**Structural and electronic effects of cation binding (Li+, Na+, K+, Mg2+ & Ca2+) to π system of ƞ6-benzene-Cr(CO)3 complex: A theoretical study**

A. KALPANA1, L. AKILANDESWARI\*2

*1,2Department of Chemistry, Sri Sarada College for Women, Salem 636 016, TamilNadu, India.*

Supplementary Material

SM TABLE I. Computed λmax (maximum absorption wavelength), f (oscillator strength), TDM (transition dipole moments),

Root mean square value (μ0n) (RMS) between the ground and nth excited state of all the system under study.

|  |  |  |
| --- | --- | --- |
| Systems | MB | MBC |
| State transition | λ (nm) | *f* | Transition dipolemoment | RMS(μ0n)(e-bohr) | State transition | λ (nm) | *f* | Transition dipolemoment | RMS(μ0n)(e-bohr) |
| x | y | z | x | y | z |
| BC | S0→S3 | 168.03 | 0.5587 | -0.1278 | -0.4628 | 0 | 0.480 | S0→S2 | 361.16 | 0.0004  | -0.0011  | -0.0122  | 0.0661  | 0.067 |
| **S0→S4** | **168.03** | **0.5588** | **-0.4629** | **0.1278** | **0** | **0.480** | S0→S3 | 361.10 | 0.0004  | -0.0006  | 0.0657  | 0.0121  | 0.067 |
| S0→S8 | 155.08 | 0.0056 | 0 | 0 | -0.0087 | 0.009 | S0→S4 | 346.01 | 0.0002  | 0.0323  | 0.0405  | -0.0043  | 0.052 |
|  |  |  |  |  |  |  | S0→S5 | 345.91 | 0.0010  | -0.0093  | 0.0202  | -0.1022  | 0.105 |
|  |  |  |  |  |  |  | S0→S6 | 345.80 | 0.0009  | -0.0117  | 0.0954  | 0.0238  | 0.099 |
|  |  |  |  |  |  |  | S0→S7 | 344.98 | 0.0005  | 0.0720  | 0.0005  | -0.0060  | 0.072 |
|  |  |  |  |  |  |  | **S0→S8** | **328.93** | **0.0016**  | **-0.0002**  | **-0.1242**  | **-0.0418**  | **0.131** |
|  |  |  |  |  |  |  | S0→S9 | 328.89 | 0.0016  | 0.0008  | -0.0419  | 0.1247  | 0.132 |
|  |  |  |  |  |  |  | S0→S10 | 308.11 | 0.0001 | 0.0006  | -0.0353  | -0.0010  | 0.035 |
| Li+-BC | S0→S2 | 193.2 | 0.0202 | 0.0085 | 0.0635 | 0 | 0.064 | S0→S4 | 390.76 | 0.0006  | -0.0051  | -0.0323  | 0.0820  | 0.088 |
| S0→S3 | 193.19 | 0.0202 | -0.0636 | 0.0084 | 0 | 0.064 | S0→S5 | 390.42 | 0.0006  | 0.0013  | -0.0824  | -0.0336  | 0.089 |
| **S0→S6** | **165.65** | **0.5223** | **-0.1315** | **0.4292** | **0** | **0.449** | **S0→S6** | **352.21** | **0.0025**  | **0.1700**  | **0.0058**  | **0.0026**  | **0.170** |
| S0→S7 | 165.65 | 0.5222 | -0.4292 | -0.1315 | 0 | 0.449 | S0→S7 | 349.04 | 0.0013  | 0.0925  | -0.0814  | 0.0041  | 0.123 |
| S0→S10 | 163.62 | 0.0066 | 0 | 0.0001 | -0.0277 | 0.028 | S0→S8 | 348.72 | 0.0012  | -0.0476  | -0.0692  | -0.0820  | 0.117 |
|  |  |  |  |  |  |  | S0→S9 | 348.49 | 0.0013  | 0.0531  | 0.0593  | -0.0911  | 0.121 |
|  |  |  |  |  |  |  | S0→S10 | 322.44 | 0.0006  | 0.0060  | 0.0061  | -0.0785  | 0.079 |
| Na+-BC | S0→S1 | 230.59 | 0.0111 | -0.0067 | 0.0494 | 0.0001 | 0.050 | S0→S2 | 398.04 | 0.0006 | 0.0000  | -0.0337  | 0.0837  | 0.090 |
| S0→S2 | 230.57 | 0.0111 | 0.0495 | 0.0069 | 0.0001 | 0.050 | S0→S3 | 397.86 | 0.0006 | 0.0018  | 0.0831  | 0.0338  | 0.090 |
| **S0→S5** | **168.36** | **0.5276** | **-0.0938** | **0.444** | **0.0009** | **0.454** | S0→S4 | 391.39 | 0.0001 | -0.0007  | -0.0035  | 0.0404  | 0.041 |
| S0→S6 | 168.35 | 0.5276 | 0.4441 | 0.0938 | 0.001 | 0.454 | S0→S5 | 391.27 | 0.0001 | 0.0007  | 0.0414  | 0.0036  | 0.042 |
|  |  |  |  |  |  |  | S0→S8 | 367.94 | 0.0012 | -0.1217  | -0.0008  | -0.0002  | 0.122 |
|  |  |  |  |  |  |  | **S0→S9** | **351.84** | **0.0015** | **0.0012**  | **-0.1334**  | **0.0118**  | **0.134** |
|  |  |  |  |  |  |  | S0→S10 | 351.64 | 0.0015 | 0.0001  | -0.0119  | -0.1333  | 0.134 |
| K+-BC | S0→S1 | 230.94 | 0.0085 | 0 | 0.0002 | -0.0395 | 0.040 | S0→S4 | 379.73 | 0.0007 | 0.0019  | 0.0929  | 0.0145  | 0.094 |
| S0→S2 | 230.93 | 0.0085 | 0 | -0.0395 | -0.0002 | 0.040 | S0→S5 | 379.42 | 0.0007 | -0.0026  | -0.0143  | 0.0924  | 0.094 |
| S0→S5 | 172.58 | 0.0001 | -0.0055 | 0 | 0.0001 | 0.006 | S0→S6 | 377.77 | 0.0001 | -0.0001  | 0.0292  | -0.0173  | 0.034 |
| S0→S7 | 171.21 | 0.1136 | 0.1767 | -0.0001 | 0 | 0.177 | S0→S7 | 377.69 | 0.0001 | -0.0002  | -0.0152  | -0.0304  | 0.034 |
| S0→S9 | 169.78 | 0.3383 | 0 | -0.2698 | 0.2307 | 0.355 | S0→S9 | 341.11 | 0.0001 | -0.0332  | -0.0051  | -0.0049  | 0.034 |
| **S0→S10** | **169.76** | **0.3436** | **-0.0001** | **0.233** | **0.2718** | **0.358** | **S0→S10** | **339.76** | **0.0013** | **-0.0026**  | **-0.0183**  | **0.1175**  | **0.119** |
| Mg2+-BC | S0→S1 | 334.30 | 0.0014 | 0.0098 | 0.0108 | 0 | 0.015 | S0→S1 | 1096.59 | 0.0002 | 0.0018  | 0.0651  | 0.0407  | 0.077 |
| S0→S2 | 334.28 | 0.0014 | -0.0107 | 0.0098 | -0.0001 | 0.015 | S0→S2 | 1095.48 | 0.0002 | 0.0018  | 0.0401  | -0.0655  | 0.077 |
| **S0→S8** | **174.03** | **0.0109** | **0** | **0** | **-0.0519** | **0.052** | **S0→S3** | **792.33** | **0.0484** | **-1.1238**  | **-0.0011**  | **0.0001**  | **1.124** |
|  |  |  |  |  |  |  | S0→S5 | 402.55 | 0.0001 | 0.0020  | -0.0285  | -0.0024  | 0.029 |
|  |  |  |  |  |  |  | S0→S6 | 402.43 | 0.0001 | -0.0014  | 0.0018  | -0.0282  | 0.028 |
|  |  |  |  |  |  |  | S0→S7 | 395.43 | 0.0001 | -0.0007  | 0.0356  | 0.0053  | 0.036 |
|  |  |  |  |  |  |  | S0→S8 | 395.14 | 0.0001 | 0.0001  | -0.0057  | 0.0363  | 0.037 |
|  |  |  |  |  |  |  | S0→S9 | 374.08 | 0.0016 | 0.0000  | 0.1391  | -0.0113  | 0.140 |
|  |  |  |  |  |  |  | S0→S10 | 373.93 | 0.0016 | 0.0010  | 0.0112  | 0.1395  | 0.140 |
| Ca2+-BC | S0→S1 | 296.74 | 0.0027 | 0 | 0 | 0.0157 | 0.016 | S0→S1 | 744.07 | 0.0003 | 0.0002  | 0.0394  | -0.0834  | 0.092 |
| S0→S2 | 296.72 | 0.0027 | 0 | 0.0157 | 0 | 0.016 | S0→S2 | 743.49 | 0.0003 | 0.0013  | 0.0835  | 0.0395  | 0.092 |
| **S0→S10** | **173.55** | **0.0069** | **0.0335** | **-0.0001** | **0** | **0.034** | **S0→S3** | **667.06** | **0.0174** | **-0.6181**  | **0.0001**  | **-0.0001**  | **0.618** |
|  |  |  |  |  |  |  | S0→S5 | 430.26 | 0.0001 | 0.0008  | -0.0075  | -0.0359  | 0.037 |
|  |  |  |  |  |  |  | S0→S6 | 430.18 | 0.0001 | -0.0001  | 0.0359  | -0.0077  | 0.037 |
|  |  |  |  |  |  |  | S0→S9 | 374.44 | 0.0009 | 0.0003  | -0.0892  | 0.0523  | 0.103 |
|  |  |  |  |  |  |  | S0→S10 | 374.36 | 0.0009 | 0.0003  | -0.0518  | -0.0892  | 0.103 |

Data corresponding to the maximum absorption wavelength are in bold letters.

SM TABLE II . NTO pictures and MO transitions corresponding to λmax of MB systems under study.

|  |  |  |  |
| --- | --- | --- | --- |
| Systems | λmax&*f* | NTO | MO transition |
| % contribution | Hole | Particle |
| B | 168.035(0.559) | 50% |  |  | HOMO-1 → LUMOHOMO → LUMO+1HOMO-1 → LUMO+1HOMO → LUMO | 0.69-0.69-0.16-0.16 | (47%)(47%)(2%)(2%) |
| 50% |  |  |
| Li+-B | 165.649(0.522) | 49% |  |  | HOMO-1 → LUMO HOMO → LUMO+1HOMO-1 → LUMO+1HOMO → LUMO  | 0.62-0.620.330.33 | (38%)(38%)(11%)(11%) |
| 49% |  |  |
| Na+-B | 168.357(0.528) | 49% |  |  | HOMO-1 → LUMO+2HOMO → LUMO+1 | 0.70-0.70 | (49%)(49%) |
| 49% |  |  |
| K+-B | 169.766(0.344) | 63% |  |  | HOMO-1 → LUMO+3HOMO → LUMO+1HOMO → LUMO+5HOMO-1→LUMO+5HOMO-1→LUMO+1 | 0.570.570.460.280.15 | (32%)(32%)(21%)(8%)(2%) |
| 34% |  |  |
| Mg2+-B | 174.029(0.011) | 53% |  |  | HOMO-2 → LUMO+1HOMO-3 → LUMO+2 | 0.730.67 | (53%)(45%) |
| 45% |  |  |
| Ca2+-B | 173.551(0.007) | 49% |  |  | HOMO-3 → LUMO+2HOMO-2 → LUMO+1 | 0.700.70 | (49%)(48%) |
|  | 48% |  |  |

SM TABLE III. NTO pictures and MO transitions corresponding to λmax of MBC systems under study.

|  |  |  |  |
| --- | --- | --- | --- |
| Systems | λmax&*f* | NTO | MO transition |
| % contribution | Hole | Particle |
| BC | 328.925(0.002) | 71% |  |  | HOMO-2 →LUMO+1 HOMO-2 → LUMO+2 HOMO-1 → LUMO+3 HOMO → LUMO+2 HOMO-2 → LUMO+13HOMO-1 → LUMO+12  | 0.71-0.370.28-0.27-0.180.15 | (51%)(14%)(8%)(7%)(3%)(2%) |
| 10% |  |  |
| Li+-BC | 352.210(0.003) | 49% |  |  | HOMO → LUMO+5HOMO → LUMO+4HOMO-1 → LUMO+4 HOMO-1 → LUMO+5HOMO → LUMO+12HOMO-1 → LUMO+11 | 0.45-0.45-0.44-0.41-0.22-0.20 | (21%)(20%)(19%)(17%)(5%)(4%) |
| 43% |  |  |
| Na+-BC | 351.840(0.002) | 77% |  |  | HOMO-2 → LUMO+3HOMO-2 → LUMO+11HOMO-2 → LUMO+1HOMO-2 → LUMO+6HOMO → LUMO+4HOMO-1 → LUMO+3 | 0.66-0.31-0.270.27-0.230.23 | (43%)(10%)(7%)(7%)(5%)(5%) |
| K+-BC | 339.759(0.001) | 70% |  |  | HOMO-3 → LUMO+2HOMO-3 → LUMO+1HOMO-3→LUMO+5HOMO-3→LUMO+14HOMO-2→LUMO+3HOMO-2→LUMO+2 | 0.560.390.390.21-0.200.17 | (31%)(15%)(15%)(4%)(4%)(3%) |
| Mg2+-BC | 792.337(0.048) | 98% |  |  | HOMO-2 → LUMO | 0.99 | (98%) |
| Ca2+-BC | 667.052(0.017) | 99% |  |  | HOMO-2 → LUMO | 1.00 | (99%) |