**Can Anti-Aufbau DFT Calculations Estimate Singlet Excited State Aromaticity?**

Correspondence on “Dibenzoarsepins: Planarization of 8π-Electron System in the Lowest Singlet Excited State”

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***Abstract:*** The simple anti-aufbau DFT approach for estimating singlet excited state aromaticity suggested in a recent Communication of Kawashima, Imoto, Ishida, Furuta, Yamamoto, Mitsuishi, Tanaka, Fujii, and Naka published in this journal is shown to produce incorrect results because it targets a linear combination of the singlet and triplet configurations involving the HOMO and LUMO rather than the first singlet excited state. If the S1 state of a molecule is dominated by the HOMO → LUMO excitation, a comparably simple but theoretically consistent and qualitatively correct approximation to the S1 wavefunction can be achieved by performing a small “two electrons in two orbitals” CASSCF(2,2) calculation which can be followed by the evaluation of magnetic aromaticity criteria such as NICS.

***Keywords:*** excited state aromaticity; Baird’s rule; NICS; anti-aufbau DFT; arsepines

Excited state aromaticity is often associated with Baird’s rule,[1] according to which the familiar Hückel’s 4*n*+ 2 and 4*n* rules for electronic ground state aromaticity in cyclic conjugated hydrocarbons are reversed in the lowest triplet state: Rings with 4*n* π electrons switch from antiaromatic to aromatic, while those with 4*n*+ 2 π electrons switch from aromatic to antiaromatic. Subsequent research has demonstrated that similar aromaticity reversals can take place in the lowest singlet excited state.[2–5]

The lowest triplet state (T1), addressed in Baird’s rule, is much easier to access computationally than the first singlet excited state (S1). A straightforward single-determinant spin-unrestricted Hartree-Fock (UHF) or density functional theory (UDFT) calculation can provide a reasonable approximation to T1, whereas the description of S1 requires a multideterminant wavefunction. However, from an experimental viewpoint, S1 aromaticity reversals are more interesting than those in T1 as such reversals can be utilized to design molecules with phototuneable behaviour.

The authors of a recent paper on S1 aromaticity in dibenzoarsepines[6] suggest that if the S1 state is dominated by the HOMO → LUMO excitation, it should be possible to estimate its aromaticity through a simple UDFT computational procedure utilizing an anti-aufbau unrestricted Slater determinant. Their procedure can be described as follows: Subsequent to a standard spin-restricted DFT (RDFT) calculation on the ground state (S0), the *β*-spin HOMO is replaced by the *β*-spin LUMO and the resulting set of orbitals is then used as a starting guess in a UDFT calculation which is carried out so as to preserve the anti-aufbau orbital ordering. The anti-aufbau DFT calculation can be combined with evaluation of magnetic properties such as nucleus-independent chemical shifts (NICS). While this procedure is simpler and more computationally efficient than a full π-space complete-active-space self-consistent field (CASSCF) calculation which is the standard approach for studying the magnetic properties of S1,[3–5] it does not produce correct results because, as it is shown below, the anti-aufbau unrestricted Slater determinant is not an approximation to the S1 wavefunction, but very much a linear combination of the singlet and triplet configurations involving the HOMO and LUMO. If the S1 state of a molecule is dominated by the HOMO → LUMO excitation, a relatively simple but theoretically consistent and qualitatively correct approximation to the S1 wavefunction can be achieved by performing a small “two electrons in two orbitals” CASSCF(2,2) calculation which can be followed by the evaluation of aromaticity criteria such as NICS.

Let us start by examining the case of two electrons in two orbitals, *ϕ*1 and *ϕ*2; the lower-energy orbital *ϕ*1 is doubly-occupied in the electronic ground state. The corresponding S1 and T1 wavefunctions can be written down in terms of two two-electron Slater determinants (in unnormalized form, for *z*-projection of the total spin *M* = 0):

The anti-aufbau procedure suggested in reference [6] would employ a single two-electron Slater determinant, , to describe S1. This determinant corresponds to a linear combination of and with equal weights, (in unnormalized form). The expectation value of the square of the total spin operator, , over can be shown to be equal to 1, which corresponds to total spin *S* = 0.618, a value intermediate between those for a singlet, *S* = 0, and a triplet, *S* = 1, but closer to that for a triplet.

The two arsepines studied in reference [6], 5-methyl-dibenzo[*b,f*]arsepine and 5-phenyl-dibenzo[*b,f*]arsepine (referred to as **3-Me** and **3-Ph**), are molecules containing 136 and 168 electrons, respectively. In anti-aufbau UDFT calculations, all 136 (**3-Me**) and 168 (**3-Ph**) occupied orbitals for electrons with different spins are different; this can be expected to introduce additional triplet spin character and shift the respective total spin values even further towards the triplet *S* = 1. Several calculations were carried out to analyse the performance of the anti-aufbau UDFT procedure for **3-Me** and **3-Ph** and compare it to that of a S1 CASSCF(2,2) wavefunction using the RHF HOMO and LUMO as a starting guess for the active space. The initial intention was to carry out these calculations using the S1 optimized geometries of **3-Me** and **3-Ph** provided in the SI of reference [6], but an examination of the S0 and S1 optimized geometries of **3-Me** showed these to be identical which is unlikely to be correct. Therefore, it was decided to perform independent gas-phase TDB3LYP-D3(BJ)/def2TZVP (time-dependent B3LYP in the def2TZVP basis with D3 dispersion corrections and Becke-Johnson damping) S1 geometry optimizations and harmonic frequency calculations for both molecules, using GAUSSIAN.[7] These calculations produced one *Cs* symmetry S1 geometry for **3-Me**, corresponding to a local minimum, and two *Cs* symmetry S1 geometries for **3-Ph**, corresponding to different local minima, one with the phenyl group in the symmetry plane and another one (higher in energy) with the phenyl group perpendicular to the symmetry plane (see the SI). The first two of these geometries, which are reasonably similar to those shown in Figures S20 and S21 in reference [6], but slightly “flatter”, are used in all calculations reported in this letter. The two different local minima located on the **3-Ph** S1 potential energy surface could provide an explanation for the two bands observed in the PL spectrum of **3-Ph**, see Figure 3 in reference [6], but this would require additional S1 geometry optimizations accounting for the solvents used in the experimental measurements.

Table 1 shows the results of ground-state RB3LYP, anti-aufbau UB3LYP, UB3LYP (with *M*= 1, as an approximation to T1), and CASSCF(2,2) S0, S1 and T1 calculations of NICS(0) and NICS(1) in **3-Me** and **3-Ph**, performed with gauge-including atomic orbitals (GIAOs) in the 6-311G(d) basis. All DFT calculations were carried out with GAUSSIAN;[7] for the CASSCF calculations use was made of Dalton.[8] Since the arsepine rings in the S1 states of **3-Me** and **3-Ph** are both non-planar, NICS(0) were calculated at the geometric centres of the arsepine rings, and NICS(1)—at 1 Å above and below NICS(0), along the *x*-axis (see the SI). The presence of substituents in **3-Me** and **3-Ph** makes the two NICS(1) positions inequivalent, hence the pairs of NICS(1) values in Table 1.

The anti-aufbau UB3LYP and *S* values for **3-Me** and **3-Ph** confirm the predicted increases of triplet spin character in comparison to the two-electron example discussed above; in contrast, the corresponding values from the UB3LYP (*M*= 1) calculations indicate almost pure triplet spin states. One of the two anti-aufbau UB3LYP NICS(1) values for **3-Ph**, −9.30 ppm, is identical to the single “S1” NICS(1) value for this molecule reported in reference [6]. However, the single “S1” NICS(1) value for **3-Me** reported in reference [6], −6.7 ppm, is smaller in magnitude than either of the corresponding NICS(1) values in Table 1. This is most likely due to the use of a S0 rather than S1 **3-Me** optimized geometry in reference [6]. The data in Table 1 show that the levels of aromaticity of the S1 states of **3-Me** and **3-Ph** are very similar, and so are the levels of aromaticity of the respective T1 states, with **3-Me** being the slightly more aromatic compound in both of S1 and T1.

The S0 and T1 RB3LYP/UB3LYP and CASSCF(2,2) NICS(0) and NICS(1) values are in good qualitative agreement. RB3LYP/UB3LYP include more correlation effects than the modest “two electrons in two orbitals” active space in CASSCF(2,2) and, therefore, place some additional emphasis on both the antiaromaticity of the S0 states of **3-Me** and **3-Ph**, and the aromaticity of the T1 states of these molecules.

Clearly, the anti-aufbau UB3LYP NICS(0) and NICS(1) values are not far from the midpoints between the corresponding CASSCF(2,2) S1 and T1 NICS(0) and NICS(1) values, and closer to the CASSCF(2,2) T1 NICS(0) and NICS(1) values, as expected from the fact that the anti-aufbau UB3LYP procedure produces a mixture of singlet and triplet states (*vide supra*). These results show that the anti-aufbau UB3LYP procedure is not capable of producing reliable results for the magnetic properties of the first singlet excited state. A more consistent option is to use CASSCF(2,2) which is more computationally demanding than anti-aufbau UB3LYP but considerably less so than full π-space CASSCF and can be applied to reasonably large conjugated molecules. Of course, full π-space CASSCF would provide more accurate results as CASSCF(2,2) incorporates nondynamic correlation effects for a single electron pair only; the wavefunction could be improved further by including dynamic correlation effects through perturbation theory based on a CASSCF reference, for example, CASPT2. However, current CASSCF codes will struggle with larger active spaces in molecules such as **3-Me** and **3-Ph** and, to date, there are no codes capable of calculating NMR shielding tensors and NICS at the CASPT2-GIAO level.

A detail worth noting is that the S1 states of **3-Me** and **3-Ph** are expected to be much more aromatic than the corresponding T1 states, in contrast to simpler examples such as square cyclobutadiene and *D*8h cyclooctatetraene, for which the levels of S1 and T1 aromaticity are very similar.[3–5] This suggests that singlet and triplet excited state aromaticities are phenomena that could have much less in common than currently assumed.

***Conflict of interest***

The authors declare no conflict of interest.

***Table 1***: NICS(0) and NICS(1) values (in ppm) for the S0, S1 and T1 electronic states of **3-Me** and **3-Ph** calculated using different theoretical methods. UB3LYP results include the expectation value of the square of the total spin operator, , and the total spin *S*. For further details, see text.

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| --- | --- | --- | --- |
| Method | Property | **3-Me** | **3-Ph** |
| RB3LYP (S0) | NICS(0) | 10.20 | 10.14 |
|  | NICS(1) | 5.43, 7.79 | 5.99, 7.94 |
| anti-aufbau UB3LYP |  | 1.0144 | 1.0140 |
|  | *S* | 0.6245 | 0.6243 |
|  | NICS(0) | −8.92 | −8.50 |
|  | NICS(1) | −9.55, −9.38 | −9.22, −9.30 |
| UB3LYP (*M* = 1, ≈T1) |  | 2.0207 | 2.0223 |
|  | *S* | 1.0069 | 1.0074 |
|  | NICS(0) | −4.95 | −4.48 |
|  | NICS(1) | −6.24, −5.87 | −5.91, −5.70 |
| CASSCF(2,2) (S0) | NICS(0) | 6.28 | 6.69 |
|  | NICS(1) | 2.72, 4.27 | 3.43, 4.76 |
| CASSCF(2,2) (S1) | NICS(0) | −20.44 | −19.50 |
|  | NICS(1) | −18.25, −19.95 | −17.68, −19.26 |
| CASSCF(2,2) (T1) | NICS(0) | −2.35 | −1.82 |
|  | NICS(1) | −3.78, −3.48 | −3.71, −3.17 |

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