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| **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 |  | |  |  | |  |

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| **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 hybrid  orbitals | orbital (occupancy) | EDA, %  EDB, % | NBO hybrid  orbitals |
| π(C2–C3)  (1.66648) | 52.13  47.87 | 0.7220(sp1.00)C  0.6919(sp1.00)C | π\*(C4–C5)  (0.42196) | 48.54  51.46 | 0.6967(sp1.00)C  -0.7174(sp1.00)C | 83.68 |
|  |  |  | π\*(C6–C7)  (0.25353) | 58.68  41.32 | 0.7660(sp1.00)C  -0.6428(sp1.00)C | 104.2 |
| π(C4–C5)  (1.67634) | 51.46  48.54 | 0.7174(sp1.00)C  0.6967(sp1.00)C | π\*(C2–C3)  (0.43340) | 47.87  52.13 | 0.6919(sp1.00)C  -0.7220(sp1.00)C | 95.60 |
|  |  |  | π\*(C15–N16)  (0.23287) | 55.48  44.52 | 0.7449(sp1.00)C  -0.6672(sp1.00)N | 79.88 |
| π(C6–C7)  (1.79042) | 41.32  58.68 | 0.6428(sp1.00)C  0.7660(sp1.00)C | π\*(C2–C3)  (0.43340) | 47.87  52.13 | 0.6919(sp1.00)C  -0.7220(sp1.00)C | 51.41 |
|  |  |  | π2\*(C8–N9)  (0.09631) | 54.76  45.24 | 0.7400(sp1.00)C  -0.6726(sp1.00)N | 87.86 |
| π(C15–N16)  (1.91775) | 44.52  55.48 | 0.6672(sp1.00)C  0.7449(sp1.00)N | π\*(C4–C5)  (0.42196) | 48.54  51.46 | 0.6967(sp1.00)C  -0.7174(sp1.00)C | 45.65 |
| π(C20–C25)  (1.60421) | 59.36  40.64 | 0.7705(sp1.00)C  0.6375(sp1.00)C | π\*(C21–C22)  (0.31606) | 51.89  48.11 | 0.7204(sp1.00)C  -0.6936(sp1.00)C | 98.44 |
|  |  |  | π\*(C23–C24)  (0.29373) | 52.94  47.06 | 0.7276(sp1.00)C  -0.6860(sp1.00)C | 57.43 |
| π(C21–C22)  (1.71913) | 48.11  51.89 | 0.6936(sp1.00)C  0.7204(sp1.00)C | π\*(C20–C25)  (0.44107) | 40.64  59.36 | 0.6375(sp1.00)C  -0.7705(sp1.00)C | 60.44 |
|  |  |  | π\*(C23–C24)  (0.29373) | 52.94  47.06 | 0.7276(sp1.00)C  -0.6860(sp1.00)C | 87.19 |
| π(C23–C24)  (1.70330) | 47.06  52.94 | 0.6860(sp1.00)C  0.7276(sp1.00)C | π\*(C20–C25)  (0.44107) | 40.64  59.36 | 0.6375(sp1.00)C  -0.7705(sp1.00)C | 99.02 |
|  |  |  | π\*(C21–C22)  (0.31606) | 51.89  48.11 | 0.7204(sp1.00)C  -0.6936(sp1.00)C | 70.02 |
| π1(C8–C9)  (1.97837) | 45.93  54.07 | 0.6777(sp99.99)C  0.7353(sp99.99)C | σ\*(N1–H27)  (0.02547) | 25.25  74.75 | 0.5025(sp2.24)N  -0.8646(sp0.00)H | 11.08 |
| σ(N1–C2)  (1.98309) | 61.72  38.28 | 0.7856(sp1.90)N  0.6187(sp2.72)C | σ\*(C5–C15)  (0.02588) | 48.92  51.08 | 0.6995(sp1.78)C  -0.7147(sp1.86)C | 16.51 |
| σ(N1–C5)  (1.98329) | 61.58  38.42 | 0.7847(sp1.89)N  0.6199(sp2.63)C | σ\*(C2–C6)  (0.02144) | 49.37  50.63 | 0.7026(sp1.66)C  -0.7116(sp1.84)C | 16.47 |
| σ(C2–C3)  (1.97445) | 51.36  48.64 | 0.7166(sp1.82)C  0.6974(sp2.05)C | σ\*(C2–C6)  (0.02144) | 49.37  50.63 | 0.7026(sp1.66)C  -0.7116(sp1.84)C | 15.22 |
| σ(C18–C20)  (1.97486) | 48.67  51.33 | 0.6976(sp1.60)C  0.7165(sp2.26)C | σ\*(C20–C21)  (0.02199) | 48.81  51.19 | 0.6986(sp1.80)C  -0.7155(sp1.89)C | 10.58 |
| σ(C21–C22)  (1.97960) | 50.74  49.26 | 0.7123(sp1.73)C  0.7018(sp1.85)C | σ\*(C18–C20)  (0.05197) | 51.33  48.67 | 0.7165(sp1.60)C  -0.6976(sp2.26)C | 13.75 |
| σ(C24–C25)  (1.97745) | 49.47  50.53 | 0.7033(sp1.96)C  0.7109(sp1.72)C | σ\*(C18–C20)  (0.05197) | 51.33  48.67 | 0.7165(sp1.60)C  -0.6976(sp2.26)C | 11.83 |
| σ(C23–C24)  (1.97925) | 49.91  50.09 | 0.7065(sp1.82)C  0.7077(sp1.77)C | σ\*(C25–O26)  (0.01784) | 65.97  34.03 | 0.8122(sp2.82)C  -0.5833(sp1.99)O | 13.33 |
| n1(N1)  (1.55481) | – | (sp1.00) | π\*(C2–C3)  (0.43340) | 47.87  52.13 | 0.6919(sp1.00)C  -0.7220(sp1.00)C | 164.5 |
|  |  |  | π\*(C4–C5)  (0.42196) | 48.54  51.46 | 0.6967(sp1.00)C  -0.7174(sp1.00)C | 188.9 |
| n1(N9)  (1.96718) | – | (sp0.84) | σ\*(C7–C8)  (0.03364) | 49.27  50.73 | 0.7019(sp2.24)C  -0.7123(sp0.89)C | 53.21 |
| n2(O11)  (1.83780) | – | (sp1.00) | σ\*(C10–O12)  (0.09671) | 68.74  31.26 | 0.8291(sp2.52)C  -0.5591(sp2.07)O | 135.6 |
| n2(O12)  (1.78646) | – | (sp1.00) | π\*(C10–O11)  (0.28967) | 70.04  29.96 | 0.8369(sp1.00)C  -0.5474(sp1.00)O | 210.1 |
| n1(N17)  (1.65131) | – | (sp99.99) | π\*(C15–N16)  (0.23287) | 55.48  44.52 | 0.7449(sp1.00)C  -0.6672(sp1.00)N | 131.5 |
|  |  |  | π\*(C18–O19)  (0.34752) | 71.13  28.87 | 0.8434(sp99.99)C  -0.5373(sp99.99)O | 250.71 |
| n2(O19)  (1.84565) | – | (sp25.39) | σ\*(N17–C18)  (0.07057) | 36.83  63.17 | 0.6069(sp1.43)N  -0.7948(sp2.31)C | 103.4 |
|  |  |  | σ\*(C18–C20)  (0.05197) | 51.33  48.67 | 0.7165(sp1.60)C  -0.6976(sp2.26)C | 47.32 |
|  |  |  | σ\*(O26–H42)  (0.06638) | 20.98  79.02 | 0.4580(sp2.84)O  -0.8889(sp0.00)H | 96.6 |

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| **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 hybrid  orbitals | orbital (occupancy) | EDA, %  EDB, % | NBO hybrid  orbitals |
| π(C2–C3)  (1.668) | 52.15  47.85 | 0.722(sp1.00)C  0.691(sp1.00)C | π\*(C4–C5)  (0.420) | 48.58  51.42 | 0.697(sp1.00)C  –0.717(sp1.00)C | 83.01 |
|  |  |  | π\*(C6–C7)  (0.251) | 58.60  41.40 | 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)C  0.697(sp1.00)C | π\*(C2–C3)  (0.430) | 47.85  52.15 | 0.691(sp1.00)C  –0.722(sp1.00)C | 95.34 |
|  |  |  | π\*(C15–N16)  (0.228) | 55.27  44.73 | 0.743(sp1.00)C  –0.668(sp1.00)N | 81.67 |
| π(C6–C7)  (1.792) | 41.40  58.60 | 0.643(sp1.00)C  0.765(sp1.00)C | π\*(C2–C3)  (0.430) | 47.85  52.15 | 0.691(sp1.00)C  –0.722(sp1.00)C | 50.70 |
|  |  |  | π2\*(C8–N9)  (0.095) | 54.78  45.22 | 0.740(sp1.00)C  –0.672(sp1.00)N | 87.52 |
| π(C15–N16)  (1.917) | 44.73  55.27 | 0.668(sp1.00)C  0.743(sp1.00)N | π\*(C4–C5)  (0.420) | 48.58  51.42 | 0.697(sp1.00)C  –0.717(sp1.00)C | 45.26 |
| π(C20–C21)  (1.647) | 49.05  50.95 | 0.700(sp99.99)C  0.713(sp1.00)C | π\*(C22–N23)  (0.363) | 57.67  42.33 | 0.759(sp1.00)C  –0.650(sp1.00)N | 110.52 |
|  |  |  | π\*(C24–C25)  (0.276) | 51.43  48.57 | 0.717(sp1.00)C  –0.696(sp1.00)C | 69.63 |
| π(C22–N23)  (1.704) | 42.33  57.67 | 0.650(sp1.00)C  0.759(sp1.00)N | π\*(C20–C21)  (0.358) | 50.95  49.05 | 0.713(sp99.99)C  –0.700(sp1.00)C | 59.10 |
|  |  |  | π\*(C24–C25)  (0.276) | 51.43  48.57 | 0.717(sp1.00)C  –0.696(sp1.00)C | 103.12 |
| π(C24–C25)  (1.616) | 48.57  51.43 | 0.696(sp1.00)C  0.717(sp1.00)C | π\*(C20–C21)  (0.358) | 50.95  49.05 | 0.713(sp99.99)C  –0.700(sp1.00)C | 96.34 |
|  |  |  | π\*(C22–N23)  (0.363) | 57.67  42.33 | 0.759(sp1.00)C  –0.650(sp1.00)N | 76.57 |
| π1(C8–N9)  (1.9788) | 45.93  54.07 | 0.677(sp99.99)C  0.735(sp99.99)N | σ\*(N1–H26)  (0.023) | 25.38  74.62 | 0.503(sp2.26)N  -0.863(sp0.00)H | 10.03 |
| σ(N1–C2)  (1.983) | 61.71  38.29 | 0.785(sp1.90)N  0.618(sp2.71)C | σ\*(C5–C15)  (0.026) | 48.84  51.16 | 0.698(sp1.76)C  –0.715(sp1.83)C | 16.38 |
| σ(N1–C5)  (1.983) | 61.60  38.40 | 0.784(sp1.88)N  0.619(sp2.65)C | σ\*(C2–C6)  (0.021) | 49.37  50.63 | 0.702(sp1.66)C  –0.711(sp1.85)C | 16.84 |
| σ(C2–C3)  (1.974) | 51.33  48.67 | 0.716(sp1.82)C  0.697(sp2.05)C | σ\*(C2–C6)  (0.021) | 49.37  50.63 | 0.702(sp1.66)C  –0.711(sp1.85)C | 14.96 |
| σ(C18–C20)  (1.975) | 47.61  52.39 | 0.690(sp1.75)C  0.723(sp2.29)C | σ\*(C24–C25)  (0.024) | 51.10  48.90 | 0.714(sp1.62)C  –0.699(sp1.87)C | 9.57 |
| σ(C24–C25)  (1.985) | 48.90  51.10 | 0.699(sp1.62)C  0.714(sp1.87)C | σ\*(C18–C20)  (0.071) | 52.39  47.61 | 0.723(sp1.75)C  –0.690(sp2.29)C | 13.54 |
| n1(N1)  (1.557) | – | (sp1.00) | π\*(C2–C3)  (0.430) | 47.85  52.15 | 0.691(sp1.00)C  –0.722(sp1.00)C | 163.23 |
|  |  |  | π\*(C4–C5)  (0.420) | 48.58  51.42 | 0.697(sp1.00)C  –0.717(sp1.00)C | 186.89 |
| n1(N9)  (1.967) | – | (sp0.84) | σ\*(C7–C8)  (0.033) | 49.26  50.74 | 0.701(sp2.24)C  –0.712(sp0.89)C | 53.12 |
| n2(O11)  (1.837) | – | (sp1.00) | σ\*(C10–O12)  (0.096) | 68.75  31.25 | 0.829(sp2.52)C  –0.559(sp2.07)O | 135.26 |
| n2(O12)  (1.785) | – | (sp1.00) | π\*(C10–O11)  (0.289) | 70.03  29.97 | 0.836(sp1.00)C  –0.547(sp1.00)O | 211.26 |
| n1(N17)  (1.662) | – | (sp99.99) | π\*(C15–N16)  (0.2288) | 55.27  44.73 | 0.743(sp1.00)C  –0.668(sp1.00)N | 125.44 |
|  |  |  | π\*(C18–O19)  (0.262) | 67.51  32.49 | 0.821(sp99.99)C  –0.570(sp99.99)O | 189.48 |
| n2(O19)  (1.852) | – | (sp99.99) | σ\*(N17–C18)  (0.087) | 36.73  63.27 | 0.606(sp1.63)N  –0.795(sp2.29)C | 126.28 |
|  |  |  | σ\*(C18–C20)  (0.071) | 52.39  47.61 | 0.723(sp1.75)C  –0.690(sp2.29)C | 85.69 |

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| **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 hybrid  orbitals | orbital (occupancy) | EDA, %  EDB, % | NBO hybrid  orbitals |
| π(C2–C3)  (1.6674) | 51.95  48.05 | 0.7208(sp1.00)C  0.6932(sp1.00)C | π\*(C4–C5)  (0.4206) | 49.07  50.93 | 0.7005(sp1.00)C  -0.7136(sp1.00)C | 84.52 |
|  |  |  | π\*(C6–C7)  (0.2436) | 58.38  41.62 | 0.7641(sp1.00)C  -0.6451(sp1.00)C | 101.1 |
| π(C4–C5)  (1.6787) | 50.93  49.07 | 0.7136(sp1.00)C  0.7005(sp1.00)C | π\*(C2–C3)  (0.4277) | 48.05  51.95 | 0.6932(sp1.00)C  -0.7208(sp1.00)C | 93.8 |
|  |  |  | π\*(C15–N16)  (0.2266) | 55.96  44.04 | 0.7481(sp1.00)C  -0.6636(sp1.00)N | 84.81 |
| π(C6–C7)  (1.7934) | 41.62  58.38 | 0.6451(sp1.00)C  0.7641(sp1.00)C | π\*(C2–C3)  (0.4277) | 48.05  51.95 | 0.6932(sp1.00)C  -0.7208(sp1.00)C | 50.7 |
|  |  |  | π2\*(C8–N9)  (0.0944) | 54.72  45.28 | 0.7397(sp1.00)C  -0.6729(sp1.00)N | 86.94 |
| π(C15–N16)  (1.9184) | 44.04  55.96 | 0.6636(sp1.00)C  0.7481(sp1.00)N | π\*(C4–C5)  (0.4206) | 49.07  50.93 | 0.7005(sp1.00)C  -0.7136(sp1.00)C | 43.72 |
| π(C31–C36)  (1.6296) | 53.15  46.85 | 0.7291(sp1.00)C  0.6845(sp99.99)C | π\*(C32–C33)  (0.32123) | 56.87  43.13 | 0.7541(sp1.00)C  -0.6568(sp1.00)C | 94.13 |
|  |  |  | π\*(C34–C35)  (0.3376) | 56.27  43.73 | 0.7501(sp1.00)C  -0.6613(sp1.00)C | 76.7 |
| π(C32–C33)  (1.6218) | 43.13  56.87 | 0.6568(sp1.00)C  0.7541(sp1.00)C | π\*(C31–C36)  (0.3213) | 46.85  53.15 | 0.6845(sp1.00)C  -0.7291(sp1.00)C | 66.96 |
|  |  |  | π\*(C34–C35)  (0.3376) | 56.27  43.73 | 0.7501(sp1.00)C  -0.6613(sp1.00)C | 103.2 |
| π(C34–C35)  (1.6334) | 43.73  56.27 | 0.6613(sp1.00)C  0.7501(sp1.00)C | π\*(C31–C36)  (0.3213) | 46.85  53.15 | 0.6845(sp1.00)C  -0.7291(sp1.00)C | 93.38 |
|  |  |  | π\*(C32–C33)  (0.3212) | 56.87  43.13 | 0.7541(sp1.00)C  -0.6568(sp1.00)C | 67.34 |
| π1(C8–C9)  (1.97867) | 45.92  54.08 | 0.6777(sp99.99)C  0.7354(sp99.99)C | σ\*(N1–H20)  (0.02374) | 25.37  74.63 | 0.5036(sp2.25)N  -0.8639(sp0.00)H | 10.32 |
| σ(N1–C2)  (1.9834) | 61.73  38.27 | 0.7857(sp1.90)N  0.6187(sp2.71)C | σ\*(C5–C15)  (0.0259) | 48.94  51.06 | 0.6996(sp1.77)C  -0.7146(sp1.82)C | 16.47 |
| σ(N1–C5)  (1.9831) | 61.58  38.42 | 0.7847(sp1.88)N  0.6198(sp2.65)C | σ\*(C2–C6)  (0.0216) | 49.34  50.66 | 0.7025(sp1.67)C  -0.7117(sp1.86)C | 16.93 |
| σ(C2–C3)  (1.9743) | 51.35  48.65 | 0.7166(sp1.82)C  0.6975(sp2.05)C | σ\*(C2–C6)  (0.0216) | 49.34  50.66 | 0.7025(sp1.67)C  -0.7117(sp1.86)C | 14.84 |
| σ(C18–C31)  (1.9740) | 46.96  53.04 | 0.6853(sp1.81)C  0.7283(sp2.25)C | σ\*(C32–C33)  (0.0208) | 51.01  48.99 | 0.7142(sp1.93)C  -0.6999(sp1.63)C | 11.08 |
| σ(C33–C34)  (1.9726) | 50.56  49.44 | 0.7110(sp1.67)C  0.7032(sp1.93)C | σ\*(C35–N40)  (0.1095) | 61.80  38.20 | 0.7861(sp3.07)C  -0.6180(sp1.81)N | 19.48 |
| n1(N1)  (1.5567) | – | (sp1.00) | π\*(C2–C3)  (0.4277) | 48.05  51.95 | 0.6932(sp1.00)C  -0.7208(sp1.00)C | 164 |
|  |  |  | π\*(C4–C5)  (0.4206) | 49.07  50.93 | 0.7005(sp1.00)C  -0.7136(sp1.00)C | 184.7 |
| n1(N9)  (1.9673) | – | (sp0.84) | σ\*(C7–C8)  (0.0337) | 49.27  50.73 | 0.7019(sp2.24)C  -0.7123(sp0.89)C | 53.13 |
| n2(O11)  (1.8373) | – | (sp1.00) | σ\*(C10–O12)  (0.0960) | 68.72  31.28 | 0.8290(sp2.51)C  -0.5593(sp2.06)O | 134.9 |
| n2(O12)  (1.7843) | – | (sp1.00) | π\*(C10–O11)  (0.28744) | 69.97  30.03 | 0.8365(sp1.00)C  -0.5480(sp1.00)O | 212.8 |
| n1(N17)  (1.6630) | – | (sp99.99) | π\*(C15–N16)  (0.2266) | 55.96  44.04 | 0.7481(sp1.00)C  -0.6636(sp1.00)N | 117.5 |
|  |  |  | π\*(C18–O19)  (0.2733) | 67.45  32.55 | 0.8213(sp99.99)C  -0.5705(sp99.99)O | 198 |
| n2(O19)  (1.8492) | – | (sp99.99) | σ\*(N17–C18)  (0.0851) | 36.99  63.01 | 0.6082(sp1.63)N  -0.7938(sp2.22)C | 123.4 |
|  |  |  | σ\*(C18–C31)  (0.0739) | 53.04  46.96 | 0.7283(sp1.81)C  -0.6853(sp2.25)C | 89.41 |
| n3(O38)  (1.4343) | – | (sp1.00) | π\*(N37–O39)  (0.6149) | 59.35  40.65 | 0.7704(sp1.00)N  -0.6376(sp1.00)O | 693.1 |
| n2(O39)  (1.4343) | – | (sp99.99) | σ\*(N37–O38)  (0.0568) | 51.36  48.64 | 0.7166(sp2.10)N  -0.6975(sp2.98)O | 80.59 |
| n3(O41)  (1.4418) | – | (sp1.00) | π\*(N40–O42)  (0.6143) | 59.38  40.62 | 0.7706(sp1.00)N  -0.6373(sp1.00)O | 679.30 |
| n2(O42)  (1.8939) | – | (sp99.99) | σ\*(N40–O41)  (0.0572) | 51.37  48.63 | 0.7167(sp2.11)N  -0.6974(sp2.99)O | 81.13 |

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| **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) | 74.75  25.25 | 0.8646(sp2.24)N  0.5025(sp0.00)H | 30.82, 69.16  99.88, 0.12 |
| σ(N1–C2)  (1.98309) | 61.72  38.28 | 0.7856(sp1.90)N  0.6187(sp2.72)C | 34.48, 65.48  26.82, 73.07 |
| σ(N1–C5)  (1.98329) | 61.58  38.42 | 0.7847(sp1.89)N  0.6199(sp2.63)C | 34.61, 65.36  27.53, 72.36 |
| σ(C8–N9)  (1.99498) | 42.61  57.39 | 0.6528(sp1.12)C  0.7576(sp1.18)N | 47.09, 52.89  45.72, 53.94 |
| σ(C15–N16)  (1.98767) | 40.38  59.62 | 0.6355(sp2.11)C  0.7721(sp1.35)N | 32.08, 67.82  42.58, 57.36 |
| σ(N17–C18)  (1.99042) | 63.17  36.83 | 0.7948(sp1.43)N  0.6069(sp2.31)C | 41.15, 58.82  30.13, 69.75 |
| σ(C25–O26)  (1.99466) | 34.03  65.97 | 0.5833(sp2.82)C  0.8122(sp1.99)O | 26.09, 73.70  33.46, 66.47 |
| σ(O26–H42)  (1.98706) | 79.02  20.98 | 0.8889(sp2.84)O  0.4580 (sp0.00)H | 26.04, 73.90  99.71, 0.29 |
| σ(C18–O19)  (1.99412) | 35.21  64.79 | 0.5934(sp2.20)C  0.8049(sp1.58)O | 31.17, 68.72  38.66, 61.03 |
| σ(C10–O11)  (1.99646) | 34.46  65.54 | 0.5870(sp1.92)C  0.8096(sp1.40)O | 34.20, 65.69  41.48, 58.15 |
| σ(C10–O12)  (1.99171) | 31.26  68.74 | 0.5591(sp2.52)C  0.8291(sp2.07)O | 28.32, 71.43  32.50, 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 |

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| **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) | 74.62  25.38 | 0.863(sp2.26)N  0.503(sp0.00)H | 30.70, 69.28  99.88, 0.12 |
| σ(N1–C2)  (1.983) | 61.71  38.29 | 0.785(sp1.90)N  0.618(sp2.71)C | 34.47, 65.49  26.92, 72.97 |
| σ(N1–C5)  (1.983) | 61.60  38.40 | 0.784(sp1.88)N  0.619(sp2.65)C | 34.73, 65.24  27.38, 72.51 |
| σ(C8–N9)  (1.995) | 42.59  57.41 | 0.652(sp1.12)C  0.757(sp1.18)N | 47.10, 52.87  45.77, 53.89 |
| σ(C15–N16)  (1.987) | 40.57  59.43 | 0.637(sp2.05)C  0.770(sp1.43)N | 32.79, 67.12  41.07, 58.87 |
| σ(N17–C18)  (1.989) | 63.27  36.73 | 0.795(sp1.63)N  0.606(sp2.29)C | 38.04, 61.93  30.33, 69.54 |
| σ(C18–O19)  (1.994) | 35.06  64.94 | 0.592(sp2.07)C  0.805(sp1.46)O | 32.56, 67.34  40.54, 59.11 |
| σ(C22–N23)  (1.986) | 40.83  59.17 | 0.639(sp2.19)C  0.769(sp1.82)N | 31.32, 68.62  35.38, 64.42 |
| σ(N23–C24)  (1.986) | 59.33  40.67 | 0.770(sp1.83)N  0.637(sp2.22)C | 35.31, 64.49  31.08, 68.86 |
| σ(C10–O11)  (1.996) | 34.46  65.54 | 0.587(sp1.92)C  0.809(sp1.40)O | 34.23, 65.66  41.47, 58.16 |
| σ(C10–O12)  (1.991) | 31.25  68.75 | 0.559(sp2.52)C  0.8291(sp2.07)O | 28.37, 71.38  32.60, 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 |

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| **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) | 74.63  25.37 | 0.8639(sp2.25)N  0.5037(sp0.00)H | 30.73, 69.25  99.88, 0.12 |
| σ(N1–C2)  (1.9834) | 61.73  38.27 | 0.7857(sp1.90)N  0.6187(sp2.71)C | 34.50, 65.46  26.95, 72.94 |
| σ(N1–C5)  (1.9831) | 61.58  38.42 | 0.7847(sp1.88)N  0.6198(sp2.65)C | 34.67, 65.29  27.38, 72.51 |
| σ(C8–N9)  (1.9950) | 42.59  57.41 | 0.6526(sp1.12)C  0.7577(sp1.18)N | 47.10, 52.87  45.76, 53.90 |
| σ(C15–N16)  (1.9874) | 40.58  59.42 | 0.6371(sp2.05)C  0.7708(sp1.43)N | 32.75, 67.16  41.08, 58.85 |
| σ(N17–C18)  (1.9894) | 63.01  36.99 | 0.7938(sp1.63)N  0.6082(sp2.22)C | 38.07, 61.90  30.97, 68.91 |
| σ(C33–N37)  (1.9890) | 38.31  61.69 | 0.6190(sp3.08)C  0.7854(sp1.83)N | 24.50, 75.36  35.36, 64.60 |
| σ(C35–N40)  (1.9892) | 38.20  61.80 | 0.6180(sp3.07)C  0.7861(sp1.81)N | 24.53, 75.33  35.57, 64.39 |
| σ(C18–O19)  (1.9942) | 35.16  64.84 | 0.5929(sp2.06)C  0.8053(sp1.47)O | 32.70, 67.20  40.40, 59.25 |
| σ(N37–O38)  (1.9957) | 48.64  51.36 | 0.6975(sp2.10)N  0.7166(sp2.98)O | 32.22, 67.68  25.07, 74.79 |
| σ(N37–O39)  (1.9956) | 48.66  51.34 | 0.6975(sp2.09)N  0.7165(sp2.97)O | 32.29, 67.61  25.12, 74.73 |
| σ(N40–O41)  (1.9956) | 48.63  51.37 | 0.6974(sp2.11)N  0.7167(sp2.99)O | 32.08, 67.82  25.03, 74.83 |
| σ(N40–O42)  (1.9957) | 48.65  51.35 | 0.6975(sp2.10)N  0.7166(sp2.97)O | 32.22, 67.68  25.15, 74.71 |
| σ(C10–O11)  (1.9964) | 34.46  65.54 | 0.5870(sp1.92)C  0.8096(sp1.40)O | 34.27, 65.63  41.47, 58.15 |
| σ(C10–O12)  (1.9917) | 31.28  68.72 | 0.5593(sp2.51)C  0.8290(sp2.06)O | 28.46, 71.29  32.62, 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 |