J. Phys. Chem. A **2000,** *104,* 6271−6276 **6271**

Density Functional Theory Study of Ultrashort and Overlong CC Single Bonds and the Lowest Nonbonding C···C Distance

V. Galasso*,†

Dipartimento di Scienze Chimiche, Università di Trieste, I-34127 Trieste, Italy

I. Carmichael‡

Radiation Laboratory, University of Notre Dame, Notre Dame, Indiana 46556

Received: January 18, 2000; In Final Form: April 13, 2000

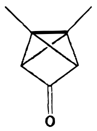
Full conformational analysis on selected organic compounds containing the ultrashort (bent and unbent) or overlong CC single bond or the shortest C···C nonbonding distance between saturated, tetravalent carbon atoms, reported in the literature so far, has been performed by means of the density functional theory (DFT) model B3LYP/6-31G(d,p). The patterns of the theoretical structural parameters are in excellent agreement with the X-ray diffraction data. The nature of these extraordinary bonds has also been rationalized with the composition of the atomic hybrid orbitals of the involved carbon atoms. Such unique structural features lead to unusual ^{13}C NMR spectroscopic properties, namely, chemical shifts and indirect nuclear spin−spin coupling constants. The theoretical values of these observables, calculated by DFT methodologies, are fully consistent with available experimental evidence and expectation. In particular, theory predicts an unusually large value of ^{1}J(CC) for the ultrashort unbent bond in the bipolyhedron systems, a normal cyclopropanic positive value of ^{1}J(CC) for the ultrashort bent bond in the tricyclo[2.1.0.0^{2,5}]pentane derivative, a reduced alkanic value of ^{1}J(CC) for the overlong bond in the cyclobutaarene derivatives, and a large negative value of ^{2}J(CC) for the lowest nonbonding C···C interaction in the quaternary 1-bicyclo[1.1.1]pentane salt.

Introduction

Within the huge family of organic compounds, a fascinating appeal stems from the molecules containing an extremely short or long single bond between two saturated, tetravalent carbon atoms as well as an extremely short nonbonding carbon···carbon distance. For these exceptional, structural records some recently synthesized molecules deserve the privilege of being registered in a kind of "Guinness Chemical Book", updated to the end of the Second Millennium.

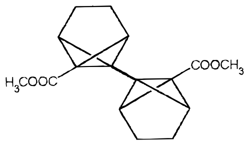
As a yardstick, the *normal* length of a strain-free single bond between two saturated tetravalent (nominally sp^3 hybridized) carbon atoms is 1.54 Å, as is observed, e.g., for the central bond in the open-chain reference system butane, $H_3CH_2CCH_2CH_3$ (1.539 Å).[1]

The shortest *endocyclic* CC single bond observed so far belongs to 1,5-dimethyltricyclo[2.1.0.0^{2,5}]pentan-3-one (TCPO), in which the distance between the two carbon bridgehead atoms, common to the three-membered rings, has the value of 1.417(1) Å measured by X-ray diffraction at −155 °C[2] and 1.408(3) Å at room temperature.[3] However, it is to be stressed that the electron density in this bridge bond is displaced by approximately 0.40 Å away from the bond axis.[2] This bond must therefore be described as a severely *bent σ* bond. Furthermore, it has been shown that in tricyclo[2.1.0.0^{2,5}]pentane derivatives this distance strongly increases with increasing folding angle in the bicyclopropyl moiety.[4]

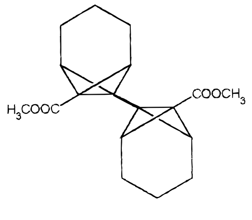


TCPO

The shortest *exocyclic* CC single bond lengths have been determined by X-ray investigations for two coupled bicyclo[1.1.0]butanes.[5] Indeed, the central bond in 1,1′-bi(tricyclo[3.1.0.0^{2,6}]hexane-6,6′-dicarboxylic acid dimethyl ester) (BTHEX) is 1.443 Å, and in 1,1′-bi(tricyclo[4.1.0.0^{2,7}]heptane-7,7′-dicarboxylic acid dimethyl ester) (BTHEP) it is 1.448 Å (librationally corrected values). These experimental results were the long-sought targets of expectation that bonds involved in widened bond angles (beyond the canonical tetrahedral value) are shortened.[5,6] In contrast to the case in TCPO, where the *bent* nature of the intra-ring bond makes the bond definition somewhat problematic, a striking aspect of these ultrashort intercage CC single bonds in BTHEX and BTHEP is that they are noncyclic or *unbent*.



BTHEX



BTHEP

A few cyclobutaarenes are situated on the other terminal step of this metric ladder.[7,8] Indeed, introduction of diphenyl

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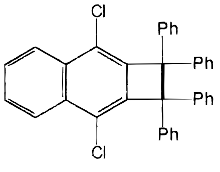
* To whom correspondence should be addressed.

† E-mail: galasso@univ.trieste.it.

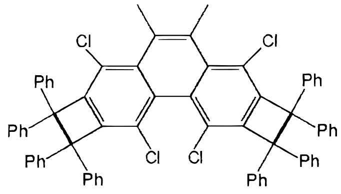
‡ E-mail: carmichael.1@nd.edu.

10.1021/jp0002291 CCC: $19.00

substituents on the peripheral carbon atoms of the cyclobutene ring causes a severe intramolecular overcrowding, manifested by an extreme stretching of the CC single bond in the cyclobutene ring. This interatomic distance has been determined by X-ray analysis to be 1.720(4) Å in 3,8-dichloro-1,1,2,2-tetraphenylcyclobuta[*b*]naphthalene (CBNA) and 1.717(5) Å in 3,6,9,10-tetrachloro-4,5-dimethyl-1,1,2,2,7,7,8,8-octaphenyldicyclobuta[*b*,*h*]phenanthrene (DCBPH).[7]



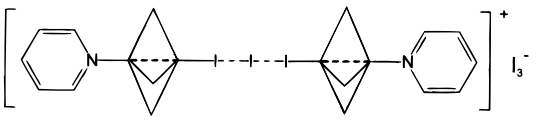
CBNA



DCBPH

With reference to the canonical value of 1.54 Å, the CC bond distance is therefore shortened by about 0.10 Å in BTHEX and BTHEP (0.13 Å in TCPO) and elongated by about 0.18 Å in CBNA and DCBPH. The full range of the CC single bond distance is thus as large as 0.28 Å (or 0.31 Å).

Extremely short nonbonding contacts between saturated, tetracoordinate carbon atoms have been documented in the simplest strained-cage molecules, bicyclo[1.1.1]pentane derivatives.[9,10] In particular, the shortest nonbonding C⋯C distance has been established by X-ray crystal analysis to be 1.80(2) Å in 1-(1-pyridinio)-3-iodobicyclo[1.1.1]pentane iodide/triiodide (PIBCP),[10] remarkably smaller than the standard alkanic value of 2.50 Å. It is worthwhile mentioning that, since the bicyclo[1.1.1]pentane framework behaves as an excellent relay for π/σ conjugation,[11] the shortest C⋯C contact may be a critical factor for the preparation of nanotechnology-important substrates.[12]



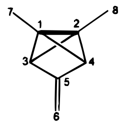
PIBCP

As far as the CC or C⋯C distances are concerned, to our knowledge, these are the *world records in chemistry* reported so far in the literature. They are of strong immediate interest from a theoretical standpoint, because their extraordinary geometric parameters also lead to peculiar spectroscopic properties. Among the spectroscopic observables, the NMR parameters have emerged as very efficient monitors of the complex interplay of the subtle stereoelectronic effects operative in a molecular system. In particular, distinguished features of the present exceptional molecules should be the ^{13}C chemical shifts and the nuclear spin−spin coupling constants *J*(CC) involving the two C atoms in the extreme single CC bond or nonbonding C⋯C contact. In this work, we report on a systematic theoretical investigation of the equilibrium structures and NMR properties of all six quoted molecules, using density functional theory (DFT) methodologies, which are intended to economically recover the important effects of electron correlation.

Computational Methods

The equilibrium structures of all molecular systems were completely optimized with the B3LYP hybrid functional[13] and the standard 6-31G(d,p) basis set using the Gaussian-94 program package.[14] For iodine the double-ζ plus polarization basis set of Strömberg et al. was used.[15] This functional, which takes into account the electron exchange-correlation effects, and the polarized basis sets are a good compromise between the size of the calculations and the accuracy of the theoretical predictions. [Full lists of atomic coordinates may be obtained from V.G. upon request.]

TABLE 1: Optimized Structural Parameters (Bond Lengths, Å; Angles, deg) for TCPO



r(1−2)	1.425	α(7−1−2)	144.18
r(1−3)	1.542	α(2−1−3)	62.49
r(1−7)	1.491	α(3−1−4)	81.64
r(3⋯4)	2.016	α(1−3−5)	91.02
r(3−5)	1.525	α(3−5−4)	82.74
r(5−6)	1.201		

The ^{13}C NMR chemical shifts were calculated at the DFT level with the continuous set of gauge transformations (CSGT) method,[16] using the 6-311+G(2d,p) basis set for TCPO, BTHEX, BTHEP, and PIBCP, the 6-311G(d,p) basis set for CBNA and DCBPH, and the B3LYP hybrid functional. The calculated magnetic shieldings were converted into the chemical shifts by noting that at the same level of theory the ^{13}C shielding in TMS is 177.54 ppm (extended basis set) and 174.99 ppm (second basis set).

The indirect nuclear spin−spin coupling constants $^{n}J(CC)$ were obtained by finite field double perturbation theory calculations[17] using a modified version of the Gaussian-94 suite of programs. Only the Fermi contact (FC) component of each coupling constant was considered. Use was made of a previously constructed basis set [5s2p1d|2s], with a shell of five-component polarizing d functions on the heavy atoms C, N, and O,[18] the 6-311G(d) basis set for Cl, and the DZ(d) basis set for I. Incidentally, we mention that these are by far the largest reported calculations of *J* values at the ab initio/DFT level.

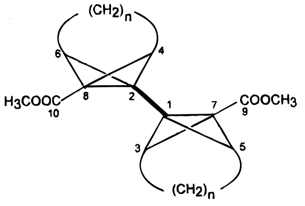
Localization of the molecular orbitals (MOs) was performed according to the Pipek−Mezey procedure.[19]

Results and Discussion

Structural Parameters. Geometries for all systems were fully optimized at the B3LYP/6-31G(d,p) level of theory. A selection of the most relevant structural parameters (bond lengths, valence and torsion angles) is presented in Tables 1-4. The most salient aspects of the DFT conformational analysis can be summarized as follows.

For TCPO the calculated structural parameters (Table 1) are in satisfactory agreement with the X-ray data of Irngartinger et al.[2,3] In particular, the ultrashort distance of the bond between the bridgehead carbon atoms C_1 and C_2 and the interplanar angle between the three-membered rings are fairly reproduced: (theoretical) 1.425 Å and 94.96° vs (experimental) 1.417(1) Å and 95.0°.[2] For this bridging bond, the picture that emerges from the MO localization is in full agreement with the electron density distribution determined from the X-ray data:[2] the CC bond has no π character and can be described as a classical two-center σ bent bond, formed by hybrid orbitals $sp^{3.63}$ pointing about 39° outward from the line joining the two carbon atoms (by reference, at the same level of theory, in ethane these hybrids are $sp^{2.28}$). As a matter of fact, the parent compound tricyclo[2.1.0.0^{2,5}]pentan-3-one has also been synthesized and fully characterized,[20] but no experimental structure has yet been reported. For this molecule, at the same level of theory, the

TABLE 2: Optimized Structural Parameters (Bond Lengths, Å; Angles, deg) for BTHEX and BTHEP

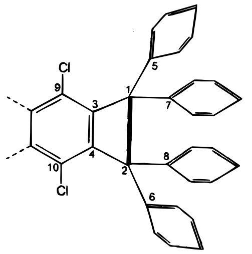


	BTHEX ($n = 2$)	BTHEP ($n = 3$)		BTHEX ($n = 2$)	BTHEP ($n = 3$)
$r(1-2)$	1.452	1.456	$\alpha(2-1-3)$	133.88	130.09
$r(1-3)$	1.507	1.509	$\alpha(2-1-5)$	133.88	130.01
$r(1-5)$	1.505	1.506	$\alpha(2-1-7)$	131.72	128.78
$r(1-7)$	1.511	1.534	$\alpha(3-1-5)$	91.95	97.70
			$\alpha(3-1-7)$	60.06	59.27
			$\alpha(5-1-7)$	60.06	59.34

DFT calculations predict a central bond of 1.426 Å and a folding angle δ of 96.2°, rather similar to the structural parameters of its dimethyl derivative TCPO. However, the hybrid orbitals in the bridging bond have a slightly greater p character in the unsubstituted compound ($sp^{4.21}$).

In the crystal, both molecules BTHEX and BTHEP are centrosymmetric and, ignoring the ester groups, C_{2h} symmetry is closely approximated.[5] However, the conformation about the central CC bond is by no means perfectly staggered: a plane may be drawn through C_1 and C_2 such that the four bonded carbon atoms lie on one side of this plane.[5] These structural features are correctly accounted for by the DFT calculations (Table 2). For both molecules, the equilibrium conformation bears C_i symmetry, the central bond is particularly short, and the exocyclic adjacent bond angles are significantly widened from the standard tetrahedral value. The theoretical structural parameters are consistent with those obtained from the X-ray data: for BTHEX, bond distance of 1.452 Å and average angle widening of 23.7° (experimental, 1.443 Å and 21.4°), and for BTHEP 1.456 Å and 20.1° (experimental, 1.448 Å and 18.7°).[5] It is to be mentioned that the present results are in better correlation with the experimental values than those previously obtained by ab initio HF calculations for the unsubstituted BTHEX molecule.[21,22] A serious drawback of these uncorrelated calculations is that one adjacent CC distance should be shorter than the intercage bond. Here, the predicted central bond distances follow the experimental ordering. According to the MO localization, the ultrashort CC central bond results from the interaction of two hybrid orbitals, $sp^{1.26}$ in BTHEX and $sp^{1.31}$ in BTHEP, along the internuclear axis. Therefore, there is a remarkable difference in the character of the ultrashort bent CC bond in TCPO and the ultrashort unbent CC bond in BTHEX and BTHEP: the s contribution to the bonding orbital increases from 21.6% in TCPO to 44.3% in BTHEX and 43.2% in BTHEP. Furthermore, it is worth noting that, on the grounds of MP2 ab initio calculations,[22] the still elusive bitetrahedrane has been claimed as a plausible candidate for the molecule incorporating the shortest possible, unbent CC intercage bond (theoretical, 1.434 Å). This expectation is also corroborated by the present DFT calculations: the shorter distance of 1.427 Å is reflected on the greater *acetylenic* character of carbon hybridization $sp^{1.07}$, as compared with the congener systems BTHEX and BTHEP. The extraordinary character of the intercage bond in these small bipolyhedra is further demonstrated by the marked shift to higher wavenumbers of the corresponding CC stretching band, as compared to the related band of ethane at 993 cm^{-1}. Indeed, according to DFT calculations, this stretching motion would give rise to a band at 1587 cm^{-1} for BTHEP, 1608 cm^{-1} for BTHEX, and 1728 cm^{-1} for bitetrahedrane.

TABLE 3: Optimized Structural Parameters (Bond Lengths, Å; Angles, deg) for CBNA and DCBPH

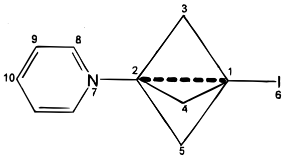


	CBNA	DCBPH		CBNA	DCBPH
$r(1-2)$	1.730	1.728	$\alpha(3-1-2)$	83.90	83.66
$r(1-3)$	1.528	1.530	$\alpha(4-2-1)$	83.90	83.56
$r(2-4)$	1.528	1.528	$\alpha(1-3-4)$	96.05	96.24
$r(3-4)$	1.406	1.388	$\alpha(2-4-3)$	96.05	96.52
$r(1-5)$	1.537	1.525	$\alpha(3-1-5)$	112.29	116.47
$r(2-6)$	1.537	1.526	$\alpha(4-2-6)$	112.29	115.00
$r(1-7)$	1.525	1.537	$\alpha(5-1-7)$	113.05	113.70
$r(2-8)$	1.525	1.536	$\alpha(6-2-8)$	113.05	112.56

In the crystal, the planar naphthocyclobutene molecule CBNA has a cyclobutene fusion bond of a normal length (1.41 Å) and considerably shortened (1.35 Å) adjacent bonds in the benzene rings.[7] On the other hand, in the twisted phenanthrodicyclobutene derivative DCBPH the fusion-annelated bonds and the adjacent aryl bonds are closer in length, about 1.37 Å. Furthermore, the aryl core of this molecule is severely distorted from planarity: the intramolecular twist is characterized by the C(Cl)−C−C−C(Cl) torsion angle along the concave surface of the molecule of 38°.[7] However, the utmost importance of these molecules is associated with their overlong CC single bonds, namely, the sterically congested benzocyclobutene bonds with four phenyl groups. The present DFT calculations correctly account for all the structural features of the two molecules (Table 3). It must be mentioned that the equilibrium structure of CBNA has previously been computed by Bettinger et al.[23] at the same level of theory; nevertheless, the present DFT results are reported here to facilitate the comparison of internally consistent geometric parameters of CBNA and DCBPH. Both cyclobutaarenes display a structure of C_2 symmetry, where the *fused* cyclobutenic rings are essentially planar. The theoretical overlong CC distances of 1.730 Å in CBNA and 1.728 Å in DCBPH are in good agreement with the corresponding experimental values of 1.720(4) and 1.717(5) Å, respectively.[7] Further information on these exceptional bonds is provided by MO localization. In CBNA, the atomic orbitals responsible for this overlong CC are hybrids $sp^{2.29}$ with 30.4% *s* character, directed along the internuclear axis. Of course, the picture $C_1(sp^{2.30})C_2(sp^{2.28})$ for DCBPH has much in common with that of CBNA. It is worth stressing that this composition looks rather similar to that predicted for the standard CC bond in ethane itself ($sp^{2.28}$). By comparison with simple model systems, Bettinger et al.[23] have attributed the exceptional lengthening of the CC bond in CBNA to a combination of cyclobutene ring strain, through-bond coupling, and steric repulsion.

The strained-cage molecule PIBCP contains the shortest 1.80(2) Å $C_1 \cdots C_2$ nonbonding distance reliably determined to date for any known organic compound.[10] The crystallographic parameters show that other structural characteristics of this molecule, such as interatomic distances and angles in the pyridine ring and the bicyclo[1.1.1]pentane moiety, are normal.[10]

TABLE 4: Optimized Structural Parameters (Bond Lengths, Å; Angles, deg) for PIBCP



$r(1\cdots2)$	1.827	$\alpha(6-1-3)$	126.25
$r(1-3)$	1.558	$\alpha(6-1-4)$	126.20
$r(1-4)$	1.559	$\alpha(1-3-2)$	71.92
$r(1-6)$	2.137	$\alpha(1-4-2)$	72.05
$r(2-3)$	1.554	$\alpha(3-2-7)$	125.90
$r(2-4)$	1.548	$\alpha(4-2-7)$	125.73
$r(2-7)$	1.481		

The pattern of the geometric parameters obtained by DFT calculations (Table 4) for the cationic unit of this salt is in reasonable agreement with the X-ray structure. The slight overestimation of the $C_1\cdots C_2$ nonbonding distance, 1.827 Å vs 1.80(2) Å, if any, may likely be traced to the limited basis set adopted for iodine. The angular deformations at the bridgehead carbon atoms of the bicyclo[1.1.1]pentane moiety are also reproduced satisfactorily: the average exocyclic angles $N-C_2-C$ and $I-C_1-C$ are predicted to be 125.8° and 126.2°, in good correlation with the experimental values of 125.2° and 126.1°, respectively.[10]

A final point of interest is the insufficiency of the SCF−HF calculations, with the standard 6-31G(d,p) basis set, for both the ultrashort and overlong CC bonds in the investigated molecules. Indeed, the ultrashort bonds are predicted about 0.03 Å longer while the overlong bonds about 0.04 Å shorter than the experimental distances. Incorporation of the effects of electron correlation in the DFT with the B3LYP exchange-correlation hybrid functional brings the theoretical predictions into much closer agreement with experiment.

As a consequence of their peculiar stereochemistry, the patterns of the NMR spectroscopic properties of the examined molecules exhibit some unusual aspects. We report now on these properties.

^{13}C Chemical Shifts. The most relevant results of the DFT calculations for the ^{13}C chemical shifts are reported in Table 5. It must be noted that highly accurate predictions of the $\delta(^{13}C)$ observables require very large basis sets and sophisticated treatment of electron correlation effects, but for the considered medium-sized molecules these requirements are computationally prohibitive. However, for all molecules, the present theoretical results are in substantial accord with the available spectroscopic data. In particular, it is to be noted that the large failure for the bridgehead carbon atom directly attached to iodine in PIBCP (about 40 ppm relative to the observed value) is due to neglect of the spin−orbit-induced heavy-atom effect on the ^{13}C chemical shift. As shown by a recent theoretical investigation on simple iodoalkanes,[24] this additional spin−orbit operator provides a shielding contribution of such magnitude for the α-carbon nucleus. Apart from this discrepancy, a comprehensive reproduction of the absolute values and main trends in the ^{13}C chemical shifts has been obtained.

In particular, with reference to the carbons involved in the “special” CC single bonds the following comments can be made. In the case of the *bent* bond in TCPO, the high shielding[25] and downfield displacement of about 16 ppm relative to its unsubstituted parent (−1.0 ppm),[20] as a consequence of replacement of H atoms by methyl groups, are correctly accounted for. On the other hand, in the case of the *unbent* bond, the resonance is predicted to move from upfield in bitetrahedrane (−23.5 ppm) toward downfield in BTHEX (32 ppm) and BTHEP (40 ppm), the observed change of 9 ppm of the signal on passing from BTHEX to BTHEP[26] being accurately reproduced by the CSGT calculations. Finally, the nearly similar values of the chemical shifts exhibited by the pair CBNA and DCBPH[27] are also accounted for by theory. Of course, no simple, direct correlation between ^{13}C chemical shifts and the length of the CC single bonds can be invoked, on the basis of elementary charge-transfer arguments. At any rate, a monotonic downfield displacement of the bridgehead signal is apparent on passing from bitetrahedrane (1.427 Å, −23.5 ppm) to BTHEX (1.443 Å, 28.9 ppm), BTHEP (1.448 Å, 37.8 ppm),[26] CBNA (1.720 Å, 75.7 ppm), and DCBPH (1.724 Å, 75.5 and 76.4 ppm);[27] thus, the overall elongation of 0.30 Å of the CC *unbent* single bond is accompanied by a parallel deshielding of 100 ppm for the carbon nuclei. As to the carbons of the lowest nonbonding distance in PIBCP,[28] apart from the abovementioned carbon linked to iodine, the resonance of the other carbon, bonded to the pyridyl fragment, is satisfactorily calculated.

TABLE 5: ^{13}C NMR Chemical Shifts Relative to TMS (ppm)

	TCPO			TCPO	
	calcd	exptl[25]		calcd	exptl[25]
C-1[a]	13.4	14.6	C-5	184.4	185.3
C-3	38.4	42.3	C-7	1.9	5.8

	BTHEX		BTHEP	
	calcd	exptl[26]	calcd	exptl[26]
C-1[b]	32.1	28.9	40.4	37.8
C-3	40.3	43.2	43.9	45.9
C-5	40.3	43.2	43.7	45.9
C-7	21.9	22.1	23.3	22.2
C-9	172.0	170.1	172.5	171.0

	CBNA		DCBPH	
	calcd	exptl[27]	calcd	exptl[27]
C-1[c]	76.8	75.7	77.1	76.4
C-2	76.8	75.7	76.9	75.5
C-3	141.4	144.4	144.9	
C-4	141.4	144.4	140.6	

	PIBCP			PIBCP	
	calcd	exptl[28]		calcd	exptl[28]
C-1[d]	38.0	−4.8	C-8	141.2	142.4
C-2	57.5	61.2	C-9	129.5	127.8
C-3,4	58.9	60.7	C-10	148.2	146.6

[a] Atom numbering in Table 1. [b] Atom numbering in Table 2. [c] Atom numbering in Table 3. [d] Atom numbering in Table 4.

$J(^{13}C^{13}C)$ Indirect Nuclear Spin−Spin Coupling Constants. The results of the DFT calculations are presented in Table 6. Before the discussion is started, some preliminary comments are in order. First, highly accurate predictions of the *J* property require very large basis sets, in particular for the FC term,[29] and more sophisticated exploitation of electron correlation effects.[30,31] Second, a full calculation of the *J* tensor requires consideration of all four electron−nucleus spin perturbations of Ramsey’s theory,[32] i.e., in addition to the FC term, also the orbital-diamagnetic, orbital-paramagnetic, and spin-dipolar terms. However, by using the present basis set and DFT perturbational approach, previous investigations have reported a satisfactory reproduction of ^1J(CC) for a variety of organic compounds.[18,33] On the other hand, the dominant importance of the FC contribution to “normal” coupling constants ^1J(CC) is well documented in the literature.[34] Moreover, with ab initio equa-

TABLE 6: Calculated Nuclear Spin−Spin Coupling Constants (Hz)

	TCPO		TCPO		TCPO
$^1J(1-2)$[a]	14.2	$^1J(1-7)$	64.6	$^2J(3-4)$	14.9
$^1J(1-3)$	13.3	$^1J(3-5)$	43.5		

	BTHEX	BTHEP		BTHEX	BTHEP
$^1J(1-2)$[b]	99.8	85.9	$^1J(3-7)$	24.3	24.7
$^1J(1-3)$	26.0	26.4	$^1J(5-7)$	25.5	25.7
$^1J(1-5)$	26.1	26.4	$^1J(7-9)$	110.1	101.5
$^1J(1-7)$	−16.6	−20.9			

	CBNA	DCBPH		CBNA	DCBPH
$^1J(1-2)$[c]	23.5	23.5	$^1J(2-6)$		50.1
$^1J(1-3)$	45.1	45.1	$^1J(1-7)$	49.4	49.2
$^1J(2-4)$		45.6	$^1J(2-8)$		52.1
$^1J(1-5)$	52.5	53.0	$^1J(3-4)$	49.7	51.6

	PIBCP		PIBCP		PIBCP
$^2J(1-2)$[d]	−19.2	$^1J(2-3)$	25.9	$^1J(7-8)$	12.3
$^1J(1-3)$	26.6	$^1J(2-4)$	27.6	$^1J(8-9)$	72.7
$^1J(1-4)$	26.1	$^1J(7-2)$	−2.2	$^1J(9-10)$	64.1

[a] Atom numbering in Table 1. [b] Atom numbering in Table 2. [c] Atom numbering in Table 3. [d] Atom numbering in Table 4.

tions-of-motion calculations, we have previously shown that this situation also holds in the case of the intercage bond of the still elusive bitetrahedrane,[35] and for the bridging bond in bicyclobutane, tricyclopentane, and related systems.[18,36] On this basis, the present theoretical predictions can be regarded with confidence.

In the pattern of the J(CC) predicted for TCPO (Table 6), three main aspects are remarkable: (i) The ^1J(CC) of the ultrashort bond C_1C_2 of 1.425 Å bears a reduced positive alkanic value of 14.2 Hz (ethane, 34.6 Hz[37]), typical of cyclopropane derivatives.[38] Contrary to naive expectation for the strongly *bent* nature of this ultrashort single bond, the calculated parameter is consistent with the p character of the carbon hybridization $sp^{3.63}$, only moderately enhanced relative to that of the standard reference compound, ethane $sp^{2.28}$. (ii) Nearly the same value is found for the coupling constants ^1J(CC) of the other intracage bonds involving the bridgehead carbons, i.e., C_1C_3 and C_1C_4, due to similar carbon hybridization. Instead, the great s component (45.4%) of the hybrid orbital of C_1 in the exocyclic bond C_1C_7 is responsible for the alkenic order of magnitude of 64.6 Hz for the associated ^1J(CC) (ethylene, 67.6 Hz[37]). (iii) Finally, the geminal coupling constant $^2J(C_3C_4)$ has a positive value of 14.9 Hz as large as that of the one-bond coupling constants of the intracage bonds involving the bridgehead carbons. This ^2J(CC), which differs from the small and negative constant generally observed in aliphatic compounds, can be justified in terms of the multiple-path coupling mechanism operating in the tricyclic framework.[39,40]

Of striking interest is the one-bond coupling over the C_1C_2 central bond of BTHEX and BTHEP. Indeed, the ultrashort *unbent* intercage bond is predicted to have an extraordinarily large $^1J(C_1C_2)$, 99.8 Hz in BTHEP (1.452 Å) and 85.9 Hz in BTHEX (1.456 Å), which reflects the great s character of the bond arising from carbon hybrid orbitals $sp^{1.26}$ in BTHEX and $sp^{1.31}$ in BTHEP. It is quite satisfying to remark on the good agreement between the DFT prediction of 85.9 Hz for BTHEP and the experimental value of 78.8 Hz determined by Lüttke and Machinek[41] for the parent system 7-methyl-1,1′-bi(tricyclo-[4.1.0.0^{2,7}]heptane). This finding is also consistent with the ab initio theoretical value of 151 Hz calculated for the related linkage in bitetrahedrane,[35] the smallest member in the class of completely saturated bipolyhedron systems, which might be the highest ^1J(CC) reported for a pure single bond between two saturated, tetravalent carbons. Comparatively smaller are the values anticipated by theory for the other three directly bonded J(CC) coupling constants, the endocage bonds C_1C_3 and C_1C_5 (about 26 Hz), and C_1C_7 (−17 Hz in BTHEX and −21 Hz in BTHEP). Again, these theoretical parameters compare quite favorably with the coupling constants measured for 7-methyl-1,1′-bi(tricyclo[4.1.0.0^{2,7}]heptane) (22 and −15 Hz, respectively).[41] The markedly lower values of $^1J(C_1C_3)$ and $^1J(C_1C_5)$ relative to $^1J(C_1C_2)$ derive from the increased p character of these intracage bonds, the hybridizations being $C_1(sp^{2.1})$ and $C_3(sp^{3.0})$ in BTHEP. Further, the sign reversal shown by $^1J(C_1C_7)$ can be accounted for with the argument that this bond is formed from two essentially pure p orbitals: in BTHEP, the hybridizations indeed are $C_1(sp^{6.08})$ and $C_7(sp^{8.32})$.

Recently, Pecul et al.[42] have investigated the dependence of ^1J(CC) upon bond length for the model system ethane with ab initio calculations at the MCSCF level. They have found that ^1J(CC) increases strongly when the CC bond is shortened from the “normal” distance of 1.53 Å, but the elongation of the bond introduces very slight changes: in the range 1.23−1.74 Å, ^1J(CC) varies from 62 to 39 Hz, being dominated by the FC term. This argument explains the experimental value of 28.2 observed for the stretched outer single bond of 1.57 Å in 3,5-dimethylcyclobutabenzene,[43] with a reduction of only 8 Hz relative to the spectroscopic parameter of ethane (34.6 Hz[37]). On this basis, not unexpected is the sizable value of about 24 Hz predicted for the ^1J(CC) of the overlong C_1C_2 bond in CBNA and DCBPH. Formally, on passing from ethane to CBNA and DCBPH, the bond elongation by 0.20 Å is thus accompanied by a reduction of about 11 Hz in ^1J(CC). On the other hand, it is worth noting that, as modeled by means of MO localization, the CC bonding situation looks rather similar, arising from hybrids $sp^{2.28}$ in ethane and $sp^{2.29}$ in CBNA. As to the lateral and fusion bonds of the cyclobutene moiety in CBNA and DCBPH, the average values of their ^1J(CC) constants are predicted to be about 10 Hz greater than the corresponding constants measured for 3,5-dimethylcyclobutabenzene,[43] despite the similarity in the bond lengths. This indicates that these bonds in the four-membered rings of the present highly strained cyclobutaarenes have still richer s character compared to cyclobutabenzene.

The most peculiar aspect in the pattern of the J(CC) constants of PIBCP concerns the nonbonding interaction $C_1\cdots C_2$, characterized by the extremely short distance of 1.80 Å, which reflects strong through-cage electronic effects. These manifest themselves in the relatively large, negative value predicted by theory for the geminal coupling constant $^2J(C_1C_2)$, −19.2 Hz. It is comparable with the experimental value of (−)25.2 Hz determined by Barfield et al.[44] for the parent system bicyclo-[1.1.1]pentane-1-carboxylic acid. The present theoretical result, therefore, rules out any similarity between this geminal coupling constant of PIBCP and, for instance, the directly bonded coupling constant of the bridgehead bond in [1.1.1]propellane, for which the exceptional nearly zero ^1J(CC) has been forecast by ab initio calculations.[45] Finally, the theoretical estimates of about 26 Hz for the ^1J(CC) coupling constants in the bicyclo-[1.1.1]pentane moiety of PIBCP are quite similar to those measured for bicyclo[1.1.1]pentane-1-carboxylic acid (25.1 Hz).[46]

Concluding Remarks

The equilibrium structures and ^{13}C NMR spectroscopic parameters of six selected organic compounds have been thoroughly investigated with DFT methodologies to rationalize the special properties of the shortest and longest CC single bonds and of the lowest C$\cdots$C nonbonding interaction between two saturated, tetravalent carbon atoms, so far reported in the literature. These molecules, therefore, are of paramount importance for theoretical understanding of chemical bonding. It is gratifying to stress that the B3LYP/DFT approach has been successful in correctly reproducing the crystallographic data reliably determined for the ultrashort bent and unbent CC single bonds, overlong CC single bonds, and the lowest nonbonding C$\cdots$C distance. The quality of this agreement markedly overcomes that obtained by previous ab initio treatments. Detailed and complimentary information on these extraordinary carbon−carbon bonding situations has been provided by computing their ^{13}C chemical shifts and J(CC) nuclear spin−spin coupling constants. The theoretical results compare favorably with the available NMR experimental data. In particular, theory forecasts a relatively small ^1J(CC) for the ultrashort bent CC single bond, an alkenic value for the ^1J(CC) of the ultrashort unbent CC single bond, a reduced alkanic value for the ^1J(CC) of the overlong CC single bond, and a large negative value for the geminal ^2J(CC) associated with the shortest C$\cdots$C nonbonding interaction. These predictions have been rationalized in terms of the hybridizations of the involved carbon atoms, as modeled by MO localization.

Acknowledgment. The research described herein has been supported by the Office of Basic Energy Sciences of the United States Department of Energy. This is Document No. NDRL-4192 from the Notre Dame Radiation Laboratory. We are grateful to Professors W. Lüttke (Universität Göttingen, Göttingen, Germany), G. Szeimies (Humboldt Universität, Berlin, Germany), and F. Toda (Ehime University, Ehime, Japan) for communicating some NMR experimental parameters prior to publication. V.G. thanks the Italian MURST for financial support.

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