.071) | 52.3947.61 | 0.723(sp1.75)C–0.690(sp2.29)C | 85.69 |

|  |
| --- |
| **S Table 2c** Second–order perturbation theory analysis of the Fock matrix in NBO basis for (**3c**): Selected donor (Lewis) and acceptor (non–Lewis) orbitals, percentage electron density over bonded atoms (ED**A**, EDB in%), NBO hybrid orbitals of bonded atoms and stabilization energy of various intramolecularinteractions(*E*(2)) |
| Donor (i)  | Acceptor (j) | *E*(2) (kJ/mol) |
| orbital / lp(occupancy) | EDA, %EDB, % | NBO hybridorbitals | orbital (occupancy) | EDA, %EDB, % | NBO hybridorbitals |
| π(C2–C3)(1.6674) | 51.9548.05 | 0.7208(sp1.00)C0.6932(sp1.00)C | π\*(C4–C5)(0.4206) | 49.0750.93 | 0.7005(sp1.00)C-0.7136(sp1.00)C | 84.52 |
|  |  |  | π\*(C6–C7)(0.2436) | 58.3841.62 | 0.7641(sp1.00)C-0.6451(sp1.00)C | 101.1 |
| π(C4–C5)(1.6787) | 50.9349.07 | 0.7136(sp1.00)C0.7005(sp1.00)C | π\*(C2–C3)(0.4277) | 48.0551.95 | 0.6932(sp1.00)C-0.7208(sp1.00)C | 93.8 |
|  |  |  | π\*(C15–N16)(0.2266) | 55.9644.04 | 0.7481(sp1.00)C-0.6636(sp1.00)N | 84.81 |
| π(C6–C7)(1.7934) | 41.6258.38 | 0.6451(sp1.00)C0.7641(sp1.00)C | π\*(C2–C3)(0.4277) | 48.0551.95 | 0.6932(sp1.00)C-0.7208(sp1.00)C | 50.7 |
|  |  |  | π2\*(C8–N9)(0.0944) | 54.7245.28 | 0.7397(sp1.00)C-0.6729(sp1.00)N | 86.94 |
| π(C15–N16)(1.9184) | 44.0455.96 | 0.6636(sp1.00)C0.7481(sp1.00)N | π\*(C4–C5)(0.4206) | 49.0750.93 | 0.7005(sp1.00)C-0.7136(sp1.00)C | 43.72 |
| π(C31–C36)(1.6296) | 53.1546.85 | 0.7291(sp1.00)C0.6845(sp99.99)C | π\*(C32–C33)(0.32123) | 56.8743.13 | 0.7541(sp1.00)C-0.6568(sp1.00)C | 94.13 |
|  |  |  | π\*(C34–C35)(0.3376) | 56.2743.73 | 0.7501(sp1.00)C-0.6613(sp1.00)C | 76.7 |
| π(C32–C33)(1.6218) | 43.1356.87 | 0.6568(sp1.00)C0.7541(sp1.00)C | π\*(C31–C36)(0.3213) | 46.8553.15 | 0.6845(sp1.00)C-0.7291(sp1.00)C | 66.96 |
|  |  |  | π\*(C34–C35)(0.3376) | 56.2743.73 | 0.7501(sp1.00)C-0.6613(sp1.00)C | 103.2 |
| π(C34–C35)(1.6334) | 43.7356.27 | 0.6613(sp1.00)C0.7501(sp1.00)C | π\*(C31–C36)(0.3213) | 46.8553.15 | 0.6845(sp1.00)C-0.7291(sp1.00)C | 93.38 |
|  |  |  | π\*(C32–C33)(0.3212) | 56.8743.13 | 0.7541(sp1.00)C-0.6568(sp1.00)C | 67.34 |
| π1(C8–C9)(1.97867) | 45.9254.08 | 0.6777(sp99.99)C0.7354(sp99.99)C | σ\*(N1–H20)(0.02374) | 25.3774.63 | 0.5036(sp2.25)N-0.8639(sp0.00)H | 10.32 |
| σ(N1–C2)(1.9834) | 61.7338.27 | 0.7857(sp1.90)N0.6187(sp2.71)C | σ\*(C5–C15)(0.0259) | 48.9451.06 | 0.6996(sp1.77)C-0.7146(sp1.82)C | 16.47 |
| σ(N1–C5)(1.9831) | 61.5838.42 | 0.7847(sp1.88)N0.6198(sp2.65)C | σ\*(C2–C6)(0.0216) | 49.3450.66 | 0.7025(sp1.67)C-0.7117(sp1.86)C | 16.93 |
| σ(C2–C3)(1.9743) | 51.3548.65 | 0.7166(sp1.82)C0.6975(sp2.05)C | σ\*(C2–C6)(0.0216) | 49.3450.66 | 0.7025(sp1.67)C-0.7117(sp1.86)C | 14.84 |
| σ(C18–C31)(1.9740) | 46.9653.04 | 0.6853(sp1.81)C0.7283(sp2.25)C | σ\*(C32–C33)(0.0208) | 51.0148.99 | 0.7142(sp1.93)C-0.6999(sp1.63)C | 11.08 |
| σ(C33–C34)(1.9726) | 50.5649.44 | 0.7110(sp1.67)C0.7032(sp1.93)C | σ\*(C35–N40)(0.1095) | 61.8038.20 | 0.7861(sp3.07)C-0.6180(sp1.81)N | 19.48 |
| n1(N1)(1.5567) | – | (sp1.00) | π\*(C2–C3)(0.4277) | 48.0551.95 | 0.6932(sp1.00)C-0.7208(sp1.00)C | 164 |
|  |  |  | π\*(C4–C5)(0.4206) | 49.0750.93 | 0.7005(sp1.00)C-0.7136(sp1.00)C | 184.7 |
| n1(N9)(1.9673) | – | (sp0.84) | σ\*(C7–C8)(0.0337) | 49.2750.73 | 0.7019(sp2.24)C-0.7123(sp0.89)C | 53.13 |
| n2(O11)(1.8373) | – | (sp1.00) | σ\*(C10–O12)(0.0960) | 68.7231.28 | 0.8290(sp2.51)C-0.5593(sp2.06)O | 134.9 |
| n2(O12)(1.7843) | – | (sp1.00) | π\*(C10–O11)(0.28744) | 69.9730.03 | 0.8365(sp1.00)C-0.5480(sp1.00)O | 212.8 |
| n1(N17) (1.6630) | – | (sp99.99) | π\*(C15–N16)(0.2266) | 55.9644.04 | 0.7481(sp1.00)C-0.6636(sp1.00)N | 117.5 |
|  |  |  | π\*(C18–O19)(0.2733) | 67.4532.55 | 0.8213(sp99.99)C-0.5705(sp99.99)O | 198 |
| n2(O19)(1.8492) | – | (sp99.99) | σ\*(N17–C18)(0.0851) | 36.9963.01 | 0.6082(sp1.63)N-0.7938(sp2.22)C | 123.4 |
|  |  |  | σ\*(C18–C31)(0.0739) | 53.0446.96 | 0.7283(sp1.81)C-0.6853(sp2.25)C | 89.41 |
| n3(O38)(1.4343) | – | (sp1.00) | π\*(N37–O39)(0.6149) | 59.3540.65 | 0.7704(sp1.00)N-0.6376(sp1.00)O | 693.1 |
| n2(O39)(1.4343) | – | (sp99.99) | σ\*(N37–O38)(0.0568) | 51.3648.64 | 0.7166(sp2.10)N-0.6975(sp2.98)O | 80.59 |
| n3(O41)(1.4418) | – | (sp1.00) | π\*(N40–O42)(0.6143) | 59.3840.62 | 0.7706(sp1.00)N-0.6373(sp1.00)O | 679.30 |
| n2(O42)(1.8939)  | – | (sp99.99) | σ\*(N40–O41)(0.0572) | 51.3748.63 | 0.7167(sp2.11)N-0.6974(sp2.99)O | 81.13 |

|  |
| --- |
| **S Table 3a** Selected Lewis orbitals (occupied bond or lone pair) of (**3a**) with their NBO hybrids: A, B–bonded atoms, lp–loan pair and (ED,%)– percentage electron density |
| Bond(A–B) / lp(EDA–B / lp) | EDA, %EDB, % | NBO hybrid orbitals | s, p, % |
| σ(N1–H27)(1.98755) | 74.7525.25 |  0.8646(sp2.24)N0.5025(sp0.00)H | 30.82, 69.1699.88, 0.12 |
| σ(N1–C2)(1.98309) | 61.7238.28 | 0.7856(sp1.90)N0.6187(sp2.72)C | 34.48, 65.4826.82, 73.07 |
| σ(N1–C5)(1.98329) | 61.5838.42 |  0.7847(sp1.89)N0.6199(sp2.63)C | 34.61, 65.3627.53, 72.36 |
| σ(C8–N9)(1.99498) | 42.6157.39 | 0.6528(sp1.12)C0.7576(sp1.18)N | 47.09, 52.8945.72, 53.94 |
| σ(C15–N16)(1.98767) | 40.3859.62 |  0.6355(sp2.11)C0.7721(sp1.35)N | 32.08, 67.8242.58, 57.36 |
| σ(N17–C18)(1.99042) | 63.1736.83 | 0.7948(sp1.43)N0.6069(sp2.31)C | 41.15, 58.8230.13, 69.75 |
| σ(C25–O26)(1.99466) | 34.0365.97 |  0.5833(sp2.82)C0.8122(sp1.99)O | 26.09, 73.7033.46, 66.47 |
| σ(O26–H42)(1.98706) | 79.0220.98 | 0.8889(sp2.84)O0.4580 (sp0.00)H | 26.04, 73.9099.71, 0.29 |
| σ(C18–O19)(1.99412) | 35.2164.79 |  0.5934(sp2.20)C0.8049(sp1.58)O | 31.17, 68.7238.66, 61.03 |
| σ(C10–O11)(1.99646) | 34.4665.54 | 0.5870(sp1.92)C0.8096(sp1.40)O | 34.20, 65.6941.48, 58.15 |
| σ(C10–O12)(1.99171) | 31.2668.74 | 0.5591(sp2.52)C0.8291(sp2.07)O | 28.32, 71.4332.50, 67.43 |
| lp1(N1) / (1.55481) | – | (sp1.00) | 0.00, 99.98 |
| lp2(O11) /(1.83780)  | – | (sp1.00) | 0.00, 99.74 |
| lp2(O12) / (1.78646) | – | (sp1.00) | 0.00, 99.90 |
| lp1(N16) / (1.92028) | – | (sp2.18) | 31.41, 68.52 |
| lp1(N17) / (1.65131) | – | (sp99.99) | 0.08, 99.91 |
| lp2(O19) / (1.84565) | – | (sp25.39) | 57.37, 57.37 |
| lp2(O26) / (1.80648) | – | (sp1.00) | 0.01, 99.87 |

|  |
| --- |
| **S Table 3b** Selected Lewis orbitals (occupied bond or lone pair) of (**3b**) with their NBO hybrids: A, B–bonded atoms, lp–loan pair and (ED,%)– percentage electron density |
| Bond(A–B) / lp(EDA–B /lp) | EDA, %EDB, % | NBO hybrid orbitals | s, p, % |
| σ(N1–H26)(1.987) | 74.6225.38 | 0.863(sp2.26)N0.503(sp0.00)H | 30.70, 69.2899.88, 0.12 |
| σ(N1–C2)(1.983) | 61.7138.29 | 0.785(sp1.90)N0.618(sp2.71)C | 34.47, 65.4926.92, 72.97 |
| σ(N1–C5)(1.983) | 61.6038.40 | 0.784(sp1.88)N0.619(sp2.65)C | 34.73, 65.2427.38, 72.51 |
| σ(C8–N9)(1.995) | 42.5957.41 | 0.652(sp1.12)C0.757(sp1.18)N | 47.10, 52.8745.77, 53.89 |
| σ(C15–N16)(1.987) | 40.5759.43 | 0.637(sp2.05)C0.770(sp1.43)N | 32.79, 67.1241.07, 58.87 |
| σ(N17–C18)(1.989) | 63.2736.73 | 0.795(sp1.63)N0.606(sp2.29)C | 38.04, 61.9330.33, 69.54 |
| σ(C18–O19)(1.994) | 35.0664.94 | 0.592(sp2.07)C0.805(sp1.46)O | 32.56, 67.3440.54, 59.11 |
| σ(C22–N23)(1.986) | 40.8359.17 | 0.639(sp2.19)C0.769(sp1.82)N | 31.32, 68.6235.38, 64.42 |
| σ(N23–C24)(1.986) | 59.3340.67 | 0.770(sp1.83)N0.637(sp2.22)C | 35.31, 64.4931.08, 68.86 |
| σ(C10–O11)(1.996) | 34.4665.54 | 0.587(sp1.92)C0.809(sp1.40)O | 34.23, 65.6641.47, 58.16 |
| σ(C10–O12)(1.991) | 31.2568.75 | 0.559(sp2.52)C0.8291(sp2.07)O | 28.37, 71.3832.60, 67.34 |
| lp1(N1)(1.557) | – | (sp1.00) | 0.00, 99.98 |
| lp2(O11)(1.837) | – | (sp1.00) | 0.00, 99.74 |
| lp2(O12)(1.785) | – | (sp1.00) | 0.00, 99.90 |
| lp1(N16)(1.917) | – | (sp1.94) | 33.93, 65.99 |
| lp1(N17)(1.662) | – | (sp99.99) | 0.64, 99.36 |

|  |
| --- |
| **S Table 3c** Selected Lewis orbitals (occupied bond or lone pair) of (**3c**) with their NBO hybrids: A, B–bonded atoms, lp–loan pair and (ED,%)– percentage electron density |
| Bond(A–B) / lp(EDA–B / lp) | EDA, %EDB, % | NBO hybrid orbitals | s, p, % |
| σ(N1–H20)(1.9878) | 74.6325.37 | 0.8639(sp2.25)N0.5037(sp0.00)H | 30.73, 69.2599.88, 0.12 |
| σ(N1–C2)(1.9834) | 61.7338.27 | 0.7857(sp1.90)N0.6187(sp2.71)C | 34.50, 65.4626.95, 72.94 |
| σ(N1–C5)(1.9831) | 61.5838.42 | 0.7847(sp1.88)N0.6198(sp2.65)C | 34.67, 65.2927.38, 72.51 |
| σ(C8–N9)(1.9950) | 42.5957.41 | 0.6526(sp1.12)C0.7577(sp1.18)N | 47.10, 52.8745.76, 53.90 |
| σ(C15–N16)(1.9874) | 40.5859.42 | 0.6371(sp2.05)C0.7708(sp1.43)N | 32.75, 67.1641.08, 58.85 |
| σ(N17–C18)(1.9894) | 63.0136.99 | 0.7938(sp1.63)N0.6082(sp2.22)C | 38.07, 61.9030.97, 68.91 |
| σ(C33–N37)(1.9890) | 38.3161.69 | 0.6190(sp3.08)C0.7854(sp1.83)N | 24.50, 75.3635.36, 64.60 |
| σ(C35–N40)(1.9892) | 38.2061.80 | 0.6180(sp3.07)C0.7861(sp1.81)N | 24.53, 75.3335.57, 64.39 |
| σ(C18–O19)(1.9942) | 35.1664.84 | 0.5929(sp2.06)C0.8053(sp1.47)O | 32.70, 67.2040.40, 59.25 |
| σ(N37–O38)(1.9957) | 48.6451.36 | 0.6975(sp2.10)N0.7166(sp2.98)O | 32.22, 67.6825.07, 74.79 |
| σ(N37–O39)(1.9956) | 48.6651.34 | 0.6975(sp2.09)N0.7165(sp2.97)O | 32.29, 67.6125.12, 74.73 |
| σ(N40–O41)(1.9956) | 48.6351.37 | 0.6974(sp2.11)N0.7167(sp2.99)O | 32.08, 67.8225.03, 74.83 |
| σ(N40–O42)(1.9957) | 48.6551.35 | 0.6975(sp2.10)N0.7166(sp2.97)O | 32.22, 67.6825.15, 74.71 |
| σ(C10–O11)(1.9964)  | 34.4665.54 | 0.5870(sp1.92)C0.8096(sp1.40)O | 34.27, 65.6341.47, 58.15 |
| σ(C10–O12)(1.9917) | 31.2868.72 | 0.5593(sp2.51)C0.8290(sp2.06)O | 28.46, 71.2932.62, 67.32 |
| lp1(N1) / (1.5567) | – | (sp1.00) | 0.00, 99.98 |
| lp2(O11) / (1.8373) | – | (sp1.00) | 0.00, 99.74 |
| lp2(O12) / (1.7843) | – | (sp1.00) | 0.00, 99.90 |
| lp1(N16) / (1.9179) | – | (sp1.91) | 34.38, 65.54 |
| lp1(N17) / (1.6630) | – | (sp99.99) | 0.59, 99.41 |
| lp2(O19) / (1.8492) | – | (sp99.99) | 0.05, 99.69 |
| lp2(O38) / (1.8943) | – | (sp99.99) | 0.11, 99.79 |
| lp2(O39) / (1.4343) | – | (sp99.99) | 0.10, 99.80 |
| lp2(O41) / (1.8953) | – | (sp99.99) | 0.14, 99.76 |
| lp2(O42) / (1.8939) | – | (sp99.99) | 0.11, 99.79 |