**Supporting Information**

**Effect of donor acceptor substitution position on the electrical responsive properties of Azulene System: A Computational study**

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|  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Mol. |  | 631G(d) | 631+G(d) | 631++G(d) | 631G(dp) | 631+G(dp) | 631++G(dp) | 6311G(d) | 6311+G(d) | 6311++G(d) | 6311G(dp) | 6311+G(dp) | 6311++G(dp) |
| AZ-1 | α | 174.42 | 202.23 | 202.86 | 175.62 | 203.54 | 204.14 | 181.98 | 200.19 | 200.83 | 183.53 | 201.69 | 202.30 |
| β | 759.18 | 994.77 | 942.31 | 766.58 | 1016.59 | 922.39 | 651.64 | 843.54 | 798.04 | 658.62 | 850.40 | 805.92 |
| AZ-2 | α | 184.07 | 217.38 | 217.95 | 188.53 | 218.59 | 219.14 | 191.88 | 215.36 | 215.83 | 196.88 | 216.81 | 217.25 |
| β | 1131.35 | 1117.17 | 1071.98 | 966.80 | 1102.72 | 1042.36 | 1078.66 | 1099.14 | 1068.35 | 909.27 | 1070.92 | 1028.96 |
| AZ-3 | α | 161.38 | 185.21 | 185.82 | 162.63 | 186.63 | 187.21 | 169.51 | 184.64 | 185.19 | 170.97 | 186.08 | 186.66 |
| β | 287.21 | 293.739 | 280.49 | 299.66 | 320.37 | 305.82 | 266.53 | 293.07 | 268.22 | 274.43 | 308.42 | 287.69 |
| AZ-4 | α | 182.28 | 208.45 | 208.93 | 183.39 | 209.54 | 210.02 | 189.91 | 207.32 | 207.54 | 191.28 | 208.64 | 209.11 |
| β | 352.67 | 501.67 | 485.69 | 350.79 | 499.47 | 479.04 | 305.52 | 496.01 | 470.79 | 300.48 | 492.76 | 464.49 |
| AZ-5 | α | 179.28 | 205.77 | 206.32 | 180.39 | 206.86 | 207.42 | 187.28 | 204.70 | 205.24 | 187.98 | 206.02 | 206.53 |
| β | 193.65 | 309.49 | 283.02 | 192.80 | 308.72 | 283.01 | 164.40 | 298.31 | 266.32 | 161.78 | 292.53 | 261.79 |
| AZ-6 | α | 170.11 | 196.32 | 196.78 | 171.09 | 197.22 | 197.71 | 177.71 | 195.08 | 195.49 | 178.91 | 196.14 | 196.53 |
| β | 96.32 | 115.76 | 118.45 | 98.56 | 119.63 | 122.08 | 110.33 | 111.65 | 115.82 | 116.86 | 115.62 | 120.05 |
| AZ-7 | α | 199.75 | 229.47 | 230.06 | 200.87 | 230.64 | 231.24 | 207.19 | 227.13 | 227.74 | 208.67 | 228.56 | 229.12 |
| β | 2206.17 | 2794.22 | 2751.41 | 2208.47 | 2794.59 | 2753.01 | 2113.87 | 2671.58 | 2625.64 | 2109.19 | 2657.75 | 2612.89 |
| AZ-8 | α | 187.99 | 215.40 | 216.04 | 189.10 | 216.55 | 217.19 | 195.88 | 213.95 | 214.52 | 197.33 | 215.33 | 215.87 |
| β | 1182.27 | 1461.99 | 1424.88 | 1184.49 | 1463.65 | 1427.31 | 1112.51 | 1395.09 | 1353.29 | 1110.73 | 1389.39 | 1348.44 |
| AZ-9 | α | 184.78 | 211.55 | 212.17 | 185.98 | 212.86 | 213.46 | 192.29 | 209.31 | 209.945 | 193.87 | 210.79 | 211.38 |
| β | 946.77 | 1183.36 | 1155.98 | 949.67 | 1186.84 | 1160.48 | 880.17 | 1071.12 | 1062.56 | 880.37 | 1093.00 | 1059.89 |
| AZ-10 | α | 189.15 | 215.82 | 216.28 | 190.21 | 216.85 | 217.32 | 196.39 | 214.39 | 214.89 | 197.71 | 215.65 | 216.11 |
| β | 972.42 | 1286.87 | 1255.79 | 970.77 | 1284.01 | 1253.34 | 886.92 | 1241.42 | 1205.56 | 879.32 | 1230.51 | 1196.11 |
| AZ-11 | α | 171.22 | 196.27 | 197 | 172.24 | 197.29 | 197.95 | 178.85 | 195.31 | 195.80 | 180.12 | 196.46 | 197.01 |
| β | 212.41 | 258.11 | 220.21 | 210.01 | 255.65 | 216.18 | 116.75 | 240.44 | 203.58 | 112.02 | 232.38 | 197.15 |
| AZ-12 | α | 175.38 | 201.83 | 202.22 | 176.40 | 202.81 | 203.19 | 182.64 | 200.29 | 200.71 | 183.90 | 201.44 | 20184 |
| β | 458.98 | 533.64 | 511.92 | 456.17 | 529.69 | 508.86 | 389.77 | 519.93 | 494.79 | 382.19 | 511.85 | 487.76 |

**TABLE-S1 : : Static Polarizability (αav,** ina.u **), First Hyperpolarizability (βav** ina.u**) of all azulene derivatives using DFT-B3LYP level of theory with different basis set.**

**TABLE-S2 : Static Polarizability (αav,** ina.u **), First Hyperpolarizability (βav** ina.u**) of all azulene derivatives using different functional with 6-31+G(d) basis set.**

|  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Molecule |  | B3LYP | CAM-B3LYP | B3PW91 | MPW91PW91 | PBEPBE | HSEH1PBE | HCTH | WB97XD |
| AZ-1 | α | **202.23** | **190.71** | **198.71** | **195.31** | **204.91** | **197.73** | **196.12** | **189.47** |
| β | **994.77** | **549.89** | **968.24** | **782.64** | **1052.55** | **884.50** | **2327.06** | **491.03** |
| AZ-2 | α | **217.38** | **200.35** | **212.95** | **210.28** | **228.59** | **211.93** | **223.79** | **197.99** |
| β | **1117.17** | **1194.07** | **1094.17** | **1078.12** | **956.11** | **1026.15** | **1073.28** | **1112.15** |
| AZ-3 | α | **185.21** | **178.81** | **182.33** | **180.33** | **198.54** | **182.10** | **192.09** | **178.39** |
| β | **293.739** | **234.93** | **307.54** | **308.29** | **680.77** | **307.23** | **507.29** | **244.28** |
| AZ-4 | α | **208.45** | **200.81** | **204.68** | **202.53** | **217.58** | **203.84** | **213.71** | **200.22** |
| β | **501.67** | **498.89** | **479.97** | **461.74** | **482.49** | **470.37** | **491.98** | **485.13** |
| AZ-5 | α | **205.77** | **198.33** | **202.06** | **199.99** | **214.89** | **201.30** | **210.52** | **197.55** |
| β | **309.49** | **267.00** | **301.73** | **278.19** | **364.34** | **295.21** | **377.64** | **262.58** |
| AZ-6 | α | **196.32** | **188.97** | **192.33** | **190.48** | **204.17** | **191.79** | **200.30** | **187.79** |
| β | **115.76** | **138.62** | **114.93** | **120.17** | **112.58** | **138.13** | **106.61** | **134.37** |
| AZ-7 | α | **229.47** | **217.33** | **225.18** | **221.99** | **244.09** | **224.23** | **237.32** | **215.18** |
| β | **2794.22** | **2549.36** | **2669.79** | **2567.49** | **2957.70** | **2600.16** | **2786.23** | **2450.30** |
| AZ-8 | α | **215.40** | **204.77** | **211.54** | **208.87** | **227.82** | **210.68** | **222.38** | **203.38** |
| β | **1461.99** | **1300.99** | **1402.24** | **1349.82** | **1539.25** | **1365.32** | **1437.93** | **1261.31** |
| AZ-9 | α | **211.55** | **202.62** | **207.72** | **205.44** | **223.58** | **207.29** | **215.13** | **200.45** |
| β | **1183.36** | **1150.52** | **1133.24** | **1097.42** | **1232.89** | **1103.90** | **1168.24** | **1116.66** |
| AZ-10 | α | **215.82** | **205.61** | **211.85** | **209.06** | **227.92** | **210.79** | **223.67** | **204.79** |
| β | **1286.87** | **987.72** | **1207.38** | **1114.33** | **1548.60** | **1166.77** | **1493.25** | **931.13** |
| AZ-11 | α | **196.27** | **188.42** | **192.69** | **190.73** | **205.44** | **191.99** | **200.75** | **187.78** |
| β | **258.11** | **155.88** | **237.21** | **199.29** | **336.07** | **211.94** | **274.21** | **139.48** |
| AZ-12 | α | **201.83** | **193.01** | **198.02** | **195.70** | **212.20** | **197.09** | **207.72** | **192.12** |
| β | **533.64** | **385.71** | **502.01** | **452.44** | **651.69** | **465.77** | **591.87** | **369.19** |

**TABLE-S3 : Dipole Moment(µ, in Debye), Static Polarizability(a.u.), First Hyperpolarizability(a.u.), HOMO-LUMO energy Gap and Hardness of all the azulene derivatives using CAM-B3LYP 6-31+G(d) basis set .**

|  |  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **MOL.** | **AZ-1** | **AZ-2** | **AZ-3** | **AZ-4** | **AZ-5** | **AZ-6** | **AZ-7** | **AZ-8** | **AZ-9** | **AZ-10** | **AZ-11** | **AZ-12** |
| µx | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| µy | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| µz | 5.47 | 5.94 | 4.13 | 11.13 | 8.74 | 6.66 | 9.09 | 7.54 | 5.92 | 12.65 | 8.34 | 8.98 |
| µ | 5.47 | 5.94 | 4.13 | 11.13 | 8.74 | 6.66 | 9.09 | 7.54 | 5.92 | 12.65 | 8.34 | 8.98 |
| E (a.u) | -723.951663 | -723.957639 | -723.941961 | -723.969802 | -723.964956 | -723.955456 | -723.968766 | -723.968725 | -723.961966 | -723.967076 | -723.953033 | -723.961368 |
| αxx | 103.657 | 155.118 | 171.998 | 94.0811 | 114.991 | 149.049 | 90.5003 | 102.468 | 178.616 | 89.5622 | 103.083 | 92.8583 |
| αyy | 179.023 | 176.234 | 172.92 | 190.727 | 195.503 | 195.98 | 168.239 | 200.904 | 189.557 | 166.365 | 174.751 | 218.967 |
| αzz | 289.456 | 269.712 | 191.506 | 317.611 | 284.485 | 221.886 | 393.26 | 310.932 | 239.687 | 360.902 | 287.42 | 267.209 |
| **αav** | **190.71** | **200.35** | **178.81** | **200.81** | **198.33** | **188.97** | **217.33** | **204.77** | **202.62** | **205.61** | **188.42** | **193.01** |
| ∆α | 161.86 | 105.63 | 19.06 | 194.17 | 146.85 | 63.95 | 272.34 | 180.63 | 56.40 | 242.25 | 160.95 | 155.93 |
| βx | -124.91713 | 490.40333 | -85.32738 | -18.149167 | 75.801667 | 65.845 | -100.76146 | -233.596 | -582.3373 | -0.044651 | 23.276667 | 20.15489 |
| βy | 139.4299 | 403.682 | -92.98546 | -82.1472 | 152.6993 | 115.99766 | 0.2024507 | 381.6667 | 455.9133 | 0.0037847 | 77.6552 | 187.1088 |
| βz | -517.04953 | -1011.1066 | 198.159 | -491.7428 | -205.49262 | 37.72903 | -2547.368 | -1221.6112 | -881.317 | -987.7228 | -133.14186 | -336.6823 |
| **βav** | **549.89** | **1194.07** | **234.93** | **498.89** | **267.00** | **138.62** | **2549.36** | **1300.99** | **1150.52** | **987.72** | **155.88** | **385.71** |
| HOMO-LUMO GAP | 0.18575 | 0.17939 | 0.20182 | 0.21899 | 0.189752 | 0.21223 | 0.16704 | 0.19377 | 0.19093 | 0.20502 | 0.19213 | 0.19702 |
| η | 0.092875 | 0.089695 | 0.10091 | 0.109495 | 0.094876 | 0.106115 | 0.08532 | 0.096885 | 0.095465 | 0.10251 | 0.096065 | 0.09851 |
| <R2> | 4.356 | 3.817 | 3.198 | 4.393 | 3.812 | 3.188 | 5.009 | 4.657 | 3.920 | 5.004 | 4.688 | 3.889 |

**TABLE-S4 : Dipole Moment(µ), Static Polarizability(au.), First Hyperpolarizability(au.), HOMO-LUMO Energy Gap and Hardness of all the azulene derivatives using CAM-B3LYP/ cc-pVTZ level of theory.**

|  |  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **MOL.** | **AZ-1** | **AZ-2** | **AZ-3** | **AZ-4** | **AZ-5** | **AZ-6** | **AZ-7** | **AZ-8** | **AZ-9** | **AZ-10** | **AZ-11** | **AZ-12** |
| µx | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| µy | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| µz | 5.0971 | 5.53 | 3.94 | 10.74 | 8.44 | 6.28 | 8.84 | 7.159 | 5.4953 | 12.41 | 8.04 | 8.3785 |
| µ | 5.0971 | 5.53 | 3.94 | 10.74 | 8.44 | 6.28 | 8.84 | 7.159 | 5.4953 | 12.41 | 8.04 | 8.3785 |
| E (a.u) | -724.18492568 | -724.189173 | -724.177961 | -724.193802 | -724.191246 | -724.186426 | -724.19814 | -724.20304882 | -724.1961553 | -724.19642 | -724.183226 | -724.1940594 |
| αxx | 94.3425 | 149.118 | 165.268 | 89.427 | 109.429 | 142.27 | 83.724 | 97.312 | 170.47 | 85.474 | 97.12 | 89.538 |
| αyy | 175.389 | 171.432 | 167.43 | 185.382 | 189.402 | 189.739 | 161.478 | 195.424 | 185.412 | 162.365 | 170.514 | 212.697 |
| αzz | 282.885 | 265.41 | 182.522 | 312.951 | 280.799 | 216.841 | 388.218 | 305.524 | 227.888 | 354.321 | 273.596 | 253.125 |
| **αav** | **184.21** | **195.32** | **171.74** | **195.92** | **193.21** | **182.95** | **211.14** | **199.42** | **194.59** | **200.72** | **180.41** | **185.12** |
| βx | -114.984 | 470.319 | -78.439 | -19.0711 | 68.7817 | 52.47 | -18.674 | -122.724 | -12.798 | -5.8972 | 12.845 | 15.407 |
| βy | 145.739 | 422.864 | -47.484 | -73.174 | 108.673 | 68.489 | 172.544 | 205.816 | 223.452 | 204.148 | 35.352 | 127.3287 |
| βz | -378.430 | -802.051 | 65.045 | -323.8795 | -62.79 | 45.50 | -2135.379 | -1095.57 | -812.173 | -728.68 | -95.317 | -209.286 |
| **βav** | **421.51** | **1021.42** | **112.42** | **332.59** | **143.12** | **97.54** | **2142.42** | **1121.47** | **849.87** | **756.76** | **102.47** | **245.46** |
| HOMO-LUMO GAP | 0.16965 | 0.15936 | 0.18182 | 0.19877 | 0.16952 | 0.19213 | 0.14714 | 0.19977 | 0.19677 | 0.19512 | 0.19645 | 0.20098 |
| η | 0.084825 | 0.07968 | 0.09091 | 0.099385 | 0.08476 | 0.096065 | 0.07357 | 0.09988 | 0.09839 | 0.09756 | 0.098215 | 0.10049 |
| <R2> | 4.32 | 3.37 | 3.06 | 4.32 | 3.76 | 2.98 | 4.97 | 4.621 | 3.888 | 4.92 | 4.628 | 3.861 |

**Table-S5: Dipole Moment(µ) of all the azulene derivatives using different functional with different basis sets.**

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Molecule** | **CIS 3-21G**  **(Excited state)** | **CAM-B3LYP/ cc-pVTZ** | **HF 6-31+G(d)** | **CAM-B3LYP 6-31+G(d)** |
| AZ-1 | 6.52 | 5.09 | 5.82 | 5.47 |
| AZ-2 | 6.31 | 5.53 | 5.97 | 5.94 |
| AZ-3 | 6.39 | 3.94 | 4.30 | 4.13 |
| AZ-4 | 9.54 | 10.74 | 11.19 | 11.13 |
| AZ-5 | 9.40 | 8.44 | 8.93 | 8.74 |
| AZ-6 | 8.44 | 6.28 | 7.10 | 6.66 |
| AZ-7 | 9.52 | 8.84 | 8.85 | 9.09 |
| AZ-8 | 5.80 | 7.16 | 6.74 | 7.54 |
| AZ-9 | 6.48 | 5.50 | 5.96 | 5.92 |
| AZ-10 | 9.83 | 12.41 | 12.92 | 12.65 |
| AZ-11 | 9.21 | 8.04 | 8.71 | 8.34 |
| AZ-12 | 9.61 | 8.38 | 9.33 | 8.98 |