POPULATION ANALYSIS OF TITANOCENE DICARBORANYL BY THE MULLIKEN AND NBO METHODS: A COMPARATIVE STUDY

G. V. Loukova*[a] and A. A. Milov[b]

[a] Federal Research Center of Problems of Chemical Physics and Medicinal Chemistry, Russian Academy of Sciences, ul. Akademika Semenova 1, Chernogolovka, Moscow Region, 142432 Russia
[b] Southern Scientific Center, Russian Academy of Sciences, ul. Chekhova 41, Rostov-on-Don, 344006 Russia

Abstract

A broad systematic analysis of the orbital populations of a structurally complex d^0 titanocene, having rare ligand-to-metal charge transfer excited states, was done in the Mulliken and NBO approximations using methods traditionally applied to simulate excited states and coordinative interactions. The Mulliken population analysis was shown to be highly sensitive to the basis set and failed to provide reliable characterization of the charge distribution in the target compound. The natural population analysis, an alternative to the Mulliken analysis, much better described atomic charges in target polar organometallics.

Key words: atomic charge, Mulliken population analysis, natural bond analysis, titanocene dicarboranyl, ligand-to-metal charge transfer.
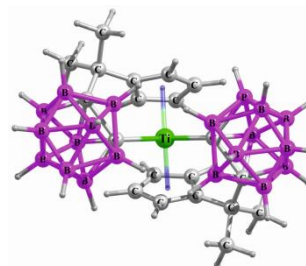
Introduction

Group IV metallocenes are promising precursors for organic synthesis catalysts, phosphorescent materials, and so on. These complexes possess the rarest and least studied ligand-to-metal charge transfer (LMCT) excited states, including unique phosphorescent ones [1–8]. Recently, we have systematically analyzed broad computing (Hartree-Fock (HF) and density functional theory (DFT)) data derived for titanocene dicarboranyl $Ti(\eta^5:\eta^1\text{-CpCMe}_2CB_{10}H_{10}C)_2$ (Fig. 1), possessing rare room-temperature emissive LMCT states, as an instructive example and revealed good agreement between most of the simulated structural and crystallographic data [9, 10].
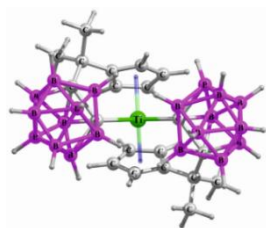

Figure 1. Optimized structure of titanocene dicarboranyl.

Evaluation of orbital populations and charge characteristics of metal ion(s) and ligands in complexes is a key problem in coordination chemistry and, in particular, photonics of charge-transfer states that cannot be solved experimentally. Charges can be used to predict dipole moment, molecular polarization, and many quantum properties of molecular systems. The distribution of charge over atoms determines pairs of donors and acceptors, including charge transfer in a molecule. In this communication, we systematically compared two popular approaches and various (HF and DFT) methods (with the use of GAUSSIAN program [11]) aimed at the broadest possible description of charge distribution in instructive $Ti(\eta^5:\eta^1\text{-CpCMe}_2CB_{10}H_{10}C)_2$ and evaluated the sensitivity of the computed charges to changes in (*i*) selection of the analysis method (the Mulliken approach [12] being historically most important), (*ii*) basis type, (*iii*) choice of the Hamiltonian, and (*iv*) molecular structure (for other compounds, different theoretical methods can be operative).

Results and discussion

According to our estimation, $Ti(\eta^5:\eta^1\text{-CpCMe}_2CB_{10}H_{10}C)_2$ has a large electric dipole moment (10–11 Debye, Table S1 in the Electronic supplementary information (ESI)) that is an extremely rare case for organometallic compounds.

The Mulliken population analysis gives very contradictory results (Table S1 in the ESI): a large variation in the values of charges on Ti and the ligands both in positive and negative ranges with a change in the basis set (mainly) and the Hamiltonian. In a series of more than 200 popular methods, computing using high basis set QZVP and the Pople basis sets: 6-311G and 3-21G provided acceptable charges (charge on Ti: +1.1... +2.2 and negative charges on ligands > −1) (for instances, see: Tables 1 and S1 in the ESI).

The shortcomings of the Mulliken analysis became apparent, for example, when applying popular basis sets with added diffuse wave functions. About 100 popular methods based on correlation-consistent (aug-cc-pVTZ, cc-pVDZ and cc-pVTZ), pseudopotential basis sets (CEP-121G, SDD and LANL2DZ), TZVP and DGDZVP basis sets suggested unreliable data. Overall, within frameworks of the Mulliken approach, *ca.* 85%

Table 1. Mulliken charge characteristics of titanocene dicarboranyl (selected methods)

Method	q(Ti)	q(Cp)	q(Carb)	q(>CMe$_2$)
HF/QZVP	+1.43	–0.40	–0.19	–0.13
B3LYP/QZVP	+1.92	–0.74	–0.02	–0.20
PBE0/QZVP	+1.41	–0.40	–0.09	–0.22
HF/6-311G	+1.77	–0.17	–0.73	+0.02
B3LYP/6-311G	+1.42	–0.10	–0.65	+0.05
CAM-B3LYP/6-311G	+1.41	–0.10	–0.69	+0.08
M06/6-311G	+1.39	–0.07	–0.70	+0.08
HF/6-31G	+1.19	–0.09	–0.68	+0.18
B3LYP/6-31+G	+1.70	–0.31	–0.78	+0.23
CAM-B3LYP/6-31+G	+1.54	–0.18	–0.76	+0.17
TPSSh/6-31+G	+1.37	–0.10	–0.88	+0.30
PBE0/6-31+G	+1.46	–0.27	–0.83	+0.37
HF/3-21G	+2.07	–0.35	–0.75	+0.06
B3LYP/3-21G	+1.72	–0.26	–0.62	+0.01

q(Ti) stands for the charge on Ti; q(Cp) is the charge on each Cp-ligand; q(Carb) is the charge on each carboranyl ligand; q(>CMe$_2$) is the charge on each >CMe$_2$ bridge; in a number of cases, the total charge of the complex differs from zero that is due to rounding of charges on the corresponding molecular fragments.

Table 2. NBO charge characteristics of titanocene dicarboranyl (selected methods)

Method	q(Ti)	q(Cp)	q(Carb)	q(>CMe$_2$)
HF/QZVP	+1.49	−0.12	−0.71	+0.10
B3LYP/QZVP	+1.13	−0.03	−0.61	+0.07
HF/6-311G	+1.88	−0.26	−0.80	+0.12
HF/6-311+G(*3df,3pd*)	+1.51	−0.11	−0.74	+0.10
B3LYP/6-311G	+1.52	−0.16	−0.70	+0.10
CAM-B3LYP/6-311G	+1.51	−0.15	−0.71	+0.10
HF/6-31G	+1.73	−0.23	−0.76	+0.13
B3LYP/6-31G	+1.42	−0.15	−0.68	+0.12
HF/cc-pVTZ	+1.86	−0.27	−0.77	+0.11
B3LYP/cc-pVTZ	+1.54	−0.18	−0.68	+0.10
HF/def2TZVP	+1.62	−0.18	−0.73	+0.10
HF/3-21G(*d*)	+1.93	−0.31	−0.79	+0.14
B3LYP/3-21G	+1.66	−0.23	−0.72	+0.12

of more than 200 popular methods (HF, DFT) failed to provide realistic values of charges on Ti and ligands in the complex.

The following tremendous objections to the Mulliken population analysis were revealed in our study:

(*i*) The Mulliken charge on the Ti(IV) cation has unphysical negative value in many cases, while those on the ligands have absurd positive values in a prevailing number of cases (for some instructive instances, see Table S1 in the ESI). The Mulliken population analysis provides unreal physical picture of the charge distribution in the target organometallic complex, probably, due to its significant ionic character.

(*ii*) the Mulliken charges are highly sensitive to the basis set that becomes evident when the basis set is systematically extended.

The natural population analysis (more generally: *NBO* [13]) *is an alternative to the Mulliken analysis*. In our study, NBO showed improved numerical stability and better described the electronic distribution in the compound of relatively high ionic character. Thus, in frames of the NBO approach, the overwhelming majority of *ca.* 100 methods (HF, DFT) suggested a physical picture of the charge distribution: charge on Ti +1.1...+1.8, charges on the ligands from –0.05 to –0.35 (Cp) and from –0.50 to –0.80 (carboranyls) (for instructive instances, see Table 2).

In contrast to the Mulliken approach, in which the values of the charges of the target organometallics change unpredictably up to unphysical ones, in the NBO case, when replacing the QZVP and 6-311G basis sets with 6-31G, cc-pVTZ, cc-pVDZ and SDD in different methods (HF, DFT), and also when adding diffuse and polarization wave functions to the 6-31G and 6-311G basis sets, numerical stability is preserved.

Conclusions

The Mulliken population analysis failed to provide reliable characterization of the charge distribution in the instructive case of a polar organometallic compound—titanocene dicarboranyl. Based on the results of on-going systematic study, we suggest that NBO is a more advanced approach that solves most of the problems of the traditional Mulliken analysis, in particular, it demonstrates appropriate numerical stability with respect to changes in the basis set. Until now, the analysis of the Mulliken approach has been carried out only for fairly simple systems that do not contain organometallic fragments with significant charge transfer, and has covered a fairly limited number of methods [14]. To the best of our knowledge, such a systematic benchmark study of charges in organometallic compounds by means of various popular *ab initio* HF and DFT methods at different levels of theory, also applying different important approaches, is conducted for the first time.

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Corresponding author

*   E-mail: gloukova@mail.ru. Tel: +7(496)522-7244 (G. V. Loukova).

Electronic supplementary information

Electronic supplementary information (ESI) available online: the dipole moment and Mulliken charges data. For ESI, see DOI: 10.32931/io2532a.

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