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Theoretical study of spiropentane, spiropentene and spiropentadiene

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Abstract—HF, MP2, and DFT calculations with 6-31G** and 6-311++G** basis sets were carried out for spiropentane, spiropentene, and spiropentadiene. The results of the calculations show that the NMR determination of HCH bond angle in spiropentane is more accurate than the value measured by electron diffraction. They also indicate that the assignment of one of the signals in the experimental NMR spectrum of spiropentene is in error. The calculations confirm earlier conclusions drawn on the basis of low-level ab initio calculations concerning the operation of spiroconjugation in the investigated molecules. They also demonstrate that there is a need for further experimental studies of these molecules. © 2001 Elsevier Science Ltd. All rights reserved.

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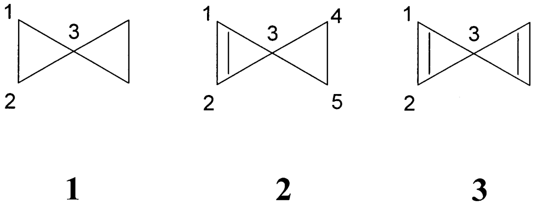
1. Introduction

Hydrocarbons with unusual spatial structure are fascinating research objects since, in addition to aesthetically pleasing shapes they have, their syntheses are challenging and reactivities exciting.[1] They can also, at longer run, find some applications.[2] In continuation of our studies of bowlane (that should have a pyramidal carbon atom), small-ring geminanes and bridged spiropentanes (one of which should possess a C–C–C bond angle of ca. 180°[3]), the present paper presents a computational study of spiropentane **1**, spiropentene **2** and spiropentadiene **3** (see Scheme 1). Spiropentane is known and well-studied.[4–10] **2**[11] and **3**[12] not only possess highly distorted double bonds but the latter molecule, having double bonds lying in perpendicular planes, is also a good model allowing one to investigate spiroconjugation, that is the interaction of perpendicular double bonds through a spiro junction. The problem has attracted considerable interest for many years[13] not only because of its theoretical significance but also due to its possible practical implications.[14,15] The syntheses of the highly unstable molecules **2** and **3**[11,12] have been reported. However, the latest calculations for them[10] have been performed at low theoretical levels some time ago. Therefore, it seemed of interest to study spiro molecules **1**–**3** using ab initio (at SCF and MP2 levels) and DFT calculations including the computation of NMR chemical shifts that were impossible to carry out in the earlier works.



1 **2** **3**

Scheme 1.

2. Results

The results of the calculations and available experimental data showing geometry of **1**–**3** are collected in Table 1, those pertaining to ^{13}C NMR chemical shifts are given in Table 2 while the calculated vibrational frequencies at MP2/6-311++G** level are summarized in Table 3. We do not address the problems with the calculation of chemical shifts of the TMS standard, since only chemical shift differences will be reported in this paper.

3. Discussion

3.1. Spiropentane 1

The experimental determination of molecular geometry have been carried out only for **1** for which ED[4], X-ray[5] and NMR[6] measurements of bond lengths and/or angles

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Keywords: strained hydrocarbons; spiranes; ab initio and DFT quantum calculations; structure; NMR.

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Table 1. The calculated and experimental values of bond lengths (Å) and angles (deg) in **1–3**

Spiropentane		C1–C2	C1–C3	C–H	HCH	CC(spiro)C			
Exp.	X-ray^5	1.527 (1.536)	1.482 (1.488)			137.1			
	ED^4	1.519	1.469	1.091	119.4±1.1	n.d.			
	NMR^6				115.0±0.7				
SCF/6-31G**		1.517	1.474	1.077	114.4	137.3			
MP2/6-31G**		1.520	1.475	1.077	114.7	137.2			
SCF/6-311++G**		1.517	1.474	1.077	114.5	137.3			
MP2/6-311++G**		1.535	1.484	1.086	115.5	137.1			
DFT1^a		1.530	1.485	1.087	114.3	137.3			
DFT2^a		1.531	1.483	1.085	114.6	137.2			
Spiropentene	C1–C2	C1–C3	C3–C4	C4–C5	C1–H	C4–H	C2C1(spiro)C4	HC4H	C3C1H
SCF/6-31G**	1.286	1.475	1.470	1.534	1.068	1.078	140.2	114.0	146.8
MP2/6-31G**	1.314	1.479	1.482	1.543	1.075	1.083	139.9	114.4	147.3
SCF/6-311++G**	1.286	1.476	1.472	1.537	1.068	1.078	140.2	114.2	146.8
MP2/6-311++G**	1.318	1.484	1.487	1.554	1.080	1.087	139.8	115.0	147.2
DFT1^a	1.304	1.485	1.485	1.547	1.080	1.088	140.1	113.8	147.0
DFT2^a	1.302	1.483	1.484	1.550	1.078	1.086	140.0	114.2	147.0
Spiropentadiene	C1–C2	C1–C3	C–H	HC1C2	C1C3(spiro)C4				
SCF/66-31G**	1.300	1.470	1.071	146.5	143.6				
MP2/6-31G**	1.327	1.481	1.079	146.1	143.1				
SCF/6-311++G**	1.298	1.471	1.071	146.5	143.6				
MP2/6-311++G**	1.331	1.485	1.083	146.2	143.1				
DFT1^a	1.316	1.484	1.083	146.2	143.5				
DFT2^a	1.314	1.482	1.081	146.2	143.5				

[a] DFT1 and DFT2 denote calculations at Becke3LYP/6-31G** or Becke3LYP/6-311++G** level, respectively.

have been reported. A comparison of calculated geometrical parameters with the corresponding experimental results is difficult since the experimental values obtained using different experimental techniques differ. For instance, the CC bond lengths determined by X-ray method[5] are larger than those measured by ED technique.[4] On the other hand, the value of HCH bond angle obtained by the latter method was shown by NMR study in nematic phase[6] to be

Table 2. The calculated (absolute) and experimental (with respect to TMS) values of isotropic magnetic shieldings (in ppm). Note, that only the differences in the calculated shifts are to be compared with experimental results

Spiropentane	δ_{C1}	δ_{C3}	$\delta_{C1}-\delta_{C3}$	δ_H				
SCF/6-31G**	197.7 (44.4)	198.2 (40.8)	−0.5	31.8 (15.3)				
MP2//6-31G**	197.6 (39.4)	197.2 (38.3)	0.4	31.2 (14.9)				
SCF/6-311++G**	190.6 (47.0)	190.8 (42.5)	−0.2	31.9 (14.8)				
MP2//6-311++G**	188.6 (43.0)	186.6 (40.9)	2.0	31.1 (14.3)				
DFT1^a	181.9 (41.4)	178.6 (41.5)	3.3	31.0 (13.2)				
DFT2^a	173.7 (44.9)	170.3 (44.7)	3.4	31.2 (12.9)				
HB//6-31G**	192.0 (47.9)	192.7 (43.4)	−0.7	31.6 (15.0)				
Exp.	186.8	180.9	5.9					
Spiropentene	δ_{C1}	δ_{C3}	δ_{C4}	$\delta_{C1}-\delta_{C3}$	$\delta_{C1}-\delta_{C4}$	δ_{H1}	δ_{H4}	$\delta_{H1}-\delta_{H4}$
SCF/6-31G**	90.9 (163.1)	191.9 (95.9)	199.8 (47.9)	−101.0	−108.9	24.8 (4.7)	32.0 (14.2)	−7.2
MP2//6-31G**	105.0 (137.3)	187.1 (90.8)	200.8 (43.7)	−82.1	−95.8	24.9 (3.2)	31.5 (13.8)	−6.6
SCF/6-311++G**	74.7 (178.0)	185.3 (101.2)	190.8 (45.8)	−110.6	−116.1	24.9 (4.4)	32.0 (13.2)	−5.1
MP2//6-311++G**	85.8 (155.9)	178.7 (100.0)	190.8 (41.9)	−92.9	−105.0	24.9 (2.6)	31.5 (13.0)	−6.6
DFT1^a	80.3 (152.9)	169.6 (95.4)	185.6 (47.1)	−89.3	−105.3	24.5 (2.2)	31.3 (12.3)	−6.9
DFT2^a	58.0 (177.7)	160.6 (101.5)	175.1 (45.8)	−102.6	−117.1	24.5 (2.4)	31.4 (11.5)	−6.9
HB//6-31G**	72.9 (178.0)	186.0 (99.9)	193.8 (48.2)	−113.1	−120.9	24.1 (4.9)	31.8 (13.8)	−7.7
Exp.	4.1	16.8	114.7	−12.7	−110.6	0.58	7.10	−6.52
Spiropentadiene	δ_{C1}	δ_{C3}	$\delta_{C1}-\delta_{C3}$	δ_H				
SCF/6-31G**	82.2 (182.8)	185.3 (52.4)	−103.1	24.6 (3.2)				
MP2//6-31G**	96.1 (158.3)	176.2 (51.7)	−80.1	24.7 (2.1)				
SCF/6-311++G**	65.6 (194.2)	178.6 (55.3)	−113.0	24.7 (3.1)				
MP2//6-311++G**	75.4 (173.5)	167.2 (56.6)	−91.8	24.5 (2.4)				
DFT1^a	71.1 (176.5)	161.3 (54.6)	−90.2	24.1 (3.7)				
DFT2^a	50.5 (193.2)	153.6 (60.2)	−103.1	24.2 (3.9)				
HB//6-31G**	67.3(194.9)	79.4(55.5)	−112.1	24.5(3.5)				
Exp.				7.62				

[a] DFT1 and DFT2 denote calculations at Becke3LYP/6-31G** or Becke3LYP/6-311++G** level, respectively.

Table 3. The calculated vibrational frequencies and intensities (in parentheses) of **1**–**3** at MP2/6-311++G** level in cm^{-1}

1	**2**	**3**
296.7 (0.0)	290.2 (2.2)	374.4 (29.4)
299.9 (0.2)	346.0 (0.0)	374.4 (29.4)
299.9 (0.2)	390.8 (11.3)	402.7 (0.0)
606.8 (0.0)	595.9 (64.0)	538.9 (34.5)
798.5 (0.5)	640.4 (0.2)	539.0 (34.5)
798.5 (0.5)	787.0 (4.2)	700.5 (0.0)
852.1 (0.0)	804.8 (1.7)	818.8 (28.0)
908.2 (6.8)	829.7 (0.0)	818.8 (28.0)
908.2 (6.8)	909.9 (0.0)	854.7 (0.0)
910.6 (18.9)	939.1 (5.9)	872.0 (0.0)
1026.4 (19.8)	984.4 (37.4)	919.7 (1.6)
1036.4 (0.0)	1014.4 (1.1)	1011.9 (0.0)
1068.0 (0.0)	1038.7 (14.0)	1082.1 (13.2)
1075.7 (1.7)	1052.5 (8.5)	1082.1 (13.2)
1075.7 (1.7)	1076.3 (0.0)	1482.5 (93.4)
1083.7 (0.0)	1076.3 (0.0)	1588.3 (0.0)
1179.8 (0.0)	1178.1 (0.0)	1621.0 (154.2)
1190.4 (0.0)	1440.0 (5.8)	3236.2 (3.1)
1196.0 (1.4)	1469.9 (1.3)	3236.2 (3.1)
1196.0 (1.4)	1527.5 (1.2)	3274.3 (0.0)
1452.5 (0.0)	1668.9 (37.8)	3279.3 (2.1)
1476.2 (1.3)	3148.0 (21.9)	
1476.2 (1.3)	3152.0 (10.9)	
1509.5 (0.0)	3240.4 (0.0)	
1613.5 (1.8)	3253.4 (21.0)	
3159.3 (17.2)	3278.5 (0.6)	
3159.3 (17.2)	3322.4 (0.1)	
3162.5 (0.0)		
3164.9 (25.4)		
3252.6 (0.0)		
3254.0 (0.0)		
3266.0 (15.1)		
3266.0 (15.1)		

overestimated by ca. 5°. Taking into account all these remarks the calculated results on spiropentane geometry (Table 1) can be summarized as follows: (1) The calculated bond lengths are much closer to X-ray than to ED data. (2) The calculated value of HCH bond angle agrees well with the result of NMR determination supporting the view that the corresponding ED value is not reliable. It should be stressed that the NMR study[6] was not later taken into account in experimental[5] and computational spiropentane studies.[8,9] (3) The calculated value of the CCC bond angle involving the spiro atom reproduces very well the experimental value for all levels of theory and the basis sets and methods used. Interestingly, on the basis of ab initio calculations with STO-3G and 4-31G basis sets Kao and Radom[10a] claim that in spiropentane there is no specific spiro interactions, that is no spiroconjugation. However, UV band at 232 nm in the spectrum of **1**[7] as compared with the spectrum of cyclopropane exhibiting bands in vacuum ultraviolet region below 170 nm[13] contradicts the latter conclusion.

SCF-level calculations yield incorrect trend in δ_{C1} and δ_{C3} values. Only MP2 values correctly give bigger, although too small, values of δ_{C1} than δ_{C3}. The biggest, still too small in comparison to experiment, value of $\delta_{C1}-\delta_{C3}$ was obtained using the DFT method.

3.2. Spiropentene 2

The synthesis of this molecule was reported by Bloch and Denis.[11] Its bond lengths and angles could not be determined, therefore only comparison of the calculated values with cyclopropane, cyclopropene and spiropentane geometry can be made. Similarly to the results for cyclopropene (not given in tables), the length of C1═C2 bond is consistently calculated too small. The calculated C1–C3 and C3–C4 bond lengths are close and the results do not allow one to decide which one should be longer. Interestingly, the C4–C5 bond is calculated longer in **2** than the corresponding bonds in **1**. In agreement with expectation, the C1H bond is calculated shorter than the C4H one.

NMR data for this compound were also given by Bloch and Denis[11] who based the structure elucidation on the observed values of ^{13}C–^{1}H coupling constants. As shown in Table 2, the calculated value of $\delta_{H1}-\delta_{H4}$ is in perfect agreement with the corresponding experimental value. Unfortunately, there are some inconsistencies in the reported carbon spectrum since the signals of equivalent carbon atoms do not agree with the atom numbering in this paper. Not knowing what standard the authors used in their measurements, we have chosen the most plausible assignment of the reported signals on the basis of cyclopropane[22], cyclopropene[23] and spiropentane **1**[7] spectra. This assignment yielded a reasonable value of $\delta_{C1}-\delta_{C4}$. However, the difference $\delta_{C1}-\delta_{C3}$ was unacceptable. This indicates that the spectrum given in Ref. 11 should be reinvestigated.

3.3. Spiropentadiene 3

Neither calculated values of bond lengths and angles nor chemical shifts can be compared with the corresponding experimental data since the structure and ^{13}C spectra was not reported.[12] On the other hand, the proton spectrum consists of one signal with little experimental information provided. However, the bond lengths and NMR spectra calculated with different basis sets and at SCF, MP2 or DFT levels exhibit similar trends. The calculated C1–C2 bond is slightly longer than the corresponding bond in spiropentene **2** but its value still seems to be too small for a double bond. Practically the same values have been obtained for C1–C3 bond in **3** and the corresponding C3–C4 bond in **2** while the corresponding CH bond in **3** is calculated slightly shorter than that in **2**. The values of CC(spiro)C bond angle increase when going from **1** to **3** for all basis sets and methods used. The calculated values of both δ_{C1} and δ_{C3} for **3** are smaller than the corresponding values for **2**. Interestingly, the lowest non-zero frequency for **3** (374.4 cm^{-1}) is considerably higher than the corresponding values for **1** and **2** (less than 300 cm^{-1}). This could indicate higher stability of **3** than **2**.

As discussed in detail by Kanda and coworkers[10b], spiroconjugation in **3** manifests itself in the splitting of the cyclopropene LUMO into two sets of *b*1 and *a*2 symmetry orbitals. The eigenvalues associated with the latter orbitals calculated at the HF/STO-3G level were equal to 0.292 and 0.311, respectively. These values decreased to 0.165 and 0.209 at the HF/6-31G** level, and were as small as 0.042 and 0.052 at the MP2/6-311++G** level. It should be noted that the direct, through space interaction of two banana ethylene bonds located at the same distance as the corresponding bonds in spiropentadiene leads to much smaller

(0.0016) energy difference. Thus, the calculations seem to indicate that **3** exhibits small, but distinct spiroconjugation. UV spectra could provide further arguments in favor of it. As mentioned above, somewhat unexpectedly **1** exhibits absorption at 232 nm[7] while cyclopropane absorbs in UV below 170 nm.[13] Unfortunately, the spectra of **2** could not be measured in view of impurities[11] and no UV spectra of **3** have been given in[12] (probably for the same reason) indicating the need for further studies of the simple spiro molecules.

4. Conclusions

Calculations for spiropentane, spiropentene, and spiropentadiene at HF, MP2 and DFT level using 6-31G** and 6-311++G** basis sets indicate that the value of HCH bond angle determined by electron diffraction is less reliable than that obtained by NMR measurements. They also suggest that NMR spectrum of spiropentene should be established once more since it cannot be reconciled with either the calculated values or the pertaining cyclopropane and cyclopropene data. The results of the calculations confirm earlier conclusions drawn on the basis of less accurate ab initio calculations concerning the operation of spiroconjugation in the molecules under investigation. They also indicate the need for further experimental studies of not only NMR but also of UV spectra of the title compounds.

5. Method

All geometry optimizations were carried out using GAUSSIAN 98 program package.[16] Initially they were performed at the SCF/6-31G** level and such optimized geometries were used as initial parameters for the geometry optimizations at the MP2 approximation with two basis sets: 6-31G** and 6-311++G**. In addition, geometrical parameters of all considered structures were reoptimized and analytical harmonic vibrational frequencies calculated at the B3LYP/6-31G** level.[17] SCF and MP2 isotropic magnetic shieldings were calculated by gauge including atomic orbitals (GIAO)[18,19] procedure using GAUSSIAN 98 program package for 6-31G** and 6-311++G** basis sets. In addition, the shieldings have been calculated for Hansen and Bouman's basis set of double-zeta quality (denoted as HB in Table 2)[20] using the program developed by Wolinski et al.[21] The latter basis set was composed of (31/1) atomic orbitals contracted to [2s1p] for the hydrogen atom and (721/221/1) atomic orbitals contracted to [3s3p1d] for the carbon atom. The latter basis set was chosen since it was developed for the calculations of magnetic shieldings. As revealed by the data collected in Table 2, the calculations with this basis set agree well with those obtained using 6-311++G** basis set.

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