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Density-Functional and Coupled-Cluster Singles-and-Doubles Calculations of the Nuclear Shielding and Indirect Nuclear Spin–Spin Coupling Constants of *o*-Benzyne

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Abstract: Density-functional theory (DFT) and coupled-cluster singles-and-doubles (CCSD) theory are applied to compute the nuclear magnetic resonance (NMR) shielding and indirect nuclear spin–spin coupling constants of *o*-benzyne, whose biradical nature makes it difficult to study both experimentally and theoretically. Because of near-equilibrium triplet instabilities that follow from its biradical character, the calculated DFT NMR properties of *o*-benzyne are unusually sensitive to details of the exchange-correlation functional. However, this sensitivity is greatly reduced if these properties are calculated at the equilibrium of the chosen functional. A strong correlation is demonstrated between the quality of the calculated indirect spin–spin coupling constants and the quality of the calculated lowest triplet excitation energy in *o*-benzyne. Orbital-unrelaxed coupled-cluster theory should be less affected by such instabilities, and the CCSD NMR properties were only calculated at the experimental equilibrium geometry. For the shielding constants, the results in best agreement with experimental results are obtained with CCSD theory and with the Keal–Tozer KT1 and KT2 functionals. For the triply bonded carbon atoms, these models yield an isotropic shielding of 1.3, –3.3, and –1.2 ppm, respectively, compared with the experimentally observed shielding of 3.7 ppm for incarcerated *o*-benzyne. For the indirect spin–spin coupling constants, the CCSD model and the Perdew–Burke–Ernzerhof functional both yield reliable results; for the most interesting spin–spin coupling constant, $^1J(\text{C}\equiv\text{C})$, we obtain 210 and 209 Hz with these two models, respectively, somewhat above the recently reported experimental value of 177.9 ± 0.7 Hz for *o*-benzyne inside a molecular container, suggesting large incarceration effects.

1. Introduction

The NMR shielding tensor of the triply bonded carbon atom of the 1,2- ^{13}C -substituted *o*-benzyne was first measured by

Orendt et al.¹ in 1996, who also presented quantum-chemical calculations using Hartree–Fock (HF) theory, second-order Møller–Plesset theory, and density-functional theory (DFT) with the Becke–Lee–Yang–Parr (BLYP) functional. These calculations indicated that there are large electron-correlation contributions to the shielding of the triply bonded carbon atom—in particular, for the individual tensor components. Moreover, only the DFT results were found to agree well

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with experimental results, and the existence of a large antisymmetric component of the shielding tensor for an atom in a distorted triple bond was confirmed. Subsequently, in 1997, the shielding and indirect nuclear spin–spin coupling constants of *o*-benzyne were studied experimentally by Warmuth² and theoretically by Jiao et al.³ In the experimental investigation of Warmuth, *o*-benzyne was trapped by guest incarceration inside a molecular container, allowing its nuclear magnetic resonance (NMR) spectrum to be recorded. In particular, the carbon–carbon triple-bond spin–spin coupling was measured at 177.9 ± 0.7 Hz—that is, within the expected range for such bonds. These findings were supported by DFT calculations,³ which gave a value of 192 Hz.

Because *o*-benzyne has a weak biradical character, with a low-lying excited triplet state, it presents a challenge for single-reference methods—in particular, for spin-restricted methods, as needed for the study of NMR parameters. Moreover, because of experimental problems related to its instability, no complete NMR spectrum has yet been recorded of the isolated *o*-benzyne molecule. Thus, the first analysis of the shielding tensor of the triply bonded carbon atom was performed in an argon matrix,¹ while the more recent experimental spectrum, providing the remaining shielding constants and a number of spin–spin coupling constants, was recorded for *o*-benzyne inside a molecular container.² Clearly, there may be significant differences between the measured NMR parameters and the corresponding values of an isolated molecule, as indicated by incarceration changes of the NMR parameters for other molecules. Therefore, the NMR parameters of the isolated *o*-benzyne molecule are not yet known precisely.

In view of the unusual character of *o*-benzyne and the difficulties it presents to both theory and experiments, we have here undertaken an independent theoretical study of this compound, with an aim to establish its NMR parameters reliably. At the same time, we analyze the performance of various popular DFT exchange–correlation functionals with respect to the calculation of NMR parameters of this difficult system.

2. Computational Details

The ACES II package was used in the coupled-cluster singles-and-doubles (CCSD) calculations;⁴ all the DFT results were obtained using Dalton.⁵ The NMR parameters and excitation energies were calculated using coupled-cluster and DFT linear response theory, using a closed-shell singlet reference wave function. The CCSD spin–spin calculations were carried out with all electrons correlated, without orbital relaxation. In the CCSD and DFT shielding calculations, London atomic orbitals were used to ensure gauge-origin invariant results.⁶

A. DFT Functionals. Concerning the choice of DFT functionals, it has over the past few years become apparent that it is preferable to use different functionals for the nuclear shielding constants and for the indirect nuclear spin–spin coupling constants. Thus, for shielding constants, recent investigations by Keal et al.⁷ have revealed that the Keal–Tozer KT1 and KT2 functionals⁸ perform very well, out-

performing the local-density approximation (LDA),⁹ the BLYP functional,^{10,11} and the Becke–3-parameter–Lee–Yang–Parr (B3LYP) hybrid functional.^{11,12} For the indirect spin–spin coupling constants, early experience indicated that performance improves in the sequence LDA, BLYP, and B3LYP;¹³ moreover, in a study of small rigid hydrocarbons,¹⁴ it was observed that B3LYP provides couplings that rival those of wave-function methods such as multiconfigurational self-consistent field theory, the second-order polarization propagator approximation, and CCSD theory. More recently, however, it has emerged that other functionals give better coupling constants than does B3LYP. Thus, from the work of Maximoff et al.¹⁵ and Keal et al.,¹⁶ it has been established that superior overall performance (at least for light atoms) is provided by the B97-2¹⁷ and B97-3¹⁸ semiempirical functionals, while hydrocarbons (especially CH couplings) are best served by the Perdew–Burke–Ernzerhof (PBE) functional.¹⁹

In view of these findings, we have, in our study of *o*-benzyne, carried out calculations using the following generalized gradient approximation (GGA) and hybrid functionals: the semiempirical BLYP GGA functional (fitted to noble-gas results) and B3LYP hybrid functional (fitted also to thermochemistry); the nonempirical Perdew–Wang 91 (PW91)²⁰ and PBE GGA functionals, both based on the properties of the slowly varying electron gas; the nonempirical KT1 and semiempirical KT2 GGA functionals; and the 10-parameter semiempirical B97-1 (fitted to thermochemistry) and B97-2 (fitted also to accurate exchange–correlation potentials) hybrid modifications of Becke’s 97 (B97) functional. We also examined the performance of the LDA, CAM-B3LYP,²¹ and B97-3 functionals but found these to be unsuitable, giving either erroneous geometries or instabilities in the calculation of the NMR parameters.

B. Basis Sets. At all levels of theory, the calculation of NMR shielding and spin–spin coupling constants is highly sensitive to the quality of the one-electron basis set. The reliable calculation of the usually dominant Fermi-contact (FC) contribution to spin–spin coupling constants, in particular, requires a flexible inner-core *s* basis, containing functions with large exponents—see, for instance, refs 22 and 23. In our calculations, we have therefore used the correlation-consistent core–valence *X*-tuple cc-pCVXZ basis sets, which combine such flexibility with the flexibility needed in coupled-cluster theory.

Unless otherwise stated, we have in the DFT calculations used the cc-pCVTZ triple- ζ basis,²⁴ consisting of a [12s7p3d1f/6s5p3d1f] carbon basis and a [5s2p1d/3s2p1d] hydrogen basis, with a total of 314 contracted Gaussians for *o*-benzyne. In the more expensive CCSD calculations, the cc-pCVTZ basis set was used for the shielding constants and for the dominant FC contribution to the indirect spin–spin coupling constants. To reduce cost, the remaining spin–spin contributions—that is, the spin–dipole (SD), the diamagnetic spin–orbit (DSO), and the paramagnetic spin–orbit (PSO) contributions—were calculated in cc-pCVDZ double- ζ basis. Finally, to examine basis-set convergence in the inner-core region, selected additional spin–spin coupling calculations

Table 1. Nuclear Shielding Constants in *o*-Benzyne (ppm)

	experimental geometry ^a									
	BLYP	PW91	PBE	KT1	KT2	B3LYP	B97-1	B97-2	HF	CCSD
C1	−34.1	−31.8	−30.6	−10.5	−12.2	−34.7	−30.4	−26.8	−42.1	1.3
C3	46.6	48.3	49.2	63.3	61.9	48.3	51.3	53.7	58.4	67.6
C4	35.3	38.1	39.2	55.5	53.9	38.1	42.2	44.9	55.4	59.0
H3	24.8	24.6	24.5	24.6	24.6	24.7	24.7	24.6	24.4	24.6
H4	24.0	23.8	23.7	23.9	23.9	24.0	24.0	24.0	24.6	24.2
	optimized geometry									
	BLYP	PW91	PBE	KT1	KT2	B3LYP	B97-1	B97-2	HF	
C1	−24.8	−21.3	−20.5	−3.3	−1.2	−20.2	−16.4	−12.0	−9.6	
C3	46.0	48.9	49.4	61.4	63.8	50.3	52.4	56.2	62.5	
C4	31.5	35.6	36.4	51.4	53.2	36.3	39.8	43.7	53.6	
H3	24.8	24.6	24.5	24.6	24.9	24.9	24.8	24.9	25.0	
H4	24.0	23.8	23.7	23.8	24.1	24.2	24.1	24.1	24.9	

^a From microwave measurements.³¹ ^b Recomputed from the experimental data of ref 2, using for the absolute shielding of C in TMS 186.37 ppm and for H in TMS 32.775 ppm.³⁷ ^c This constant is −6.6 ppm in ref 1, see text and Table 2. ^d Use of incarceration shifts of 1.23 and 3.48 ppm from Table 1 of ref 2 gives 26.6 and 25.0 ppm for H3 and H4, respectively.

Table 2. Shielding Tensor of the Triply Bonded Carbon Atom in *o*-Benzyne (ppm)

component ^a	CCSD ^b	HF ^b	KT1 ^b	exp. ^c
σ_n	−53.6	−58.3	−62.2	−53.6
σ_\perp	−84.7	−150.4	−63.9	−79.6
σ_\parallel	142.0	179.8	116.2	113.4
angle	12.9	18.4	14.1	±6.7
σ_{antisym}	−90.5	−143.6	−73.3	not available
σ_{aniso}	211.2	284.1	179.3	180.0
σ_{ave}	1.3	−9.6	−3.3	−6.6

^a σ_n is the out-of-plane tensor component; σ_\perp and σ_\parallel are the in-plane components, approximately (see the line “angle”) perpendicular and parallel to the triple bond. ^b CCSD results at the experimental geometry,³¹ HF and KT1 at the optimized geometries. ^c Recomputed from the experimental data of ref 1, using for the absolute carbon shielding in TMS 186.37 ppm.

were carried out in the larger cc-pCVQZ quadruple- ζ basis, in contracted and uncontracted forms.

For DFT calculations of indirect nuclear spin–spin coupling constants, the HIIIsu3 basis set¹³ has been shown to yield good results and has been extensively used for hydrocarbons²⁵ and, in particular, for the calculation of vibrational corrections to spin–spin coupling constants.²⁶ This basis consists of Huzinaga’s HIII basis set^{27,28} with the polarization functions and contractions of van Wüllen²⁹ and Kutzelnigg et al.³⁰ To ensure flexibility near the nuclei, the *s* functions have been decontracted and three steep *s* functions added in an even-tempered manner. We have used the HIIIsu3 basis to check the convergence of the cc-pCVTZ and cc-pCVQZ calculations and also for the calculation of vibrational corrections to the spin–spin coupling constants.

C. Geometries. The choice of molecular geometry is often a critical one in theoretical studies of molecular properties. A good approach is often to use consistently the experimental geometry. For *o*-benzyne, an experimental gas-phase geometry is available from recent microwave measurements.³¹ However, because of its biradical character, *o*-benzyne has a low-lying triplet excited state that is poorly described by single-reference spin-restricted methods. In particular, in the spin-restricted reference wave functions used here (the HF

reference wave function of CCSD and the Kohn–Sham noninteracting reference wave function of DFT), triplet instabilities are found near the minimum of the potential-energy surface. In such situations, the best description of triplet perturbations is obtained at the minimum of the chosen electronic-structure model—for example, the minimum of a specific DFT functional. Even small deviations from this geometry (when the experimental geometry or a geometry optimized with a different functional is used) may seriously affect the quality of calculated triplet properties such as the FC contributions to spin–spin coupling constants and triplet excitation energies. For this reason, we have in our *o*-benzyne study carefully considered the effect of calculating triplet properties at both the experimental geometry and the optimized geometry.

For DFT, two sets of calculations were therefore carried out for each functional—one at the experimental geometry, another one at the geometry obtained by energy minimization, using the same functional as in the subsequent NMR calculation. This minimization shortened the triple bond in all cases, by up to 2.4 pm from the experimental value of 126.4 pm, whereas the C–C≡C bond angle increased by up to 1.1° from the experimental value of 126.4°. In HF theory, the triple bond of 121.5 pm is much too short, while the C–C≡C bond angle is 127.6°. The all-electron CCSD/cc-pCVTZ geometry minimization was prohibitively expensive. For the CCSD model, therefore, we report here only NMR parameters calculated at the experimental geometry.

Although the geometry changes upon DFT energy minimization are relatively small, they significantly improve the calculated shielding and spin–spin coupling constants—in particular, for the atoms involved in the triple bond (see below). However, because we have not uncovered any general correlations (valid for all functionals) between the geometry changes and the changes in the NMR parameters upon energy minimization, we do not discuss the geometry changes further here, noting only that a good agreement with the experimental geometry does not necessarily translate into good NMR parameters.

In the following, the carbon atoms are numbered clock-

Table 3. Indirect Nuclear Spin–Spin Coupling Constants in *o*-Benzyne, Calculated in the cc-pCVTZ Basis at the Experimental Geometry^a (Hz)

	BLYP	PW91	PBE	KT1	KT2	B3LYP	B97-1	B97-2	CCSD
¹ <i>J</i> (C1≡C2)	236.4	664.9	225.9	213.0	434.1	577.3	448.5	566.4	210.2
¹ <i>J</i> (C2–C3)	75.4	121.9	69.4	69.8	96.7	108.9	109.3	110.1	83.4
¹ <i>J</i> (C3=C4)	59.7	68.8	54.1	55.8	63.9	68.8	74.3	69.4	63.3
¹ <i>J</i> (C4–C5)	77.9	90.0	71.8	73.8	83.9	90.1	93.2	89.2	77.2
² <i>J</i> (C1C3)	3.2	−45.3	1.5	1.9	−21.0	−24.4	−16.3	−24.9	2.0
² <i>J</i> (C1C5)	−15.4	−90.4	−16.4	−15.2	−53.1	−73.2	−52.0	−68.7	−13.8
² <i>J</i> (C3C5)	−0.8	−11.9	−1.4	−1.3	−7.4	−7.2	−6.4	−7.6	−3.3
³ <i>J</i> (C1C4)	14.2	83.7	14.4	13.6	48.2	69.3	49.7	66.2	13.5
³ <i>J</i> (C3C6)	2.1	9.8	2.2	1.8	5.8	6.6	6.4	7.4	4.8
¹ <i>J</i> (C3H3)	166.5	174.2	152.4	159.4	180.0	170.4	166.6	157.9	155.8
¹ <i>J</i> (C4H4)	147.5	146.3	134.6	141.0	155.4	144.6	143.9	134.7	137.4
² <i>J</i> (C2H3)	−6.3	−51.7	−7.3	−4.0	−22.8	−36.9	−23.3	−31.1	−5.8
² <i>J</i> (C3H4)	8.9	8.6	8.1	9.9	9.9	8.9	7.1	7.1	4.0
² <i>J</i> (C4H3)	7.4	−1.8	6.6	8.4	4.8	1.3	3.0	1.7	4.5
² <i>J</i> (C4H5)	11.3	12.8	10.5	12.4	13.7	13.1	10.5	10.9	6.5
³ <i>J</i> (C1H3)	11.3	57.5	11.6	9.6	28.4	44.5	28.8	36.8	8.6
³ <i>J</i> (C1H5)	15.5	−7.9	14.4	16.6	5.2	−6.8	3.1	−2.1	13.1
³ <i>J</i> (C3H5)	14.2	12.4	13.4	15.1	15.1	11.9	12.6	11.8	11.5
³ <i>J</i> (C4H6)	5.5	13.3	5.3	5.5	9.1	11.1	8.9	9.7	5.6
⁴ <i>J</i> (C1H4)	11.9	37.9	11.9	12.2	26.8	32.6	21.8	26.6	4.7
⁴ <i>J</i> (C3H6)	−2.6	−8.3	−2.6	−2.7	−5.4	−5.8	−5.0	−5.5	−3.3
³ <i>J</i> (H3H4)	5.1	3.3	4.6	4.5	4.2	3.1	3.9	3.4	4.6
³ <i>J</i> (H4H5)	3.7	5.5	3.3	2.9	4.3	5.4	4.4	4.4	4.0
⁴ <i>J</i> (H3H5)	0.5	2.4	0.5	0.5	1.3	2.2	1.1	1.3	−0.4
⁵ <i>J</i> (H3H6)	2.8	7.7	2.8	2.6	4.6	5.6	4.0	4.4	2.0

^a From microwave measurements.³¹

wise, beginning with the triple bond C1≡C2. The hydrogen atoms are numbered likewise, with H*n* attached to C*n*.

3. Results

A. NMR Shielding Constants. A comparison of the experimental and calculated shielding constants in Table 1 indicates that the best results are obtained with the KT1 and KT2 functionals, in agreement with the conclusions of ref 8. For the carbon atoms, the KT1 and KT2 shielding constants (at the optimized geometries) are fairly close to both the CCSD values and the experimental values. However, because we have not calculated vibrational corrections for the shielding constants and because the experimental values of refs 1 and 2 differ noticeably, we cannot draw any definite conclusions regarding the quality of the calculated shielding constants.

For all DFT functionals, geometry relaxation increases the C1 shielding and reduces the C4 shielding, while the C3 changes are smaller and less systematic. For the triply bonded C1 atom, the shortening of the triple bond upon relaxation significantly improves agreement with experimental results, as also observed in ref 3. This effect is particularly pronounced in HF theory, where the C1 shielding changes by more than 30 ppm upon geometry relaxation.

The hydrogen shielding constants in Table 1 differ from the experimental values by more than is usual for such constants. Also, unlike the experimental values, all of our calculations (except the HF calculation at the experimental geometry) indicate that H3 is more shielded than H4. However, one should bear in mind that the experimental

values quoted in Table 1 (25.2 and 25.8 ppm for H3 and H4, respectively) were obtained by assuming the same large incarceration shift of 2.7 ppm for the two protons in *o*-benzyne, equal to the incarceration shift in benzene.² For other molecules, the two incarceration shifts differ significantly—for example, using the shifts of 1.23 and 3.48 ppm in Table 1 of ref 2, we obtain instead 26.6 and 25.0 ppm, respectively, for the H3 and H4 shieldings in *o*-benzyne.

As seen from Table 2, the CCSD, HF, and KT1 shielding constants σ_{ave} calculated for the triply bonded carbon atom are in reasonable agreement both with experiment and with one another. However, for the HF model, this agreement arises from a fortuitous cancellation of the errors in the in-plane tensor components. Moreover, whereas the HF anisotropy is too large, the CCSD and KT1 anisotropies are closer to the experimental values. Consequently, it appears that the HF antisymmetric component is too large—the much lower (in absolute value) CCSD and KT1 results are in better agreement with each other. The KT1 shielding components of the triply bonded carbon atom agree also with the BLYP results of ref 1.

B. Indirect Nuclear Spin–Spin Coupling Constants. 1. Calculation of Spin–Spin Coupling Constants. In Tables 3 and 4, we have listed the indirect nuclear spin–spin coupling constants in *o*-benzyne, calculated at the experimental geometry of ref 31 and at the optimized geometry, respectively. There is an unusually large variation among the results obtained with the different DFT functionals. A comparison with CCSD suggests that the most accurate DFT values are those obtained with the PBE functional, at its optimized

Table 4. Indirect Nuclear Spin–Spin Coupling Constants in *o*-Benzyne, Calculated in the cc-pCVTZ Basis at the Optimized Geometry^a (Hz)

	BLYP	PW91	PBE ^b	KT1	KT2	B3LYP	B97-1	B97-2	vib. ^c	exp.
¹ J (C1≡C2)	222.3	389.2	208.7	205.7	309.7	322.2	310.3	334.0	−1.0	177.9 ± 0.7
¹ J (C2–C3)	80.6	103.7	74.7	74.0	92.4	96.8	104.4	99.0	−2.6	75.7 ± 0.9
¹ J (C3=C4)	54.2	60.0	48.9	49.9	57.3	61.5	67.8	62.4	−1.1	50.9 ± 0.8
¹ J (C4–C5)	76.0	84.1	71.3	72.9	81.6	82.6	88.7	83.6	−0.7	71.0 ± 0.8
² J (C1C3)	5.5	−18.1	4.1	3.6	−8.3	−3.9	−3.8	−5.8	−3.2	
² J (C1C5)	−12.5	−47.7	−13.0	−13.6	−33.3	−31.3	−29.3	−33.0	−3.0	
² J (C3C5)	−1.0	−8.2	−1.5	−1.7	−5.8	−4.2	−4.9	−5.1	−0.8	
³ J (C1C4)	12.0	43.8	11.9	12.6	30.2	30.1	28.6	32.6	3.7	
³ J (C3C6)	2.2	7.2	2.2	1.9	4.8	4.9	5.5	5.9	0.3	
¹ J (C3H3)	167.4	172.2	153.7	162.9	177.1	166.6	165.2	154.4	3.5	
¹ J (C4H4)	149.1	148.6	135.3	142.8	153.7	145.6	144.5	134.1	1.8	
² J (C2H3)	−1.3	−21.9	−2.3	0.8	−10.3	−11.6	−9.2	−11.6	−0.3	
² J (C3H4)	9.1	7.3	8.1	10.1	9.1	7.6	6.6	6.1	0.0	
² J (C4H3)	6.2	0.5	5.4	7.4	4.3	3.0	3.0	2.4	−0.4	
² J (C4H5)	11.6	11.0	10.9	13.1	12.7	10.7	9.5	9.3	0.4	
³ J (C1H3)	9.0	28.0	9.1	8.1	17.4	19.1	16.1	17.9	3.4	
³ J (C1H5)	15.3	6.5	14.5	15.8	11.4	8.2	9.7	8.3	−0.6	
³ J (C3H5)	13.5	13.0	12.9	14.4	14.7	12.1	12.3	11.7	0.7	
³ J (C4H6)	4.7	8.7	4.6	4.7	7.0	6.9	6.6	6.6	0.5	
⁴ J (C1H4)	9.8	20.5	9.9	11.1	17.6	14.7	12.8	13.6	1.5	
⁴ J (C3H6)	−2.5	−5.8	−2.5	−2.6	−4.4	−4.0	−4.0	−4.2	−0.1	
³ J (H3H4)	4.8	4.6	4.4	3.9	4.6	4.4	4.3	4.2	0.4	
³ J (H4H5)	3.2	4.4	3.0	2.5	3.7	4.2	3.8	3.7	0.4	
⁴ J (H3H5)	0.2	0.8	0.2	0.3	0.5	0.6	0.3	0.3	0.2	
⁵ J (H3H6)	2.4	5.0	2.6	2.3	3.7	3.5	3.0	3.1	0.1	

^a Experimental data of ref 2. ^b Very similar results are obtained in the cc-pCVQZ basis—for instance, ¹J (C1≡C2) = 205.4 Hz, ¹J (C2–C3) = 74.6 Hz, ¹J (C3=C4) = 49.2 Hz, and ¹J (C4–C5) = 71.4 Hz—and in the uncontracted cc-pCVQZ basis—see Table 7. ^c Zero-point vibrational corrections calculated at the PBE/cc-pCVTZ level of theory.

Table 5. Lowest Triplet Excitation Energy in *o*-Benzyne, Calculated at the Experimental and Optimized Geometry (eV)^a

geometry	BLYP	PW91	PBE	KT1	KT2	B3LYP	B97-1	B97-2
experimental ^b	1.687	0.824	1.608	1.783	1.134	0.915	1.163	1.044
optimized	1.889	1.181	1.828	1.912	1.469	1.425	1.587	1.544

^a The experimental³³ and EOM-CCSD excitation energies are 1.656 and 2.037 eV, respectively. ^b Ref 31.

geometry. Except for the very small ⁴J (H3H5) constant, all PBE coupling constants have the correct sign and are similar to the CCSD constants. Moreover, when PBE and CCSD differ, the PBE values are sometimes closer to the experimental values, indicating that the difference may arise from a CCSD error. Recently, in a comparison of 20 density functionals, the PBE functional was shown to yield the best ¹J (CH) constants.¹⁵ Although, in a subsequent study, PBE did not show the same good performance for other coupling constants and other molecules,¹⁶ it performs very well indeed for hydrocarbons.

The accuracy of the calculated spin–spin coupling constants, which is usually dictated by the accuracy of the FC contribution, correlates strongly with the quality of the lowest vertical triplet excitation energies listed in Table 5, computed with linear response theory using the same functional as in the energy optimization.³² In all cases, geometry optimization increases the triplet excitation energy, indicating that the optimization moves the molecule away from the nearby triplet instability. Thus, whenever the lowest calculated triplet excitation energy at the experimental geometry is much too small (for PW91, KT2, B3LYP, B97-1, and B97-2), the corresponding ¹J (C1≡C2) coupling constant is too large by

a factor of 2–3. At the optimized geometry, where the calculated excitation energy is much closer to the accurate (experimental and theoretical) value of about 1.65 eV,^{33,34} the calculated coupling constant is smaller and closer to the experimental value. These correlations between the lowest triplet excitation energy and the spin–spin coupling constants are easily understood from Ramsey's theory,³⁵ where the dominant FC contribution is expressed as a sum over triplet states, with excitation energies in the denominator. Among the DFT functionals, the very poor performance of the PW91 functional is striking—in particular, in comparison with the good performance of the similarly constructed PBE functional. Apparently, the PW91 functional provides a poor description of triplet perturbations in this molecule, giving a FC contribution to the ¹J (C1≡C2) coupling constant that is 3 times larger than that obtained with the PBE functional.

To understand better the reasons for the large errors in the DFT spin–spin coupling constants of *o*-benzyne, we have calculated, at the same levels of theory, the coupling constants of acetylene, both at the *D_{∞h}* equilibrium geometry and at a bent *C_{2v}* geometry with an H–C≡C bond angle of 135.0°. At equilibrium, the DFT acetylene results are all consistent with one another—in the cc-pCVTZ basis, for

Table 6. 1J ($C1\equiv C2$) Coupling Constant in Acetylene and *o*-Benzyne (Hz)^a

	BLYP	PW91	PBE	KT1	KT2	B3LYP	B97-1	B97-2	CCSD	exp.
linear C_2H_2	222.1	221.0	209.8	211.3	220.1	225.2	235.8	224.6	202.5	185.0 ^b
bent $C_2H_2^a$	221.0	267.2	206.5	210.1	261.7	253.7	259.6	271.0	196.9	
<i>o</i> -benzyne	236.4	664.9	225.9	213.0	434.1	577.3	448.5	566.4	210.2	177.9 ± 0.7

^a All calculations in the cc-pCVTZ basis. The H–C≡C angle is 135.0° in the bent C_2H_2 model, compared with 126.4° in *o*-benzyne. ^b See ref 38 for a discussion of this (derived) C_2H_2 equilibrium spin–spin coupling constant and ab initio results. The experimental gas-phase value of 1J ($C1\equiv C2$) is 174.78 ± 0.02 Hz.³⁷

Table 7. Carbon–Carbon Indirect Nuclear Spin–Spin Coupling Constants in *o*-Benzyne and Benzene (Hz)

	<i>o</i> -benzyne							benzene ^a
	PBE ^b	PBE ^c	PBE ^d	PW91 ^e	PW91 ^f	CCSD ^g	exp. ^h	PBE ^b
1J ($C1\equiv C2$)	208.7	203.0	211.7	389.2	191.9	210.2	177.9 ± 0.7	50.6
1J ($C2-C3$)	74.7	73.8	76.7	103.7	72.8	83.4	75.7 ± 0.9	
1J ($C3=C4$)	48.9	48.5	50.4	60.0	49.8	63.3	50.9 ± 0.8	
1J ($C4-C5$)	71.3	70.5	72.8	84.1	69.0	77.2	71.0 ± 0.8	
2J ($C1C3$)	4.1	3.5	3.7	18.1	3.4 ⁱ	2.0		−0.5
2J ($C1C5$)	−13.0	−14.0	−14.5	−47.7	−10.9 ⁱ	−13.8		
2J ($C3C5$)	−1.5	−1.9	−1.9	−8.2	−1.3	−3.3		
3J ($C1C4$)	11.9	13.2	13.7	43.8	10.8	13.5		9.2
3J ($C3C6$)	2.2	2.9	2.9	7.2	2.1	4.8		

^a Only the unique 1J (CC), 2J (CC), and 3J (CC) coupling constants are tabulated. ^b Calculation in the cc-pCVTZ basis at optimized geometry. ^c Calculation in the uncontracted cc-pCVQZ basis at optimized geometry. ^d Calculation in the HIIIsu3 basis at optimized geometry. ^e Calculation in the cc-pCVTZ basis at PW91 optimized geometry. ^f Calculation by Jiao et al.³ ^g FC term calculated in the cc-pCVTZ basis, the remaining terms in the cc-pCVDZ basis. ^h Experimental results from ref 2. ⁱ It appears from this compilation that in ref 3 the 2J ($C1C3$) and 2J ($C1C5$) constants have been interchanged.

example, all 1J ($C1\equiv C2$) values are between 209 and 236 Hz, see Table 6. Moreover, the DFT couplings are noticeably closer to the CCSD value of 203 Hz than to the experimental value of 185 Hz. At this geometry, the error relative to the experiment arises from basis-set incompleteness—when the FC contribution is recalculated in the cc-pCVQZ basis, we obtain 189 Hz at the PBE level and 180 Hz at the CCSD level. By contrast, in bent acetylene, the differences among the DFT functionals become large, albeit not as large as in *o*-benzyne (the C–C≡C angle in *o*-benzyne is 126.4°).

In Table 7, we have listed the carbon–carbon spin–spin coupling constants of *o*-benzyne calculated at different levels of theory, together with the experimental values and the coupling constants in benzene. First, comparing the cc-pCVTZ, uncontracted-cc-pCVQZ, and HIIIsu3 coupling constants calculated with the PBE functional, we find good agreement overall, with the largest differences for the 1J ($C\equiv C$) coupling. For this coupling, the three basis sets yield 208.7, 203.0, and 211.7 Hz, respectively. Noting that the cc-pCVTZ and HIIIsu3 results never differ by more than 3 Hz, we conclude that the cc-pCVTZ basis set has sufficient flexibility in the core region.

Next, we note that the PBE/cc-pCVTZ value of 209 Hz for 1J ($C\equiv C$) differs dramatically from the PW91/cc-pCVTZ value of 389 Hz. By contrast, Jiao et al.³ obtained 192 Hz for this coupling, also with the PW91 functional. The reason for their better agreement with the experimental value of 178 Hz is the use of a shorter triple-bond length—interested primarily in the bonding of *o*-benzyne, these authors deduced the geometry from a comparison of the calculated and experimental NMR parameters. For many functionals, including PW91, the one-bond spin–spin coupling constant

decreases strongly with a shortening of the triple bond, explaining the discrepancy between our results and those of Jiao et al.³

2. Survey of Spin–Spin Coupling Constants. In the following, we shall survey the indirect nuclear spin–spin coupling constants of *o*-benzyne, basing our discussion on the CCSD results and on the PBE results obtained at the optimized geometry, taking these to be the most reliable complete sets of coupling constants for this molecule.

For the one-bond carbon–carbon coupling constants, we first note the strong coupling across the triple bond. Indeed, our PBE/cc-pCVTZ value of 209 Hz, close to the CCSD value of 210 Hz, suggests that 1J ($C1\equiv C2$) in isolated *o*-benzyne at equilibrium is larger than both the DFT result of Jiao et al. (192 Hz) and the experimental result of Warmuth (178 Hz). Whereas the discrepancy with Jiao et al. arises from different geometries in the calculations, the discrepancy with the experiment arises because we have neglected the effects of incarceration inside a molecular container. Because incarceration is likely to affect the geometry of *o*-benzyne, it will also affect the geometry-sensitive coupling across the triple bond.

The remaining PBE one-bond carbon–carbon coupling constants are, like those of Jiao et al.,³ in good agreement with the experimental measurements, differing by only 1–2 Hz. On the other hand, the agreement with the CCSD values, which are too high by 5–15 Hz, is now poorer. (We note that the rovibrational corrections discussed below make the agreement of all these constants with the experimental values slightly poorer.) Finally, in agreement with the experimental values, the PBE 1J ($C3=C4$) value of 49 Hz is closest to the one-bond carbon–carbon coupling of 51 Hz in benzene, the

PBE values of 1J (C2—C3) and 1J (C4—C5) being 75 and 71 Hz, respectively.

Regarding the geminal and vicinal carbon—carbon spin—spin coupling constants in *o*-benzyne, we note that the PBE constants agree well with our CCSD results and almost as well with the PW91 results of Jiao et al.,³ provided we interchange their 2J (C1C3) and 2J (C1C5) values. Interestingly, whereas the geminal coupling is only -0.5 Hz in benzene, it is much stronger in *o*-benzyne, varying from -13 to $+4$ Hz; furthermore, whereas the vicinal coupling is 9 Hz in benzene, the two distinct vicinal couplings are 2 and 12 Hz in *o*-benzyne. Clearly, all carbon—carbon couplings are strongly affected by the triple bond in *o*-benzyne, not just those close to the triple bond.

Turning our attention to the carbon—proton interactions, we note from Table 4 that the value of the one-bond coupling 1J (C4H4) of 135 Hz differs little from that in benzene (136 Hz), whereas the coupling next to the triple bond 1J (C3H3) is enhanced by about 20 Hz. By contrast, the geminal and vicinal carbon—proton couplings are more strongly affected, as can be rationalized from the more delocalized character of these couplings. Thus, the geminal carbon—proton couplings in *o*-benzyne vary between -2.3 and 10.9 Hz (compared with 2.5 Hz in benzene); similarly, the vicinal couplings of *o*-benzyne vary between 4.6 and 14.5 Hz (compared with 6.7 Hz in benzene). Finally, we note that the long-range 4J (C1H4) coupling of 12 Hz differs significantly both from the 4J (C3H6) coupling of -2.6 Hz and from the corresponding benzene coupling of -0.7 Hz. Regarding the proton—proton interactions, the differences between *o*-benzyne and benzene are smaller, the values of 3J (HH), 4J (HH), and 5J (HH) in benzene being 6.0, 1.2, and 0.5 Hz, respectively.

The relative importance of the different Ramsey contributions—that is, the FC, SD, DSO, and PSO contributions—is essentially the same at all levels of theory. We base the following discussion on the geometry-optimized PBE results, because we were unable to carry out the all-electron CCSD calculations of all four contributions in the cc-pCVTZ basis. The FC term dominates most of the coupling constants—in particular, the large ones. The PSO contribution is relatively large for the one-bond carbon—carbon couplings and constitutes, for example, about 13% of 1J (C=C). The PSO term is important also for the proton—proton coupling constants, although it is here canceled by the DSO term as happens also in many other molecules—see, for example, ref 36. Except when it cancels the PSO term, the DSO term is always small. The SD term is significantly smaller but relevant (in relative terms) for some of the smaller constants. For the coupling across the triple bond, the PSO and SD terms both contribute about 2% but cancel coincidentally.

We have estimated the zero-point vibrational corrections to the spin—spin coupling constants as described by Ruden et al.,²⁶ including anharmonic as well as harmonic contributions. In evaluating the vibrational corrections, the first and second derivatives of the spin—spin coupling constants are calculated numerically, while the force constants are obtained numerically from analytically calculated gradients.

In Table 4, we have listed the corrections calculated at the PBE/cc-pCVTZ level of theory. A comparison with the HIIIsu3 results reveals a large uncertainty in the vibrational correction to 1J (C1≡C2), due to a near cancellation of the harmonic and anharmonic contributions. In particular, for this coupling constant, the cc-pCVTZ and HIIIsu3 vibrational corrections are -1.0 and 0.5 Hz, respectively. [The remaining corrections are much less basis-set-dependent, except for an uncertainty of about 1 Hz in the 1J (C3H3) and 1J (C4H4) corrections.] Thus, although the sign of the vibrational correction to 1J (C1≡C2) is unknown, its magnitude is small, modifying the coupling constant by less than 1%. Clearly, the large difference between the calculated and measured 1J (C1≡C2) values does not arise from vibrations.

From Table 4, we note that the vibrational corrections to the one-bond spin—spin coupling constants in *o*-benzyne are all small, never exceeding 3% of the total coupling. By contrast, the geminal and vicinal corrections are large—reducing, for example, 2J (C1C3) from 4.1 to 0.7 Hz and increasing 3J (C1H3) from 9.1 to 12.5 Hz. Interestingly, the vibrational corrections to the small geminal and vicinal 2J (C1C3), 3J (C1C4), and 2J (C1C5) coupling constants are all larger in magnitude than the vibrational correction to the much larger one-bond 1J (C1C2) coupling constant. Although these corrections may be unimportant for the comparison with incarcerated *o*-benzyne, they do illustrate that indirect nuclear spin—spin coupling constants can sometimes be dramatically affected by molecular vibrations.

4. Conclusions

We have carried out an extensive theoretical study of the NMR parameters in *o*-benzyne, using DFT and coupled-cluster theory. Because of its special structure and biradical character, the calculation of these parameters for *o*-benzyne is difficult, the results depending critically on the choice of exchange—correlation functional and on the reference geometry. In general, we find that the DFT results become significantly more reliable when calculated at the optimized geometry, using the same functional for the geometry optimization and the calculation of NMR parameters. At these optimized geometries, the electronic structure (as described by restricted theories) appears to be less strained and less affected by, for example, triplet instabilities, as seen by comparing the lowest triplet excitation energy in *o*-benzyne calculated at the experimental and optimized geometries. We note that unrestricted electronic-structure theory cannot be used in our calculations to describe the unperturbed reference state because the associated spin contamination would make the calculation of NMR parameters meaningless.

Comparing the performance of the different exchange—correlation functionals at the optimized geometries, we find that the best results (in comparison with CCSD theory) are obtained with the KT1 and KT2 functionals for the shielding constants and by the PBE functional for the indirect spin—spin coupling constants. These findings are reassuring in the sense that these conclusions, regarding the relative performance of different functionals for NMR parameters, agree

with recent benchmark studies on other molecules. We are therefore confident that the results obtained with these functionals, at the optimized geometries, are qualitatively correct and may be meaningfully compared with experimental and previous theoretical results. Indeed, with these functionals, the agreement with the available experimental results is good.

Numbering the atoms consecutively, beginning with the triply bonded carbon atoms, we obtain -3.3 , 61 , and 51 ppm for the C1, C3, and C4 shieldings, respectively, at the KT1/cc-pCVTZ level of theory, compared with the experimental values of 3.7 , 60 , and 48 ppm. Particularly noteworthy is the small shielding constant of the triply-bonded carbon atom, in agreement with the experimental results. The differences may arise either from an inadequacy of the exchange–correlation functional or from incarceration.

For the spin–spin coupling constants, we find the performance of the single-reference PBE method similar to the performance of CCSD. At the PBE/cc-pCVTZ level of theory, we obtain 205 Hz for 1J across the triple bond in isolated *o*-benzyne at equilibrium, 49 Hz across the double bond, and 75 and 71 Hz across the single bonds adjacent and not adjacent to the triple bond, respectively; the corresponding experimental values for the incarcerated molecule are 178 , 51 , 76 , and 71 Hz, respectively. Comparing also with CCSD theory, we believe that the discrepancy with the experimental triple-bond spin–spin coupling is again due to incarceration and that the true equilibrium carbon–carbon triple-bond spin–spin coupling in *o*-benzyne is about 200 Hz.

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