LETTERS TO THE EDITOR

CHARGE CHARACTERISTICS OF STRUCTURALLY COMPLEX TITANOCENE BY THE NBO METHOD

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Determining orbital populations and charge characteristics of coordination compounds is a key task in photonics of charge transfer states, which cannot be solved experimentally. Charges are used to estimate the dipole moment, molecular polarization, many quantum properties of molecular systems, etc. Modeling the electronic-structural properties of transition metal compounds is a complex, sometimes unsolvable problem. Recently, it was demonstrated [1-2] that the most popular Mulliken orbital population analysis [3] does not work in the indicative case of the polar metal complex $Ti(\eta^5:\eta^1\text{-}CpCMe_2CB_{10}H_{10}C)_2$ (Cp – cyclopentadienyl, Fig. 1). It should be noted that in

the Mulliken approximation, over 80% of more than two hundred methods of systematic analysis provided [1, 2] unphysical results (negative charge on the metal, positive charges on ligands, etc.).

Metallocenes of the titanium subgroup (Ti, Zr, Hf) − a class of organometallic compounds possessing the rarest and least studied ligand-to-metal charge transfer states (**LMCT**), including unique phosphorescent ^{3}LMCT [4-11]. Carboranes $C_2B_{10}H_{12}$ possess a unified electronic system; the properties of carboranes and their carboranyl derivatives are of fundamental interest for the theory of chemical bonding and molecular photonics.

In this work, for the first time in the approximation of natural population analysis (**NPA** , or in general form - **NBO**) [12, 13], orbital occupancies and atomic charges were systematically evaluated using a hundred methods, using titanocene dicarboranyl $Ti(\eta^5:\eta^1\text{-}CpCMe_2CB_{10}H_{10}C)_2$ (Fig. 1) as an example, which possesses unique MLCT emissive states. It is demonstrated that NBO is a good alternative to the traditional Mulliken approach, and significantly better describes the charge distribution in a compound with high ionic character.

The magnitude of the dipole moment $Ti(\eta^5:\eta^1\text{-}CpCMe_2CB_{10}H_{10}C)_2$ in the S_0-state, obtained by different computational methods, is in the range of 10-11 Debye, which corresponds to a polar molecule and is not characteristic of organometallic compounds.

Table 1 shows the results of atomic charge calculations for a structurally complex titanocene using the NBO approximation with 40 popular *ab initio* Hartree-Fock (**HF**) and density functional theory (**DFT**) methods using the GAUSSIAN 16 software package [14]. All results were obtained for structures corresponding to minima on potential energy surfaces. Unlike the Mulliken approach, where the charge values of the target compound change unpredictably to the point of absurdity [2], in the case of the NBO approach, when replacing different levels of theory (HF, DFT) basis sets QZVP and 6-311G with 6-31G, cc-pVTZ, cc-pVDZ and SDD, as well as when adding diffuse and polarization wave functions to the 6-31G and 6-311G basis sets, numerical stability is maintained

(Table 1). Meanwhile, as in the case of the Mulliken approach, within the NBO framework, methods with TZVP and LANL2DZ basis sets provided (Table 1) unreliable results: low charge on the metal (+0.1...+0.5) and high charge on the Cp ligands (+0.25...+0.35). Nevertheless, the vast majority of the hundred methods of different theory levels used provided realistic data: charge on the metal: +1.1...+1.8, charges on ligands: - 0.05...-0.35 (cyclopentadienyls) and -0.50...-0.80 (carboranyls). Accordingly, the NBO approximation describes the atomic charges of the target polar molecule much more reliably and is largely independent of the basis set.

Thus, the distribution of charge across atoms determines donor and acceptor pairs, including charge transfer in the molecule. For the same molecular system, the charge value on atoms can vary significantly depending on the approach used (Mulliken, NBO, etc.), calculation method (HF, DFT, etc.), and basis set. Based on preliminary results of a systematic study of the polar compound — titanocene dicarboranyl, it can be said that natural population analysis NBO is a more advanced approach that apparently solves most of the problems of the traditional Mulliken scheme, in particular, demonstrates numerical stability with respect to changes in the basis set.

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FIGURE CAPTION

Figure 1. Optimized structure of titanocene dicarboranyl in the S_0-state.

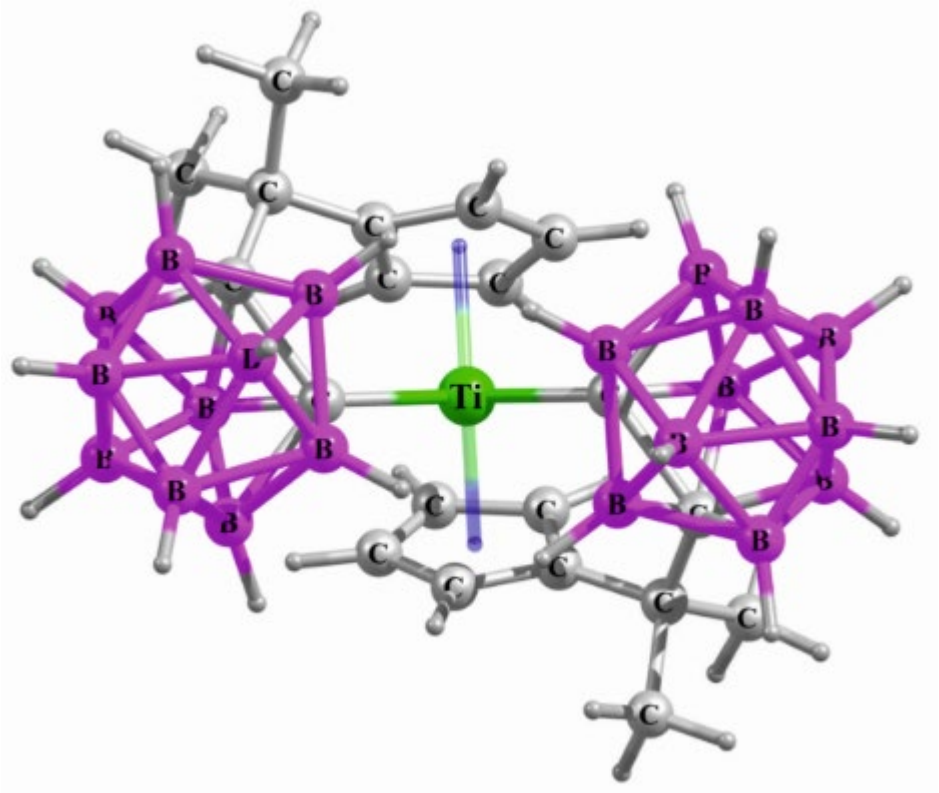

Figure 1.

Table 1 . Charge characteristics (NBO) of Ti(η^5:η^1-$CpCMe_2CB_{10}H_{10}C)_2$

Method	*q* (Ti)	*q* (Cp)	*q* (Carb)	*q* (>CMe_2)
HF/QZVP	+1.485	−0.122	−0.712	+0.094
B3LYP/QZVP	+1.131	−0.029	−0.605	+0.072
HF/6-311G	+1.877	−0.255	−0.800	+0.118
HF/6-311G(*3df* , *3pd*)	+1.872	−0.224	−0.822	+0.107
HF/6-311+G	+1.458	−0.104	−0.733	+0.106
HF/6-311+G(*3df* , *3pd*)	+1.511	−0.114	−0.739	+0.098
B3LYP/6-311G	+1.518	−0.160	−0.701	+0.103
B3LYP/6-311+G(*3df* , *3pd*)	+1.193	−0.036	−0.644	+0.082
CAM-B3LYP/6-311G	+1.509	−0.149	−0.709	+0.100
CAM-B3LYP/6-311++G(*d* , *p*)	+1.190	−0.034	−0.647	+0.089
M06/6-311G(*3df* , *3pd*)	+1.462	−0.101	−0.731	+0.100
HF/6-31G	+1.726	−0.233	−0.761	+0.134
HF/6-31+G(*3df* , *3pd*)	+1.537	−0.168	−0.729	+0.128
B3LYP/6-31G	+1.421	−0.153	−0.678	+0.120
B3LYP/6-31+G(*3df* , *3pd*)	+1.157	−0.058	−0.627	+0.110
CAM-B3LYP/6-31G	+1.401	−0.140	−0.680	+0.118
CAM-B3LYP/6-31++G(*d* , *p*)	+1.208	−0.069	−0.633	+0.102
PBE0/6-31G	+1.362	−0.125	−0.672	+0.119
TPSSH/6-31G	+1.342	−0.122	−0.675	+0.127
M06/6-31G	+1.379	−0.132	−0.679	+0.123
M06/6-31+G(*3df* , *3pd*)	+1.205	−0.074	−0.642	+0.112
HF/cc-pVTZ	+1.855	−0.267	−0.770	+0.110
B3LYP/cc-pVTZ	+1.536	−0.184	−0.681	+0.097
TPSSh/cc-pVTZ	+1.433	−0.152	−0.664	+0.101
M06/cc-pVTZ	+1.504	−0.167	−0.683	+0.097
B3LYP/cc-pVDZ	+1.719	−0.256	−0.730	+0.127
TPSSh/cc-pVDZ	+1.685	−0.245	−0.731	+0.133
M06/cc-pVDZ	+1.737	−0.261	−0.736	+0.130
HF/def2TZVP	+1.618	−0.176	−0.726	+0.094
CAM-B3LYP/def2TZVP	+1.390	−0.115	−0.652	+0.072
HF/TZVP	+0.475	+0.257	−0.573	+0.079
B3LYP/TZVP	+0.148	+0.323	−0.458	+0.061
CAM-B3LYP/TZVP	+0.121	+0.345	−0.464	+0.058
HF/DGDZVP	+1.730	−0.186	−0.814	+0.138
B3LYP/DGDZVP	+1.510	−0.143	−0.741	+0.129
HF/3-21G(*d*)	+1.931	−0.310	−0.793	+0.139
B3LYP/3-21G	+1.658	−0.233	−0.723	+0.122
CAM-B3LYP/3-21G(*d*)	+1.656	−0.226	−0.723	+0.122
B3LYP/SDD	+1.628	−0.202	−0.739	+0.130
B3LYP/LANL2DZ	+0.355	+0.235	−0.540	+0.128

Carb – carboranyl $C_2B_{10}H_{10}$. >CMe_2 – bridge between ligands: Cp and $C_2B_{10}H_{10}$. In some cases, the total charge of the molecule differs from zero, which is due to rounding of Mulliken charges on the corresponding molecular fragments.