**Electronic supplementary information**

**population analysis of titanocene dicarboranyl  
by the Mulliken and NBO methods:  
a comparative study**

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**Table S1**. Dipole moment and Mulliken charge characteristics of titanocene dicarboranyl  
obtained by HF and DFT methods at different levels of theory

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| **Method** | ***µ*g, Debye** | ***q*(Ti)** | ***q*(Cp)** | ***q*(Carb)** | ***q*(>CMe2)** |
| HF/QZVP | 11.78 | +1.43 | –0.40 | –0.19 | –0.13 |
| B3LYP/QZVP | 10.52 | +1.92 | −0.74 | −0.02 | −0.19 |
| CAM-B3LYP/QZVP | 10.88 | +1.54 | −0.63 | +0.10 | −0.24 |
| PBE0/QZVP | 10.49 | +1.41 | −0.40 | −0.09 | −0.22 |
| LC-ωPBE/QZVP | 11.04 | +0.88 | –0.12 | –0.10 | –0.21 |
| TPSSh/QZVP | 10.19 | +1.06 | –0.10 | –0.35 | –0.09 |
| M06/QZVP | 10.61 | **–0.12** | +0.34 | –0.07 | –0.22 |
| M11/QZVP | 10.64 | +0.13 | +0.98 | −0.93 | −0.12 |
|  |  |  |  |  |  |
| HF/6-311G | 11.41 | +1.77 | –0.17 | –0.73 | +0.02 |
| B3LYP/6-311G | 10.53 | +1.42 | –0.10 | –0.65 | +0.05 |
| CAM-B3LYP/6-311G | 10.74 | +1.41 | –0.10 | –0.69 | +0.08 |
| M06/6-311G | 10.39 | +1.39 | –0.07 | –0.70 | +0.08 |
|  |  |  |  |  |  |
| HF/6-311+G | 11.61 | **+5.13** | –2.33 | –1.44 | +1.20 |
| B3LYP/6-311+G | 10.61 | **+4.18** | –1.46 | –1.36 | +0.74 |
| CAM-B3LYP/6-311+G | 10.84 | **+3.19** | –1.28 | –0.80 | +0.48 |
| M06/6-311+G | 10.57 | +2.24 | –0.85 | –1.16 | +0.89 |
|  |  |  |  |  |  |
| HF/6-311++G(*d*,*p*) | 11.84 | +0.40 | –0.09 | –0.73 | +0.61 |
| B3LYP/6-311++G(*d*,*p*) | 10.54 | **–0.28** | +0.25 | –0.48 | +0.37 |
| PBE0/6-311++G(*d*,*p*) | 10.50 | +0.49 | +0.17 | –0.80 | +0.38 |
| HF/6-311+G(*3df*,*3pd*) | 11.81 | +2.88 | –0.85 | –0.34 | –0.25 |
| HF/6-311G(*3df*,*3pd*) | 11.86 | +1.67 | –0.04 | +0.10 | –0.90 |
| HF/6-311G(*d*,*p*) | 11.77 | +1.64 | –0.11 | –0.76 | +0.05 |
| B3LYP/6-311G(*d*,*p*) | 10.54 | +1.32 | −0.08 | −0.66 | +0.08 |
| CAM-B3LYP/6-311G(*d*,*p*) | 10.83 | +1.32 | –0.07 | –0.70 | +0.11 |
| PBE0/6-311G(*d*,*p*) | 10.46 | +1.30 | –0.03 | –0.68 | +0.05 |
| TPSSh/6-311G(*d*,*p*) | 10.18 | +1.26 | −0.04 | −0.70 | +0.10 |
| M06/6-311G(*d*,*p*) | 10.48 | +1.28 | −0.03 | −0.68 | +0.07 |
| M06-L/6-311G(*d*,*p*) | 10.00 | +1.36 | −0.06 | −0.64 | +0.02 |
| M06-2X/6-311G(*d*,*p*) | 10.48 | +1.45 | –0.10 | –0.68 | +0.06 |
| M06-HF/6-311G(*d*,*p*) | 9.98 | +1.51 | –0.18 | –0.81 | +0.24 |
| M11/6-311G(*d*,*p*) | 10.38 | +1.47 | –0.12 | –0.73 | +0.12 |
| N12/6-311G(*d*,*p*) | 9.90 | +1.11 | +0.01 | –0.69 | +0.06 |
| HF/6-31++G(*d*,*p*) | 11.89 | **–2.23** | +0.55 | +0.35 | +0.22 |
| B3LYP/6-31++G(*d*,*p*) | 10.75 | **–0.95** | +0.71 | –0.17 | –0.06 |
| CAM-B3LYP/6-31++G(*d*,*p*) | 11.01 | **–1.03** | +0.75 | +0.02 | –0.26 |
| HF/6-31+G(*3df*,*3pd*) | 11.81 | +2.36 | –1.31 | –1.67 | +1.81 |
| B3LYP/6-31+G(*3df*,*3pd*) | 10.64 | +1.06 | –0.48 | –1.76 | +1.71 |
| HF/6-31+G(*d*) | 11.92 | **–2.29** | +0.43 | +0.75 | –0.03 |
| B3LYP/6-31+G(*d*) | 10.81 | **–1.12** | +0.51 | +0.04 | +0.01 |
| CAM-B3LYP/6-31+G(*d*) | 11.07 | **–1.34** | +0.63 | +0.08 | –0.04 |
|  |  |  |  |  |  |
| HF/6-31G | 11.23 | +1.19 | –0.09 | –0.68 | +0.18 |
| B3LYP/6-31G | 10.54 | +0.65 | +0.04 | –0.49 | +0.13 |
| CAM-B3LYP/6-31G | 10.73 | +0.58 | +0.06 | –0.50 | +0.15 |
| M06/6-31G | 10.51 | +0.72 | +0.03 | –0.55 | +0.16 |
| TPSSh/6-31G | 10.42 | +0.74 | +0.04 | –0.55 | +0.15 |
| PBE0/6-31G | 10.53 | +0.75 | +0.03 | –0.54 | +0.14 |
|  |  |  |  |  |  |
| B3LYP/6-31+G | 10.60 | +1.70 | –0.31 | –0.78 | +0.23 |
| CAM-B3LYP/6-31+G | 10.81 | +1.54 | –0.18 | –0.76 | +0.17 |
| M06/6-31+G | 10.56 | +1.05 | +0.15 | –1.21 | +0.54 |
| TPSSh/6-31+G | 10.44 | +1.37 | –0.10 | –0.88 | +0.29 |
| PBE0/6-31+G | 10.61 | +1.46 | –0.27 | –0.83 | +0.37 |
|  |  |  |  |  |  |
| HF/6-31G(*3df*,*3pd*) | 11.91 | +1.29 | –0.39 | –1.22 | +0.97 |
| B3LYP/6-31G(*3df*,*3pd*) | 10.75 | +0.36 | –0.26 | –0.10 | +1.08 |
| HF/6-31G(*3df*,*p*) | 11.95 | +1.23 | –0.32 | –1.18 | +0.88 |
| B3LYP/6-31G(*3df*,*p*) | 10.76 | +0.33 | –0.21 | –0.92 | +0.96 |
| HF/6-31G(*d*,*p*) | 11.86 | +1.07 | –0.03 | –0.68 | +0.17 |
| B3LYP/6-31G(*d*,*p*) | 10.74 | +0.60 | +0.08 | –0.47 | +0.10 |
| CAM-B3LYP/6-31G(*d*,*p*) | 10.98 | +0.53 | +0.10 | –0.48 | +0.11 |
| TPSSh/6-31G(*d*,*p*) | 10.53 | +0.66 | +0.08 | –0.54 | +0.13 |
| PBE0/6-31G(*d*,*p*) | 10.70 | +0.66 | +0.08 | –0.52 | +0.12 |
| M06/6-31G(*d*,*p*) | 10.81 | +0.63 | +0.08 | –0.51 | +0.12 |
| M11/6-31G(*d*,*p*) | 10.50 | +0.70 | +0.03 | –0.51 | +0.12 |
| N12/6-31G(*d*,*p*) | 9.95 | +0.42 | +0.14 | –0.46 | +0.11 |
| HF/aug-cc-pVTZ | 11.80 | **–0.84** | +0.30 | +0.46 | –0.34 |
| B3LYP/aug-cc-pVTZ | 10.53 | +1.35 | –0.69 | +0.39 | –0.37 |
| PBE0/aug-cc-pVTZ | 10.49 | +0.33 | –0.30 | +0.15 | –0.02 |
| TPSSh/aug-cc-pVTZ | 10.2 | **–0.42** | +0.05 | +0.33 | –0.17 |
| BP86/aug-cc-pVTZ | 9.93 | +1.45 | –0.70 | +0.33 | –0.36 |
| HF/cc-pVTZ | 11.82 | +0.53 | +0.15 | –0.54 | +0.12 |
| B3LYP/cc-pVTZ | 10.67 | +0.58 | +0.10 | –0.44 | +0.05 |
| CAM-B3LYP/cc-pVTZ | 10.92 | +0.41 | +0.17 | –0.45 | +0.07 |
| PBE0/cc-pVTZ | 10.66 | +0.24 | +0.22 | –0.39 | +0.06 |
| TPSSh/cc-pVTZ | 10.46 | +0.02 | +0.26 | –0.40 | +0.13 |
| HF/cc-pVDZ | 11.95 | +0.60 | +0.19 | –0.52 | +0.03 |
| B3LYP/cc-pVDZ | 10.77 | **–0.24** | +0.32 | –0.22 | +0.02 |
| CAM-B3LYP/cc-pVDZ | 11.04 | **–0.39** | +0.37 | –0.22 | +0.04 |
| PBE0/cc-pVDZ | 10.73 | **–0.13** | +0.33 | –0.29 | +0.02 |
| TPSSh/cc-pVDZ | 10.51 | **–0.18** | +0.34 | –0.29 | +0.04 |
| HF/TZVP | 11.89 | **–0.06** | +0.00 | –0.93 | +0.95 |
| B3LYP/TZVP | 10.57 | **–0.11** | +0.11 | –0.78 | +0.72 |
| CAM-B3LYP/TZVP | 10.90 | **–0.14** | +0.21 | –0.78 | +0.64 |
| PBE0/TZVP | 10.55 | **–0.24** | +0.19 | –0.90 | +0.83 |
| LC-ωPBE/TZVP | 11.08 | **–0.24** | +0.35 | –0.86 | +0.63 |
| TPSSh/TZVP | 10.26 | **–0.19** | +0.18 | –0.96 | +0.87 |
| M06/TZVP | 10.71 | **–0.39** | +0.26 | –0.77 | +0.70 |
| M06-L/TZVP | 10.34 | **–0.05** | –0.18 | –1.10 | +1.31 |
| M06-2X/TZVP | 10.62 | +0.04 | +0.20 | –0.76 | +0.55 |
| M06-HF/TZVP | 10.11 | +0.60 | +0.64 | –0.65 | –0.29 |
| M11/TZVP | 10.56 | +0.22 | +0.28 | –0.67 | +0.28 |
| M11-L/TZVP | 10.01 | +0.05 | –0.20 | –1.16 | +1.33 |
| HF/DGDZVP | 11.76 | +0.74 | +0.22 | –0.57 | –0.01 |
| B3LYP/DGDZVP | 10.67 | +0.06 | +0.40 | –0.42 | –0.01 |
| CAM-B3LYP/DGDZVP | 10.98 | **–0.04** | +0.43 | –0.42 | +0.02 |
| TPSSh/DGDZVP | 10.34 | +0.20 | +0.39 | −0.49 | –0.01 |
| PBE0/DGDZVP | 10.57 | +0.21 | +0.40 | –0.47 | –0.04 |
| LC-ωPBE/DGDZVP | 11.14 | +0.00 | +0.46 | –0.48 | +0.01 |
| M06/DGDZVP | 10.68 | +0.20 | +0.37 | –0.42 | –0.04 |
| M06-HF/DGDZVP | 10.39 | **−0.03** | +0.25 | −0.47 | +0.24 |
| M06-2X/DGDZVP | 10.64 | +0.27 | +0.28 | –0.46 | +0.04 |
| M06-L/DGDZVP | 10.15 | +0.71 | +0.23 | −0.45 | −0.14 |
| M11/DGDZVP | 10.52 | +0.24 | +0.26 | –0.42 | +0.04 |
| M11-L/DGDZVP | 9.54 | +1.04 | +0.08 | –0.51 | +0.05 |
| N12/DGDZVP | 10.09 | **–0.17** | +0.55 | –0.48 | +0.02 |
| HF/3-21G | 10.84 | +2.07 | –0.35 | –0.75 | +0.06 |
| B3LYP/3-21G | 10.18 | +1.72 | –0.26 | –0.62 | +0.01 |
| B3LYP/3-21G(*d*) | 10.22 | +1.72 | –0.26 | –0.61 | +0.02 |
| CAM-B3LYP/3-21G | 10.37 | +1.68 | –0.25 | –0.62 | +0.03 |
| PBE0/3-21G | 10.13 | +1.85 | –0.29 | –0.66 | +0.02 |
| PBE0/3-21G(*d*) | 10.17 | +1.85 | –0.29 | –0.65 | +0.02 |
| LC-ωPBE/3-21G(*d*) | 10.43 | +1.71 | –0.25 | –0.66 | +0.06 |
| TPSSh/3-21G | 9.92 | +1.82 | –0.28 | –0.66 | +0.03 |
| M06/3-21G | 10.58 | +1.86 | –0.30 | –0.67 | +0.04 |
| M06-L/3-21G(*d*) | 10.20 | +2.19 | –0.36 | –0.75 | +0.02 |
| M06-2X/3-21G(*d*) | 10.07 | +1.71 | –0.28 | –0.63 | +0.05 |
| M06-HF/3-21G(*d*) | 9.32 | +1.24 | –0.19 | –0.54 | +0.11 |
| M11/3-21G | 9.89 | +1.71 | –0.26 | –0.67 | +0.08 |
| N12/3-21G | 9.39 | +1.71 | –0.25 | –0.62 | +0.01 |
| HF/CEP-121G | 11.87 | **–0.37** | +0.75 | –0.87 | +0.31 |
| B3LYP/CEP-121G | 10.82 | **−1.00** | +0.79 | –0.67 | +0.38 |
| CAM-B3LYP/CEP-121G | 11.10 | **–1.19** | +0.87 | –0.68 | +0.40 |
| PBE0/CEP-121G | 10.95 | **–0.91** | +0.90 | –0.79 | +0.35 |
| LC-ωPBE/CEP-121G | 11.42 | **–1.24** | +0.10 | –0.78 | +0.40 |
| TPSSh/CEP-121G | 10.81 | **–1.05** | +0.90 | –0.75 | +0.38 |
| M06/CEP-121G | 11.000 | **–0.98** | +0.91 | –0.84 | +0.42 |
| M06-2X/CEP-121G | 10.88 | **–0.84** | +0.80 | –0.73 | +0.36 |
| M06-HF/CEP-121G | 10.86 | **–1.53** | +0.78 | –0.41 | +0.39 |
| M06-L/CEP-121G | 10.63 | **–0.63** | +0.89 | –0.95 | +0.39 |
| M06-2X/CEP-121G | 10.88 | **–0.84** | +0.80 | –0,73 | +0.36 |
| M11/CEP-121G | 10.80 | **–0.82** | +0.79 | –0.81 | +0.43 |
| M11-L/CEP-121G | 10.40 | **+0.11** | +0.64 | –0.89 | +0.20 |
| N12/CEP-121G | 10.63 | **–1.43** | +1.00 | –0.71 | +0.43 |
| HF/SDD | 11.88 | +0.50 | +0.51 | –0.83 | +0.06 |
| B3LYP/SDD | 11.07 | +0.10 | +0.60 | –0.79 | +0.15 |
| CAM-B3LYP/SDD | 11.34 | **–0.11** | +0.66 | –0.78 | +0.17 |
| PBE0/SDD | 11.15 | +0.27 | +0.64 | –0.88 | +0.11 |
| TPSSh/SDD | 11.00 | +0.20 | +0.63 | –0.86 | +0.13 |
| M06/SDD | 11.19 | +0.31 | +0.59 | –0.89 | +0.14 |
| M06-2X/SDD | 11.70 | +0.21 | +0.57 | –0.84 | +0.17 |
| M06-HF/SDD | 10.82 | **–0.58** | +0.59 | –0.56 | +0.26 |
| M06-L/SDD | 10.81 | +0.93 | +0.48 | –1.01 | +0.06 |
| M11/SDD | 10.77 | +0.14 | +0.54 | –0.81 | +0.20 |
| N12/SDD | 10.70 | +0.13 | +0.72 | –0.97 | +0.18 |
| HF/LANL2DZ | 11.84 | +0.32 | +0.44 | –0.70 | +0.10 |
| B3LYP/LANL2DZ | 11.05 | +0.28 | +0.44 | –0.71 | +0.13 |
| CAM-B3LYP/LANL2DZ | 11.33 | +0.11 | +0.49 | –0.70 | +0.16 |
| PBE0/LANL2DZ | 11.10 | +0.39 | +0.49 | –0.79 | +0.11 |
| LC-ωPBE/LANL2DZ | 11.58 | +0.11 | +0.55 | –0.77 | +0.16 |
| TPSSh/LANL2DZ | 10.95 | +0.37 | +0.47 | –0.76 | +0.14 |
| M06/LANL2DZ | 11.13 | +0.44 | +0.45 | –0.81 | +0.13 |
| M06-2X/LANL2DZ | 11.00 | +0.29 | +0.43 | –0.75 | +0.18 |
| M11/LANL2DZ | 10.66 | +0.32 | +0.42 | –0.77 | +0.19 |

*Notes.* **Carb** stands for carboranyl C2B10H10 and >CMe2 is the bridging group; ***q*(Ti)** stands for the charge on Ti ion; ***q*(Cp)** is the charge on each Ср-ligand; ***q*(Carb)** is the charge on each carboranyl ligand; ***q*(>CMe2)** is the charge on each >CMe2 bridge; in a number of cases, the total charge of the complex differs from zero that is due to rounding of the Mulliken charges on the corresponding molecular fragments.