Tetra-*tert*-butyl-*s*-indacene is a Bond Localized C_{2h} Structure: Even More Bad News for B3LYP

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Abstract: Whether tetra-*tert*-butyl-*s*-indacene (T*t*B-*s*-indacene) is a symmetric D_{2h} structure or a bond alternating C_{2h} structure remains a standing puzzle. Agreement between ¹H NMR data and computed proton chemical shifts based on minima structures optimized at the M06-2X, ω B97X-D, and M11 levels confirm a bond localized C_{2h} symmetry—consistent with its antiaromaticity. X-ray structures and computed B3LYP geometries of D_{2h} T*t*B-*s*-indacene poorly reproduce experimental NMR data. The limitations and complications of using B3LYP geometries for interpreting the structures and paratropicities of π -expanded antiaromatic systems are discussed.

Tetra-*tert*-butyl-*s*-indacene (T*t*B-*s*-indacene) represents one of the first few critical examples of a kinetically trapped antiaromatic compound.^[1,2] It is expected to have a bond localized C_{2h} structure, resulting from antiaromaticity of the planar, cyclic, 12π -electron conjugated core, but a large number of experimental and theoretical works indicate a possible bond delocalized D_{2h} structure.^[3–9] Unsubstituted *s*-indacene, first prepared in 1963,^[10] decomposes readily and no structural data could be acquired. Hafner later prepared T*t*B-*s*-indacene in 1986 showing that while the compound still was sensitive to oxygen and traces of acid in solution, it could be obtained as red needles that were air stable in the solid state.^[1,2] ¹H NMR spectra of T*t*B-*s*indacene revealed upfield shifted ring protons compared to those of a non-aromatic methyl-dihydro derivative (Figure 1), consistent with its antiaromatic character.

The exact structure of T*t*B-*s*-indacene nonetheless was difficult to determine. The presence of four peaks in the ¹³C NMR spectrum at –130 °C for the twelve ring C atoms could point to either a completely delocalized 12 π -electron system or a low energy barrier between two valence isomers. Evidence from X-ray data, both at room temperature and at 100 K, indicated a symmetric D_{2h} structure,^[2,4] yet the possible roles of residual disorder could not be ruled out. It was suggested that the crystal structure of T*t*B-*s*-indacene might be a "frozen transition state structure" resulting from solid-state packing and thus did not necessarily reflect its symmetry as a free molecule. We now show that T*t*B-*s*-indacene indeed has a bond localized C_{2h} structure as expected by its antiaromaticity.

Although early Hückel molecular orbital theory and semiempirical calculations predicted a C_{2h} structure for unsubstituted *s*-indacene,^[5,11,12] Koch et al. concluded based on

ab initio and density functional theory (DFT) calculations that agreement between the computed D_{2h} structure of s-indacene and the X-ray structure of TtB-s-indacene must mean that TtB-sindacene is a "completely delocalized 12 π -electron system".^[6,7] MP2 calculations found the C_{2h} structure to be lower in energy than the D_{2h} structure by 0.7 kcal/mol, but single point calculations at the CASPT2 level indicated a lower energy D_{2h} structure by 3.1 kcal/mol.^[6] At the LDA and LDA+BP levels, only a D_{2h} minimum could be located.^[6] Subsequent studies performed for unsubstituted s-indacene based on various DFT computations were indecisive. B3LYP/6-31G(d) calculations predicted a "quasidelocalized" structure.^[8] The C_{2h} structure is a minimum and is 0.1 kcal/mol lower in energy than the D_{2h} form, which is a transition state structure; however, zero-point energy correction reverses the relative energy, and the D_{2h} form becomes 0.6 kcal/mol lower. BLYP predicted a bond localized C_{2h} structure.^[7] Heilbronner and Yang,^[3] and later Salvi et al.,^[5] recognized that TtB-s-indacene exhibits a stronger tendency towards bond delocalization than the parent s-indacene, but neither provided conclusive evidence for a D_{2h} geometry. Since X-ray structures can be influenced by crystal packing as well as static and dynamic disorders even at low temperatures, agreement with X-ray data does not provide decisive evidence for the structure of TtB-s-indacene. Proton chemical shifts, however, can show large responses even to subtle geometric variations.

Excellent agreement between computed and experimental proton chemical shifts can be found only when the expected geometries are correct. Bühl and Schleyer examined the reported chemical shifts for many boranes, carboranes, and nonclassical carbocations, revealing numerous structural misassignments and finding that computed and experimental proton chemical shifts match only when the assigned geometries were correct.^[13] For example, [18]annulene was expected to have a symmetric D_{6h} structure for over four decades; however, experimental match to ab initio-NMR data identified the correct C2 symmetry.^[14] Whereas the computed proton chemical shifts of D_{6h} [18]annulene structures at various DFT levels were in gross disagreement with experiment,^[15,16] the computed averaged proton chemical shifts of C₂ minima geometries of [18]annulene at the KMLYP (outer: 8.9 ppm, inner: -2.5 ppm) and BHLYP (outer: 9.2 ppm, inner: -2.8 ppm) levels matched closely with experiment (outer: 9.3 ppm, inner: -3.0 ppm). Using the same approach, computed proton

chemical shifts for a partially optimized X-ray geometry of T*t*B-*s*indacene (H8: 6.61 ppm, H2: 4.70 ppm, black dashed line, see also Table 1, footnote [e]) shows signals far upfield from the reported experimental ¹H NMR shifts (H8: 6.90 ppm, H2: 5.29 ppm, black solid line, Figure 1A).^[1,2] T*t*B-*s*-indacene cannot have a symmetric D_{2h} structure!

Proton chemical shifts computed at B97-2/6-311+G(d,p) for minima geometries obtained at the B3LYP (H8: 6.20 ppm, H2: 4.60 ppm, D_{2h}), M06-2X (H8: 6.62 ppm, H2: 4.97 ppm, C_{2h}), ωB97X-D (H8: 6.59 ppm, H2: 4.93 ppm, C_{2h}), and M11 (H8: 6.81 ppm, H2: 5.20 ppm, C_{2h}) levels spread over a range of 0.61 ppm for H8 and 0.60 ppm for H2 (cf. H8: 6.90 ppm, H2: 5.29 ppm, expt., see Figure 1A). The M11 structure displays the most bond length alternation (Ar = 0.086 Å, see footnote [c] in Table 1, cf. values for other functionals) and the computed proton chemical shifts match best with experiment. The D_{2h} minimum geometry of B3LYP (Δr = 0) most closely resembles the X-ray structure of TtB-s-indacene (Δr = 0.001 Å), but the computed proton chemical shifts are significantly upfield shifted and far off from the experimental ¹H NMR data. Accordingly, NICS-XY-scans^[17] computed for the D_{2h} B3LYP geometry of TtB-s-indacene show a higher paratropicity (more positive NICS values) compared to results obtained with the C_{2h} minimum geometries of M06-2X, wB97X-D, and M11 (Figure 1C). Notably, the delocalization errors of B3LYP are less severe for a non-aromatic analogue of TtB-s-indacene. Computed proton chemical shifts for methyl-dihydro-TtB-s-indacene (Figure 1B) show a narrow spread (0.17 ppm for H8 and 0.11 ppm for H2) and the computed proton chemical shifts match better with ¹H NMR data for all functionals: B3LYP (H8: 7.41, H2: 6.40 ppm), M06-2X (H8: 7.49 ppm, H2: 6.34 ppm), ωB97X-D (H8: 7.47 ppm, H2: 6.30 ppm), and M11 (H8: 7.58 ppm, H2: 6.41 ppm) (cf. H8: 7.56 ppm, H2: 6.36 ppm, expt.).

Errors in predicting ¹H NMR shifts based on B3LYP geometries have been reported previously.[14,18-23] Choi and Kertz noted that the proton chemical shifts of many higher annulenes, computed using geometries optimized at the B3LYP/6-31G(d) level, disagree with experiment.^[15] Proton chemical shifts computed using B3LYP geometries for a porphyrin nanobelt structure reported by Anderson and Peeks in 2017 matched poorly with experimental ¹H NMR data.^[21-24] The cause of this discrepancy is the large delocalization error of B3LYP.[25] Functionals like B3LYP have a low percentage of HF exchange at long interelectronic ranges and are prone to overestimating electron delocalization.^[25] Such errors compromise theoretical interpretations of the structures of large annulenes and extended π -conjugated macrocycles. We show here that the delocalization errors of B3LYP apply also to π -expanded antiaromatic systems and worsen for strongly antiaromatic species.

Besides *ab-initio* NMR evidence, M06-2X, ω B97X-D, and M11 all predict a *C*_{2h} minimum structure for *TtB-s*-indacene that is, respectively, 0.97, 1.10, and 2.65 kcal/mol lower in energy than the *D*_{2h} transition state structure (Table 1). No *C*_{2h} minimum structure was found at the B3LYP/6-311+G(d,p) level. Since the barrier to interconverting the two equivalent *C*_{2h} structures of *TtB-s*-indacene is small (less than 3 kcal/mol for all three functionals), dynamic disorder (even at 100 K) can give rise to a time-averaged *D*_{2h} structure, undermining interpretations of the X-ray data. Eigenvectors of the imaginary frequencies for the *D*_{2h} transition state structure at M06-2X (645*i* cm⁻¹), ω B97X-D (688*i* cm⁻¹), and M11 (1001*i* cm⁻¹) are all substantial and indicate a strong tendency towards ring bond length alternation.



Figure 1. Experimental ¹H NMR (data from reference [2]) and computed proton chemical shifts for H8 and H2 in A) TtB-s-indacene (H8: 6.90 ppm, H2: 5.29 ppm, expt.) and B) methyl-dihydro-TtB-s-indacene (H8: 7.56 ppm, H2: 6.36 ppm, expt.). Proton chemical shifts were computed at B97-2/6-311+G(d,p) for minima geometries optimized at the B3LYP, M06-2X, ω B97X-D and M11/6-311+G(d,p) levels and for a partially optimized X-ray structure (see footnote [e], Table 1). C) NICS-XY-scans for TtB-s-indacene at B97-2/6-311+G(d,p), based B3LYP, M06-2X, ω B97X-D, and M11/6-311+G(d,p) geometries. Note overlapping M06-2X and ω B97X-D scans.

Table 1. Computed C–C bond length difference (Δr), and relative energies (ΔE_{rei}) between the C_{2h} and D_{2h} structures of T*t*B-s-indacene at the B3LYP, M06-2X, ω B97X-D, and M11/6-311+G(d,p) levels.

Level	HF ^[a] (%)	PG ^[b]	∆r ^[c] (Å)	∆ <i>E</i> _{rel} (kcal/mol)	δ H8 ^[d] (ppm)	δ H2 ^[d] (ppm)
B3LYP	20	$C_{2h} D_{2h}$	_ 0	_ 0.00	_ 6.20	_ 4.60
M06-2X	54	$C_{2h} D_{2h}$	0.066 0	0.00 0.97	6.62 6.32	4.97 4.60
ωB97X-D	SR:22 LR:100 ω:0.20	C_{2h} D_{2h}	0.069 0	0.00 1.10	6.59 6.26	4.92 4.53
M11	SR:42.8 LR:100 ω:0.25	$C_{2h} D_{2h}$	0.086 0	0.00 2.65	6.81 6.40	5.20 4.67
X-ray ^[e]	-	D_{2h}	0.001	-	6.61	4.70

[a] Short range (SR) and long range (LR) percentages of HF exchange. [b] Point Group. [c] Δr is the difference between the two C–C bond lengths of the central sixmembered ring connected to C4/C8. [d] Proton chemical shifts were computed at B97-2/6-311+G(d,p) using the computed chemical shielding for hydrogen in benzene as a reference. [e] Based on X-ray crystal structure at 100 K (reference [4]). All ring C–C bonds and the four C–C_{tbutyt} bonds were fixed to reported X-ray data, all other parameters were optimized at M11/6-311+G(d,p).



Figure 2. Experimental ¹H NMR (data from reference [26]) and computed proton chemical shifts for the central hydrogens in A) *syn*-IDBF (H_{syn} : 5.60 ppm, expt.) and B) *anti*-IDBF (H_{anti} : 6.15 ppm, expt.). Computed NICS-XY-scans based on geometries optimized at the C) B3LYP and D) M11 levels. NICS-XY-scans for *s*-indacene using geometries optimized at the respective levels are included for comparison. Δr values indicate the difference between the two C–C bond lengths connected to C4/C8.

Some of us recently published a joint experimental and theoretical study of indacenodibenzofurans (IDBFs).[26] We found that syn-IDBF shows a high degree of paratropicity exceeding that of the parent s-indacene, while anti-IDBF exhibits weaker paratropicity. Indeed, experimental ¹H NMR signals for the hydrogens on the central six-membered ring of syn-IDBF are shifted upfield (H_{syn}: 5.60 ppm, Figure 2A) compared to those of anti-IDBF (Hanti: 6.15 ppm, Figure 2B). Computed proton chemical shifts reproduce these trends, indicating a more antiaromatic synisomer. However, proton chemical shifts based on M11 geometries (H_{syn}: 5.51 ppm, H_{anti}: 6.04 ppm) are in much better agreement with experiment than those based on B3LYP geometries (H_{syn}: 4.74 ppm, H_{anti}: 5.74 ppm, note greater mismatch for the more antiaromatic syn-isomer) (see Figures 2A-2B and results for M06-2X and ω B97X-D in the Supporting Information, SI). These results suggest that M11 geometries most properly capture the degree of bond localization in syn- and antiIDBF. Note the more bond alternated structures predicted by M11 ($\Delta r_{syn} = 0.100 \text{ Å}$, $r_{anti} = 0.081 \text{ Å}$) compared to B3LYP geometries ($\Delta r_{syn} = 0.047 \text{ Å}$, $\Delta r_{anti} = 0.004 \text{ Å}$).

In our previous study, NICS-XY-scans were computed using optimized B3LYP geometries of *syn-* and *anti-* IDBF. We now contrast these results to NICS-XY-scans obtained using M11 geometries. Figure 2C reproduces the published results^[26] showing a higher paratropicity for *syn-*IDBF and a lower paratropicity for *anti-*IDBF, compared to the parent *s-*indacene. NICS XY-scans based on M11 geometries (Figure 2D) confirm that *syn-*IDBF is more antiaromatic than *anti-*IDBF, but show in contrast to B3LYP results, that *anti-*IDBF is as antiaromatic as *s-*indacene based on comparisons of the NICS values at the five membered rings. Computations for indacenodibenzothiophenes (IDBT) and their sulfone analogs (IDBT-sulfone) are included in the SI, and further illustrate the limitations of predicting the ¹H NMR shifts and paratropicities of antiaromatic compounds based alone on B3LYP geometries.

M11 stands out as an especially suitable functional for the study of expanded π -conjugated [4n] antiaromatic systems. Comparisons of experimental ¹H NMR measurements to ab initio NMR calculations for expanded pentalene cores also show that M11 geometries performs the best for describing the degree of bond localization in antiaromatic systems and therefore gives the closest match for proton chemical shifts. Tri-t-butyl-pentalene^[27] shows a clear tendency for bond length alternation and experimental ¹H NMR measurements show highly shielded signals for the equivalent H1 and H3 protons and for H5 (H1/H3_{avg}: 5.07 ppm, H5: 4.72 ppm, expt., Figure 3A). Computed proton chemical shifts based on the M11 geometry (H1/H3ava: 5.15 ppm, H5: 4.67 ppm) give a closer match with experiment compared to results based on the B3LYP geometry (H1/H3avg: 4.93 ppm, H5: 4.39 ppm). π-Expanded pentalene cores can result in "fulvene-like exopentalene structures" with reduced antiaromaticity.^[28,29] London et al. recently reported a series of substituted benzopentalenes (BP)[29] that can have two unique olefinic protons on the pentalene core. Computed proton chemical shifts for a selected BP structure is shown in Figure 3B. Again, results based on the M11 geometry (H1: 5.89 ppm, H5: 6.12 ppm) agree best with experimental ¹H NMR data (H1: 6.12 ppm, H5: 6.36 ppm), while computations based on the B3LYP geometry give a poor match (H1: 5.68 ppm, H5: 5.94 ppm). Results for M06-2X and wB97X-D are included in the SI.

A caveat is treatment for expanded [4n] π -systems with diradical character. Multireference systems, such as diradicals, cannot be properly described by the HF approximation, and thus the errors arising from static correlation increase for functionals with a higher percentage of HF exchange.^[30] These are cases where B3LYP can give the right answer for the wrong reason. Here, we consider an example of dicyclopenta[b,g]naphthalene (DCN) recently reported by Chi et al.[31] DCN is a core expanded s-indacene isomer with an open-shell singlet ground state (y₀ = 30%).[31] Structures of DCN were optimized with unrestricted (U)-DFT with a broken-symmetry approach. Notably, computed proton chemical shifts based on the B3LYP geometry (H9: 7.26 ppm, H10: 6.64 ppm) agree exceedingly well with experimental ¹H NMR data (H9: 7.25 ppm, H10: 6.72 ppm, expt., Figure 3C). and the errors increase progressively for ω B97X-D (H9: 7.38 ppm, H10: 6.79 ppm), M06-2X (H9: 7.39 ppm, H10: 6.81 ppm), and M11 (H9: 7.48 ppm, H10: 6.92 ppm). Use of a local functional, for example, M11-L (H9: 7.20 ppm, H10: 6.64 ppm, Figure 3C)-a



meta-NGA functional with zero percent HF exchange^[32]—reduces the errors arising from static correlation and is recommended for diradical systems.

Figure 3. Experimental ¹H NMR and computed proton chemical shifts for: A) H1/H3_{avg} and H5 in tri-*t*-butyl-pentalene (H1/H3_{avg}: 5.07 ppm, H5: 4.72 ppm, expt., reference [27]), B) H1 and H5 in benzopentalene (H1: 6.12 ppm, H5: 6.36 ppm, expt., reference [29]), C) H9 and H10 in DCM (H9: 7.25 ppm, H10: 6.72 ppm, expt., reference [31]), and D) H1, H2, and H10 in anthracene (H1: 7.98 ppm, H2: 7.44 ppm, H10: 8.39 ppm, expt., reference [32]). Proton chemical shifts were computed at B97-2/6-311+G(d,p) for minima geometries optimized at B3LYP, M06-2X, ω B97X-D and M11/6-311+G(d,p), and additionally for DCN, at M11-L/6-311+G(d,p). Geometries and proton chemical shifts for DCN were computed with U-DFT with broken symmetry.

In contrast to their antiaromatic congeners, polycyclic aromatic hydrocarbons have inherently delocalized π -systems and thus are *not* subject to the same problems inflicted by use of B3LYP geometries for studying magnetic properties. Computed proton chemical shifts for anthracene, based on geometries optimized at the B3LYP (H1: 8.06 ppm, H2: 7.47 ppm, H10: 8.51 ppm) and M11 (H1: 7.95 ppm, H2: 7.40 ppm, H10: 8.37 ppm) levels both show perfect agreement with experimental data (H1: 7.98 ppm, H2: 7.44 ppm, H10: 8.39 ppm) (Figure 3D).^[33] Results for M06-2X and ω B97X-D are included in the SI.

In the last decade, there has been a surge of interest in the synthesis and characterization of polycyclic antiaromatic hydrocarbons containing [4n] cores, such as π -expanded indacenes, indenofluorenes, pentalenes, cyclooctatetraenes, and cyclobutadienes.^[29,31,34-42] Polycyclic antiaromatic hydrocarbons can show strong bond length alternation, paratropicity, possible diradical character, and small HOMO-LUMO energy gaps, making them interesting candidates for organic electronics applications.^[36,43-47] In all of these endeavours, B3LYP continues to be the choice method for many synergistic experimental and computational studies. We emphasize that even though time dependent (TD)-DFT calculations with B3LYP can provide satisfactorily estimates for HOMO-LUMO energy gaps,^[48] B3LYP geometries poorly describe bond delocalization in polycyclic antiaromatic systems, and the errors become more severe for highly antiaromatic systems. Fruitful explorations into the vast chemical space of functional antiaromatic compounds rely on careful computational guidance, and use of B3LYP geometries for such studies should be abandoned in favor of functionals like M11.

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Entry for the Table of Contents



Even more bad news for B3LYP! Despite known pitfalls and limitations, B3LYP continues to be a workhorse in leading joint experimental and computational investigations of functional carbon-rich and expanded π -conjugated systems. The popular DFT functional is subject to large delocalization errors, and we show now that the consequence is worse for antiaromatic systems.

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