

Indirect Nuclear Spin-Spin Coupling Constants $^1J(^{17}\text{O}, ^{13}\text{C})$ in Derivatives of Carbon Dioxide and Carbon Monoxide – Density Functional Theory (DFT) Calculations

Bernd Wrackmeyer

Anorganische Chemie II, Universität Bayreuth, D-95440 Bayreuth, Germany

Reprint requests to Prof. Dr. B. Wrackmeyer. E-mail: b.wrack@uni-bayreuth.de

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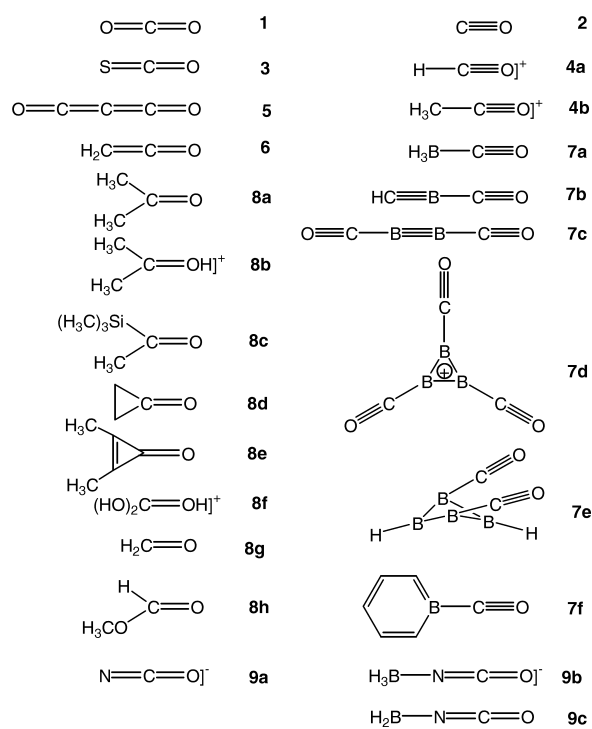
Calculations of spin-spin coupling constants $^1J(^{17}\text{O}, ^{13}\text{C})$ in carbon dioxide (1) carbon monoxide (2) and several derivatives using density functional theory (DFT) have been carried out. This coupling constant possesses a positive sign [reduced coupling constant $^1K(^{17}\text{O}, ^{13}\text{C}) < 0$] except for the parent acylium cation $[\text{H-CO}]^+$ (4a). It is shown that the Fermi contact term (FC) is positive [> 0 for $^1K(^{17}\text{O}, ^{13}\text{C})$] and that there are significant contributions from spin-dipole (SD) and paramagnetic spin-orbital (PSO) interactions.

Key words: Carbon Dioxide, Carbon Monoxide, NMR, Coupling Signs, MO Calculations

Introduction

In contrast to the large data set of one-bond ^{13}C -X spin-spin coupling constants available for numerous common nuclei X throughout the Periodic Table [1] (e.g., X = ^1H , $^6,7\text{Li}$, ^{11}B , ^{15}N , ^{19}F , ^{29}Si , ^{31}P , ^{77}Se , ^{51}V , ^{55}Mn , ^{57}Fe , ^{103}Rh , $^{117,119}\text{Sn}$, ^{123}Te , ^{195}Pt , ^{207}Pb), very few data $^1J(^{17}\text{O}, ^{13}\text{C})$ have been obtained experimentally [2, 3]. This is due to the small natural abundance of ^{17}O (0.037%) and its sizeable quadrupole moment ($I = 5/2$; $Q = -2.6 \cdot 10^{-28} \text{ m}^2$). While the former problem can be overcome by using ^{17}O labelled compounds, the latter is more difficult. In most oxygen compounds, the quadrupolar ^{17}O relaxation rate is fast, leading to broad ^{17}O NMR signals, and in general, scalar ^{17}O -X spin-spin coupling is averaged which means that neither ^{17}O nor X resonance signals show resolved splitting owing to $J(^{17}\text{O}, \text{X})$, except in favourable cases, when the electric field gradient at the oxygen atom is small or the magnitude of the coupling constant $J(^{17}\text{O}, \text{X})$ is large.

Recent progress in the quantum chemical treatment of molecular structures is promising also with respect to calculations of indirect nuclear spin-spin coupling constants $J(\text{X}, \text{Y})$ [4, 5]. In particular, density functional methods (DFT) such as B3LYP [6] provide fairly accurate J values as has been shown already for polyhedral boranes [7], cyclic hydrocarbons [8], carbenes [9], nitriles and phosphalkynes [10] to name just a



Scheme 1. Molecules studied by B3LYP/6-311+G(d,p) calculations for geometry and NMR parameters.

few applications. In the present work, the geometries of carbon dioxide, carbon monoxide and some of their derivatives (Scheme 1) were optimized [B3LYP/6-

Table 1. Calculated and experimental ^{17}O NMR parameters^a of carbon dioxide **1**, carbon monoxide **2** and derivatives **3–9** (see Scheme 1 for the structures).

Compound No.	$\delta^{17}\text{O}$ (found)	$\delta^{17}\text{O}$ (calcd.)	$^1J(^{17}\text{O}, ^{13}\text{C})$ (calcd.) [Hz]	FC (calcd.) [Hz]	SD (calcd.) [Hz]	PSO (calcd.) [Hz]
1	350.1	350.1	+17.1 ^b	+14.8	−2.7	+5.0
2	+65.0	+63.4	+17.2 ^c	+9.0	−5.7	+12.8
3	+200.2	+201.5	+21.5	+15.9	−3.0	+8.7
4a	—	+316.2	−8.2	+2.4	−12.2	+1.6
4b	+299.5	+303.2	+0.6	+6.5	−9.6	+3.7
5	—	+144.5	+12.1	+5.2	−2.3	+9.2
6	—	+301.8	+16.5	+5.4	−2.2	+13.4
7^o	—	+304.4	+13.1	+2.5	−6.1	+9.4
7b	—	+237.6	+19.3	+5.2	+0.2	+13.9
7c	—	+229.0	+40.5	+13.8	+6.3	+20.3
7d^d	—	+399.2	+8.8	+7.2	−7.2	+8.7
7e^e	—	+336.6	+16.7	+9.1	−4.1	+11.7
7f	—	+385.5	+17.9	+9.0	−3.5	+12.4
8a	+596.6	+613.7	+32.1	+15.1	−2.3	+19.4
8b	+310.3 ^f	+294.2	+31.8	+17.0	−0.5	+15.3
8c	+740.0 ^g	+763.2	+43.2	+18.6	−0.5	+25.2
8d	+524.0 ^h	+574.1	+39.7	+20.0	−1.6	+21.4
8e	+233.0 ^h	+237.5	+38.2	+27.6	−0.9	+11.6
8f	—	+125.5	+20.1	+12.1	−0.3	+8.4
8g	—	+716.5	+33.2	+13.4	−2.3	+22.1
8h (C=O)	+364.1	+383.8	+28.2	+17.3	−2.3	+17.3
(C-OMe) ⁱ	+140.6	+153.0	+40.1	+32.5	+0.2	+7.5
9^o	+43.0 ^j	−5.6	+29.0	+20.2	+1.0	+7.8
9b	—	+16.4	+22.2	+14.4	+0.5	+7.4
9c	—	+146.3	+13.0	+8.0	−2.1	+7.1

^a Calculated $\sigma(^{17}\text{O})$ data are converted to $\delta^{17}\text{O}$ data by $\delta^{17}\text{O} = \sigma(^{17}\text{O})[\text{CO}] - \sigma(^{17}\text{O}) + 350.1$, with $\sigma(^{17}\text{O})[\text{CO}] = -72.3$, $\delta^{17}\text{O}[\text{CO}] = 350.1$ and $\delta^{17}\text{O}[\text{H}_2\text{O}(\text{liquid})] = 0$; experimental data are taken from [12] if not stated otherwise. FC, SD and PSO mean Fermi contact, spin-dipole and paramagnetic spin-orbital term. All contributions to the reduced coupling constant $^1K(^{17}\text{O}, ^{13}\text{C})$ have the opposite sign.

^b Experimental: 16.1 Hz [2]; ^c Experimental: 16.4 Hz [2]. ^d Calculated $^1J(^{11}\text{B}, ^{11}\text{B}) = +70.7$ Hz and $^1J(^{13}\text{C}, ^{11}\text{B}) = +135.0$ Hz. ^e Calculated $^1J(^{11}\text{B}, ^{11}\text{B}) = +41.9$ Hz and $^1J(^{13}\text{C}, ^{11}\text{B}) = +99.6$ Hz. ^f See [19] and G. A. Olah, A. Burrichter, G. Rasul, R. Gnann, K. O. Christe, C. K. S. Prakash, J. Am. Chem. Soc. **119**, 8035 (1997). $^1J(^{17}\text{O}, ^1\text{H}) = 74.0$ Hz; this work: calc.: $^1J(^{17}\text{O}, ^1\text{H}) = -75.0$ Hz (FC: −68.4; SD: −0.2; PSO: −6.0 Hz). ^g S. Chimichi, C. Mealli, J. Mol. Struct. **271**, 133 (1992). ^h For $\delta^{17}\text{O}$ data of cyclopropanones and cyclopropenones see [18].

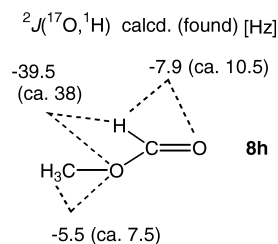
ⁱ Calculated $^1J(^{17}\text{O}, ^{13}\text{C}_{\text{Me}}) = +20.0$ Hz (FC: +23.5 Hz; SD: −1.9 Hz; PSO: −1.4 Hz). ^j Aqueous solution; B. Wrackmeyer, R. Köster, Chem. Ber. **112**, 2022 (1982).

311+G(d,p) level [6,11]], and NMR parameters such as chemical shifts and coupling constants were calculated at the same level of theory.

Results and Discussion

Calculated chemical shifts $\delta^{17}\text{O}$ and coupling constants $^1J(^{17}\text{O}, ^{13}\text{C})$ of **1–9** are listed in Table 1. The agreement of the calculated $\delta^{17}\text{O}$ data with experimental values is satisfactory, indicating that the optimized gas phase geometries do not deviate significantly from the molecular structures in solution. The agreement with $\delta^{17}\text{O}$ values determined experimentally for some of the compounds in the gas phase [12] is even better.

$^1J(^{17}\text{O}, ^{13}\text{C})$ has been measured accurately for carbon dioxide (**1**: 16.4 ± 0.1 Hz) and carbon monoxide (**2**: 16.1 ± 0.1 Hz) [2], whereas an estimated value



Scheme 2. Comparison of calculated and experimental geminal coupling constants $^2J(^{17}\text{O}, ^1\text{H})$ in methyl formate. The calculated value $^2J(^{17}\text{O}, ^1\text{H}_{\text{Me}})$ is the mean value (−1.7, −1.7, and −13.0 Hz), since the hydrogen atoms of the methyl group occupy non-equivalent positions according to the optimized geometry.

of 22 Hz was reported for acetone **8a** [3]. The calculated data $^1J(^{17}\text{O}, ^{13}\text{C})$ for **1** (17.1 Hz) and **2** (17.2 Hz) agree very well with the experimental values, whereas

in the case of **8a**, the calculated value (32.1 Hz) is markedly greater. The general reliability of the calculations of spin-spin couplings involving ^{17}O can also be shown by the agreement with experimental data [13] for $^2J(^{17}\text{O}, ^1\text{H})$ in **8h** (Scheme 2).

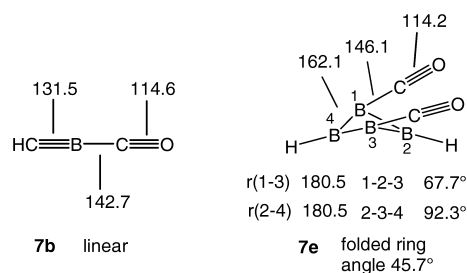
A positive sign of $^1J(^{17}\text{O}, ^{13}\text{C})$ has been suggested for **1** and **2** [2], and this is confirmed here by the DFT calculations. The reduced coupling constant $^1K(^{17}\text{O}, ^{13}\text{C}) = 4\pi^2 ^1J(^{17}\text{O}, ^{13}\text{C}) [\gamma(^{13}\text{C})\gamma(^{17}\text{O})]^{-1}$ is negative, since $\gamma(^{17}\text{O}) < 0$. In fact, all calculated values $^1J(^{17}\text{O}, ^{13}\text{C})$ possess a positive sign except for $[\text{H-CO}]^+$ (**4a**). In contrast with the experimental data, the calculations provide information on the relative contributions of the three major coupling mechanisms [14]. Usually the Fermi contact term (FC) is regarded as the dominant mechanism, except for scalar coupling involving the ^{19}F nucleus [15]. It is well known [16] that lone pairs of electrons at one of the nuclei in one-bond scalar nuclear spin-spin coupling may cause the Fermi contact term to change its sign from positive to negative (for 1K). In the compounds considered here, there is at least one lone pair of electrons at the ^{17}O nucleus. This explains why the FC contribution to $^1J(^{17}\text{O}, ^{13}\text{C})$ is positive [< 0 for $^1K(^{17}\text{O}, ^{13}\text{C})$] in all cases studied. The calculations indicate that the contribution from the paramagnetic spin-orbital term (PSO) to $^1J(^{17}\text{O}, ^{13}\text{C})$ can be large and positive [< 0 for $^1K(^{17}\text{O}, ^{13}\text{C})$]. Frequently, the PSO contribution is even larger than the FC contribution. The diamagnetic spin-orbital term (DSO) is small (≤ 0.1 Hz, of either sign) in all cases studied, and will not be considered further. The magnitude of the spin-dipole contribution (SD) to $^1J(^{17}\text{O}, ^{13}\text{C})$ can also be substantial, in some cases larger than FC or PSO contributions, and it can be of either sign.

Both the PSO and the SD contributions to $^1J(^{17}\text{O}, ^{13}\text{C})$ arise from the presence of the lone pair of electrons at oxygen and from multiple bonding [17], and have to be considered in general, when occupied and virtual orbitals are close in energy and the external field B_0 can induce electronic currents. The magnitude of the SD contribution is smaller for formal $\text{C}=\text{O}$ bonds and it is larger and negative [> 0 for $^1K(^{19}\text{O}, ^{13}\text{C})$], in most cases, for $\text{C}\equiv\text{O}$ bonds. Noteworthy exceptions are the molecules **7b** and **7c**, in which the nature of the $\text{C}\equiv\text{O}$ bond is affected by interactions of the $\pi^*(\text{C}\equiv\text{O})$ orbitals with π orbitals of the $\text{C}\equiv\text{B}$ and $\text{B}\equiv\text{B}$ bond, respectively. The PSO term becomes particularly large and positive [< 0 for $^1K(^{17}\text{O}, ^{13}\text{C})$] in CO itself and in ketones and derivatives, where magnetic-dipole al-

lowed $n \rightarrow \pi^*$ transitions are important. This is evident from the PSO values for ketene (**6**: +13.4 Hz), acetone (**8a**: +19.4 Hz), cyclopropanone (**8d**: +21.4 Hz), and acetyl trimethylsilane (**8c**: +25.2 Hz). Interestingly, the PSO term in 2,3-dimethyl-cyclopropanone **8e** (+11.6 Hz) is much smaller than in **7d** which indicates a different bonding situation in **8e** as a result of the contribution of a low-energy zwitterionic structure to the ground state. This is also indicated by the increased ^{17}O nuclear shielding in **8e** when compared with **8d** [18]. It should be noted that even for coupling constants $^1J(^{17}\text{O}, ^1\text{H})$, as shown in the case of **8b**, the PSO contribution is significant (−6.0 Hz), although much smaller than the Fermi contact term (−68.4 Hz); the agreement between the calculated (−75.0 Hz) and experimental value (74 Hz [19]) of $^1J(^{17}\text{O}, ^1\text{H})$ is almost perfect.

The molecules **7** containing the B-CO fragment deserve attention. The long known borane adduct $\text{H}_3\text{B-CO}$ (**7a**) reminds of transition metal carbonyl complexes. Isolobal [20,21] replacement of one CH unit in benzene by the B-CO fragment leads to the borabenzene-adduct **7f**, which has been isolated [22] and described by theory [23]. Other intriguing examples are **7b–e**, demonstrating the isolobal relationship [20] between the CH and the B-CO fragments [21]. Compound **7c** has been isolated in an argon matrix [22], described by theory [22,23,25], as has the cation **7d** [25]. The compound **7b** (still unknown) was included here for comparison, and **7e** (also unknown) is the analogue of the non-classical 1,3-dihydro-1,3-diborete [26], constructed by isolobal replacement of both CH fragments by the B-CO units (Scheme 3).

The wealth of information on spin-spin coupling, hardly accessible by experiments, is revealed by the calculations as shown in Scheme 4 for the linear molecule **7c** as an example. Evidence from vibrational spectroscopy [24] and the short B-B bond (144.4 pm)



Scheme 3. Structural parameters (bond lengths given in pm) of the compounds **7b** and **7e** containing B-CO fragments.

OC—B≡B—CO		[Hz]	FC	SD	PSO
7c	$^1J(^{17}\text{O}, ^{13}\text{C})$	+40.5	+13.8	+6.3	+20.3
	$^1J(^{13}\text{C}, ^{11}\text{B})$	+113.6	+127.6	-6.4	-7.8
	$^1J(^{11}\text{B}, ^{11}\text{B})$	+233.4	+219.2	+8.0	+6.1
	$^2J(^{17}\text{O}, ^{11}\text{B})$	+12.3	-9.2	+10.5	+10.9
	$^3J(^{17}\text{O}, ^{11}\text{B})$	-23.5	+6.4	-13.4	-16.5
	$^4J(^{17}\text{O}, ^{13}\text{C})$	-29.0	-6.4	-11.2	-11.4
	$^5J(^{17}\text{O}, ^{17}\text{O})$	+35.1	-2.3	+17.7	+19.6
	$^2J(^{13}\text{C}, ^{11}\text{B})$	+77.0	+56.5	+9.3	+11.2
	$^3J(^{13}\text{C}, ^{13}\text{C})$	-3.2	-16.0	+6.4	+6.3

Scheme 4. List of all calculated coupling constants in the linear molecule **7c**.

suggest a Lewis structure with a B≡B bond. This is in full agreement with the magnitude of the calculated coupling constant $^1J(^{11}\text{B}, ^{11}\text{B}) = +233.4$ Hz which is large when compared with $^1J(^{11}\text{B}, ^{11}\text{B})$ for polyhedral boranes (≤ 30 Hz) and for compounds containing typical B-B single bonds (≤ 120 Hz) [7, 27]. The predicted magnitude of long range coupling constants across up to five bonds in **7c** is fairly large, typical of extended π systems, and both SD and PSO contributions can be dominant, as in the case of $^5J(^{17}\text{O}, ^{17}\text{O})$. In the linear π system in **7c**, the magnitude of the long range coupling constants is much larger than for the cyclic molecules **7d** and **7e** (the aromatic character of **7d** has been demonstrated by theory [24]).

Conclusion

The calculations of the coupling constants $^1J(^{17}\text{O}, ^{13}\text{C})$ show that the contribution of the Fermi contact term to the reduced coupling constants $^1K(^{17}\text{O}, ^{13}\text{C})$ is always negative except for the acylium cation **4a**. This is the result of the influence of the lone pair(s) of

electrons at the oxygen atoms and the inherent electronegative character of oxygen. These findings bridge the gap between $^1K(^{15}\text{N}, ^{13}\text{C})$, for which numerous examples with positive or negative sign are known, and $^1K(^{19}\text{F}, ^{13}\text{C})$ which is invariably negative. The calculations allow to evaluate the contributions arising from spin-dipole (SD) and spin-orbital interactions (SO) in addition to the Fermi contact term. This information is not available from experiments. The calculated data clearly show that both SD and SO contributions can be even more important than the Fermi contact term. Previously it had been assumed that this situation is typical only for spin-spin coupling involving the ^{19}F nucleus.

Experimental Section

All calculations were performed using the Gaussian 03 package [28]. The gas phase geometries were optimized with DFT methods (B3LYP) [6] and the 6-311+G(d,p) basis set [11]. The calculated structures were found to be minima on the respective potential energy surface as checked by the stability of the wave function and by the absence of imaginary frequencies ($\text{Nimag} = 0$). Expectedly [4, 5], HF calculations of the coupling constants gave poor results, pure DFT methods gave better results, but still less convincing when compared with the B3LYP method. This was checked for **1** and **2**, for which accurate experimental data are available [2]. Table 1 contains the paramagnetic spin-orbital (PSO) contribution; the diamagnetic spin-orbital (DSO) contribution was < 1 Hz in all cases studied.

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