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**Competitive tetrel bond and hydrogen bond in benzaldehyde-CO₂:
Characterization by rotational spectroscopy**

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Contents:

1. **Table S1.** The calculated spectroscopic parameters of the three isomers of the BA-CO₂ complex at different levels of theory.
2. **Table S2.** Measured intensities (in arbitrary units) of the two isomers for several μ_a -type selected transitions.
3. **Tables S3-4.** Partial r_0 and B3LYP-D3(BJ)/6-311++G(d,p) calculated geometries of isomers I and II of BA-CO₂.
4. **Tables S5-8.** NBO energies (> 0.2 kJ mol⁻¹) of complexes between CO₂ and different molecules with aldehyde group (including H₂CO-CO₂, FM-CO₂, BA-CO₂-I, BA-CO₂-II) at the RHF/aug-cc-pVTZ level.
5. **Tables S9-10.** Experimental transition frequencies of the observed isomers (I and II) of benzaldehyde-CO₂ (BA-CO₂).

Table S1. The calculated spectroscopic parameters of the three isomers of the BA-CO₂ complex at different levels of theory.

		<i>A/B/C</i> MHz	Max ^{<i>a</i>} (%)	$\Delta E_0/\text{cm}^{-1}$	$\Delta E_{0,\text{BSSE}}/\text{cm}^{-1}$	
EXP	I	3652.812/403.737/363.943				
	II	2541.70/503.5558/421.4520		-		
MP2	6-311++G(d,p)	I	3616/401/361	1.6%	0	0
		II	2488/506/420	-2.1%	17	29
		III	1173/1082/241	-	543	631
	aug-cc-pVTZ	I	3644/410/369	1.6%	0	0
		II	2525/516/429	2.6%	84	126
		III	1224/1095/759	-	417	593
B3LYP-D3(BJ)	6-311++G(d,p)	I	3672/407/366	0.8%	0	0
		II	2545/513/427	1.8%	47	53
		III	1151/1075/738	-	138	196
	aug-cc-pVTZ	I	3681/407/366	0.8%	0	0
		II	2546/513/426	1.8%	61	76
		III	1160/1070/733	-	167	190
M06-2X	6-311++G(d,p)	I	3702/418/376	3.3%	0	0
		II	2657/517/733	3.3%	137	149
		III	1240/1098/770	-	179	268
	aug-cc-pVTZ	I	3709/418/376	4.5%	0	0
		II	2643/515/431	4.0%	157	175
		III	1235/1099/765	-	298	345

^a The values in parentheses are percentage differences defined as: $100\% \times (\text{experimental-theoretical})/\text{experimental}$.

Table S2. Measured intensities (in arbitrary units) of the two observed isomers for several μ_a -type selected transitions.

Transition	Isomer	Frequency (MHz)	Intensity
$8_{08} \leftarrow 7_{07}$	I	6111.0790	0.0488
	II	7211.4173	0.0358
$8_{18} \leftarrow 7_{17}$	I	5975.1630	0.0442
	II	7028.2600	0.0165
$9_{09} \leftarrow 8_{08}$	I	6865.9630	0.0194
	II	8409.4478	0.0146
$12_{012} \leftarrow 11_{011}$	I	9112.0734	0.0290
	II	10589.8151	0.0137
$12_{112} \leftarrow 11_{111}$	I	8949.7003	0.0522
	II	10476.5107	0.0164
$13_{013} \leftarrow 12_{012}$	I	9854.2714	0.0192
	II	11424.3947	0.0171
$13_{113} \leftarrow 12_{012}$	I	9691.3632	0.0396
	II	11331.5250	0.0141

Table S3. Partial r_0 and B3LYP-D3(BJ)/6-311++G(d,p) calculated geometries of isomer I.

Bond lengths (Å)		Valence angles (°)		Dihedral angles (°)	
C1O2	1.163				
C1O3	1.159	O2C1O3	177.1		
C1O4	2.804(7)^a	O3C1O4	93.3(1)	O4C1O3O2	180.0
O4C5	1.214	C1O4C5	112.1	O2C1O4C5	0.0
C5C6	1.475	O4C5C6	124.7	C1O4C5C6	180.0
C6C7	1.398	C5C6C7	119.3	C4C5C6C7	-180.0
C7O8	1.392	C6C7O8	120.1	C5C6C7O8	180.0
C8C9	1.394	C7O8C9	119.6	C6C7O8C9	0.0
C9O10	1.398	O8C9O10	120.4	C7O8C9O10	0.0
C6C11	1.401	C7C6C11	120.0	C8C7C6C11	0.0
C11H12	1.083	C6C11H12	118.7	C7C6C11H12	180.0
C10H13	1.084	C9C10H13	119.9	C8C9C10H13	-180.0
C9H14	1.084	C8C9H14	119.8	C7C8C9H14	-180.0
C8H15	1.083	C9C8H15	120.1	C10C9C8H15	-180.0
C7H16	1.085	C8C7H16	120.3	C9C8C7H16	180.0
C5H17	1.108	O6C5H17	115.1	C7O6C5H17	0.0

^a Error in parentheses in units of the last digit. The parameters in bold have been adjusted to reproduce the experimental values of rotational constants. Their theoretical values are 2.788 Å and 94.87°, respectively.

Table S4. Partial r_0 and B3LYP-D3(BJ)/6-311++G(d,p) calculated geometries of isomer II.

Bond lengths (Å)		Valence angles (°)		Dihedral angles (°)	
C1O2	1.163				
C1O3	1.159	O2C1O3	177.8		
C1O4	2.893(9)^a	O3C1O4	90.7(3)	O4C1O3O2	180.0
O4C5	1.213	C1O4C5	151.5	O2C1O4C5	0.0
C5C6	1.476	O4C5C6	125.3	C1O4C5C6	0.0
C6C7	1.399	C5C6C7	119.1	C4C5C6C7	-180.0
C7O8	1.394	C6C7O8	120.2	C5C6C7O8	180.0
C8C9	1.394	C7O8C9	119.6	C6C7O8C9	0.0
C9O10	1.398	O8C9O10	120.4	C7O8C9O10	0.0
C6C11	1.401	C7C6C11	120.0	C8C7C6C11	0.0
C11H12	1.082	C6C11H12	119.1	C7C6C11H12	180.0
C10H13	1.084	C9C10H13	119.9	C8C9C10H13	180.0
C9H14	1.084	C8C9H14	119.8	C7C8C9H14	-180.0
C8H15	1.083	C9C8H15	120.1	C10C9C8H15	-180.0
C7H16	1.085	C8C7H16	120.3	C9C8C7H16	180.0
C5H17	1.108	O6C5H17	115.1	C7O6C5H17	0.0

^a Error in parentheses in units of the last digit. The parameters in bold have been adjusted to reproduce the experimental values of rotational constants. Their theoretical values are 2.871 Å and 90.5°, respectively.

Table S5 NBO energies (> 0.21 kJ mol⁻¹) of the H₂CO-CO₂ complex.

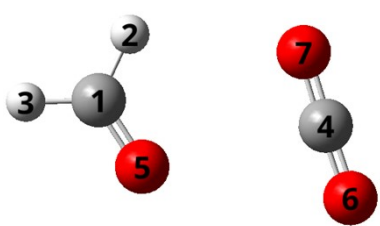
Donor NBO	Acceptor NBO	E (kJ mol ⁻¹)	Complexes
From H ₂ CO to CO ₂			
σ(1) C1 - H3	RY*(7) C4	0.38	
σ(1) C1 - O5	RY*(1) C4	0.75	
σ(1) C1 - O5	RY*(5) C4	0.21	
LP (1) O5	RY*(5) C4	0.38	
LP (1) O5	RY*(7) C4	0.25	
LP (1) O5	π*(3) C4 – O6	1.80	
LP (2) O5	RY*(6) C4	0.25	
LP (2) O5	π*(3) C4 – O6	4.69	
From CO ₂ to H ₂ CO			
LP (2) O7	σ*(1) C1 - H2	0.38	
LP (2) O7	σ*(1) C1 – H3	0.46	

Table S6. NBO energies ($> 0.21 \text{ kJ mol}^{-1}$) of the FM-CO₂ complex.

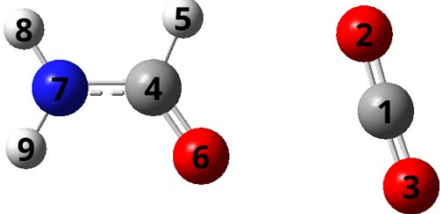
Donor NBO	Acceptor NBO	E (kJ mol ⁻¹)	Complexes
From FM to CO ₂			
σ(1) C4 – H5	RY*(6) C1	0.29	
σ(1) C4 – H5	RY*(9) C1	0.59	
π(1) C4 – O6	π*(1) C1 – O3	0.21	
π(2) C4 – O6	RY*(1) C1	0.67	
π(2) C4 – O6	RY*(5) C1	0.25	
σ(1) C4 – N7	RY*(5) C1	0.21	
LP (1) O6	RY*(5) C1	0.92	
LP (1) O6	RY*(3) O3	0.21	
LP (1) O6	RY*(4) O3	0.25	
LP (1) O6	π*(3) C1 – O3	2.51	
LP (2) O6	RY*(6) C1	0.50	
LP (2) O6	π*(3) C1 – O3	6.90	
From CO ₂ to FM			
π(1) C1 – O2	RY*(1) C4	0.25	
π(1) C1 – O2	RY*(4) C4	0.33	
LP (1) O2	σ*(1) C4 – H5	0.92	
LP (1) O2	σ*(1) C4 – N7	0.25	
LP (2) O2	σ*(1) C4 – H5	0.80	
LP (2) O2	σ*(1) C4 – N7	0.24	

Table S7. NBO energies (> 0.21 kJ mol⁻¹) of the BA-CO₂-I complex.

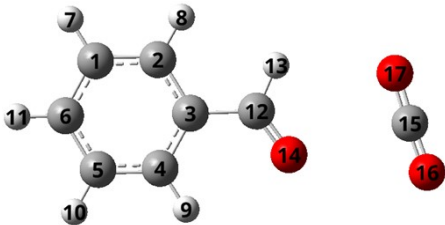
Donor NBO	Acceptor NBO	E (kJ mol ⁻¹)	Complexes
From BA to CO ₂			
σ(1) C3 – C12	RY*(5) C15	1.76	
π(1) C12 – O14	RY*(1) C15	0.54	
π(1) C12 – O14	RY*(5) C15	0.29	
π(1) C12 – O14	RY*(3) O16	0.29	
π(2) C12 – O14	LP*(2) C15	0.25	
LP (1) O14	π*(1) C15 – O16	3.01	
LP (1) O14	RY*(5) C15	0.59	
LP (1) O14	RY*(3) O16	0.25	
LP (2) O14	π*(1) C15 – O16	8.66	
LP (2) O14	RY*(7) C15	0.33	
From CO ₂ to BA			
π(1) C15 – O17	RY*(1) C12	0.25	
π(1) C15 – O17	RY*(5) C12	0.25	
π(1) C15 – O17	RY*(3) H13	0.21	
LP (1) O17	RY*(3) H13	1.67	
LP (1) O17	σ*(1) C12 – H13	0.25	
LP (2) O17	σ*(1) C3 – C12	0.67	
LP (2) O17	σ*(1) C12 – H13	0.29	

Table S8. NBO energies (> 0.21 kJ mol⁻¹) of the BA-CO₂-II complex.

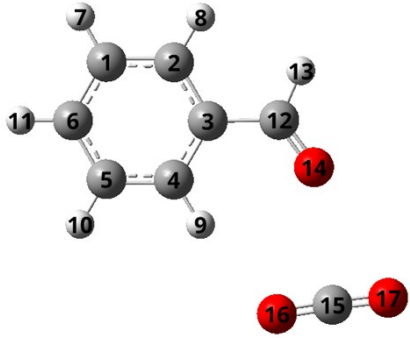
Donor NBO	Acceptor NBO	E (kJ mol ⁻¹)	Complexes
From BA to CO ₂			
σ(1) C3 – C4	RY*(5) O16	0.33	
σ(1) C4 – C5	RY*(6) C15	0.25	
π(1) C12 – O14	RY*(4) C15	0.25	
π(1) C12 – O14	RY*(5) C15	0.75	
π(1) C12 – O14	RY*(6) C15	0.33	
π(1) C12 – O14	RY*(3) O17	0.29	
π(2) C12 – O14	RY*(7) C15	0.21	
LP (1) O14	π*(1) C15 – O16	3.68	
LP (1) O14	RY*(5) C15	0.38	
LP (1) O14	RY*(3) O17	0.33	
LP (2) O14	π*(1) C15 – O16	1.72	
From CO ₂ to BA			
π(1) C15 – O17	RY*(2) H9	0.21	
LP (1) O16	RY*(1) H9	1.42	
LP (1) O16	RY*(3) H9	0.25	
LP (1) O16	σ*(1) C4 – H9	1.97	
LP (2) O16	RY*(1) H9	1.38	
LP (2) O16	σ*(1) C4 – H9	2.55	

Table S9. Experimental transition frequencies ν of the parent species of isomer I with quantum numbers and difference to calculated frequencies $\Delta\nu$ in the least squares fit.

Transition		ν/MHz	$\Delta\nu/\text{kHz}$
$J' K_a' K_c'$	$\leftarrow J'' K_a'' K_c''$		
8 0 8	7 0 7	6111.0812	0.6
8 1 8	7 1 7	5975.1636	-0.1
8 1 7	7 1 6	6292.9963	0.7
9 0 9	8 0 8	6865.9630	-1.5
9 1 9	8 1 8	6719.9006	-1.2
9 1 8	8 1 7	7077.0880	-0.6
9 2 8	8 2 7	6902.4601	0.5
9 2 7	8 2 6	6945.4757	-1.4
9 3 7	8 3 6	6914.5910	-0.9
9 3 6	8 3 5	6915.5479	0.2
9 4 6	8 4 5	6912.4970	3.9
9 5 5	8 5 4	6911.4014	-1.4
10 0 10	9 0 9	7617.8733	10.2
10 1 9	9 1 8	7860.2267	-0.9
10 2 9	9 2 8	7667.4534	-1.1
10 2 8	9 2 7	7726.1991	0.9
10 3 8	9 3 7	7684.0042	-0.9
10 3 7	9 3 6	7685.6411	-0.8
10 4 7	9 4 6	7681.2882	8.3
10 5 6	9 5 5	7679.7843	-0.1
11 0 11	10 0 10	8366.5989	-1.0
11 1 10	10 1 9	8642.2713	-1.6
11 2 10	10 2 9	8431.8347	-2.8
11 2 9	10 2 8	8509.4497	-1.7
11 3 9	10 3 8	8453.6988	0.0
11 3 8	10 3 7	8456.3536	-1.2
11 4 8	10 4 7	8450.2944	-1.3
11 4 7	10 4 6	8450.3308	1.5
11 5 7	10 5 6	8448.3051	-2.4
11 5 6	10 5 5	8448.3051	-2.6
12 0 12	11 0 11	9112.0737	-0.2
12 1 12	11 1 11	8949.7010	0.2
12 1 11	11 1 10	9423.0739	-0.3
12 2 11	11 2 10	9195.5493	0.3
12 2 10	11 2 9	9295.2720	-0.3
12 3 10	11 3 9	9223.6655	0.1
12 3 9	11 3 8	9227.7880	-1.0
12 4 9	11 4 8	9219.5607	-0.8

12 4 8	11 4 7	9219.6239	-0.6
12 5 8	11 5 7	9216.9866	0.3
12 5 7	11 5 6	9216.9866	-0.2
12 6 7	11 6 6	9215.6301	-1.7
12 6 6	11 6 5	9215.6301	-1.7
13 0 13	12 0 12	9854.2713	0.0
13 1 13	12 1 12	9691.3638	0.4
13 1 12	12 1 11	10202.4701	0.2
13 2 12	12 2 11	9958.5302	-0.5
13 2 11	12 2 10	10083.6078	-0.6
13 3 11	12 3 10	9993.8902	1.8
13 3 10	12 3 9	10000.0581	-0.6
13 4 10	12 4 9	9989.0970	-0.6
13 4 9	12 4 8	9989.2095	0.0
13 5 9	12 5 8	9985.8371	2.1
13 5 8	12 5 7	9985.8371	1.1
14 0 14	13 0 13	10593.2724	1.2
14 1 14	13 1 13	10432.1808	0.3
14 1 13	13 1 12	10980.2868	0.1
14 2 13	13 2 12	10720.7259	0.8
14 2 12	13 2 11	10874.3128	0.4
14 3 12	13 3 11	10764.3413	-0.9
14 3 11	13 3 10	10773.2894	0.0
14 4 11	13 4 10	10758.9229	-0.2
14 4 10	13 4 9	10759.1124	-0.8
14 5 10	13 5 9	10754.8679	0.3
14 5 9	13 5 8	10754.8679	-1.7
15 0 15	14 0 14	11329.2448	-0.4
15 1 15	14 1 14	11172.1391	-0.3
15 1 14	14 1 13	11756.3395	0.1
15 2 14	14 2 13	11482.0759	-0.3
15 2 13	14 2 12	11667.1426	0.0
15 3 13	14 3 12	11534.9924	0.2
15 3 12	14 3 11	11547.6180	-0.5
15 4 12	14 4 11	11529.0563	0.6
15 4 11	14 4 10	11529.3688	2.4
15 5 11	14 5 10	11524.1003	1.9
15 5 10	14 5 9	11524.1003	-1.9
2 2 1	1 1 0	11322.3520	-0.4
2 2 0	1 1 1	11362.5134	1.4
3 2 1	3 1 2	9689.5499	-0.7
3 2 2	3 1 3	9926.5071	-2.2
3 2 2	2 1 1	12050.2338	0.6

3 2 1	2 1 2	12171.4387	0.1
3 3 0	3 2 1	16343.1653	1.0
3 3 1	3 2 2	16344.9780	-0.7
3 3 1	2 2 0	18647.6492	-0.4
4 1 4	3 0 3	6141.5701	2.3
4 2 2	4 1 3	9614.0438	1.6
4 2 3	4 1 4	10006.5402	-0.2
4 2 3	3 1 2	12758.1591	-0.1
4 2 2	3 1 3	13002.3821	-0.2
4 3 1	4 2 2	16340.5505	-0.3
4 3 2	4 2 3	16345.9826	-1.6
5 1 5	4 0 4	6811.8132	1.0
5 2 3	5 1 4	9522.6144	-2.3
5 2 4	5 1 5	10106.7915	-0.2
5 2 4	4 1 3	13446.1632	-0.9
5 2 3	4 1 4	13856.8153	-0.1
5 3 2	5 2 3	16335.3754	0.8
5 3 3	5 2 4	16348.0216	-0.3
6 1 6	5 0 5	7464.4997	-0.3
6 2 4	6 1 5	9417.2479	1.6
6 2 5	6 1 6	10227.3944	0.7
6 2 5	5 1 4	14114.3177	-0.6
6 2 4	5 1 5	14736.5861	-0.3
6 3 3	6 2 4	16326.3874	0.2
6 3 4	6 2 5	16351.6009	0.0
7 1 7	6 0 6	8100.9209	-0.5
7 2 5	7 1 6	9300.2901	2.0
7 2 6	7 1 7	10368.4918	-0.1
7 2 6	6 1 5	14762.7334	-0.1
7 2 5	6 1 6	15643.9019	-0.2
7 3 4	7 2 5	16312.1231	0.4
7 3 5	7 2 6	16357.3218	0.8
8 1 8	7 0 7	8722.6342	-1.6
8 2 6	8 1 7	9174.4690	0.5
8 2 7	8 1 8	10530.2401	-1.0
9 1 9	8 0 8	9331.4563	-0.7
9 2 7	9 1 8	9042.8567	-0.4
9 2 8	9 1 9	10712.8007	1.8
10 1 10	9 0 9	9929.4281	0.8
10 2 9	10 1 10	10916.3183	-0.3
11 1 11	10 0 10	10518.7788	0.3
12 1 12	11 0 11	11101.8777	-1.7

Table S10. Experimental transition frequencies ν of the parent species of isomer II with quantum numbers and difference to calculated frequencies $\Delta\nu$ in the least squares fit.

Transition		ν/MHz	$\Delta\nu/\text{kHz}$
$J' K_a' K_c'$	$\leftarrow J'' K_a'' K_c''$		
6 0 6	5 0 5	5467.1305	-0.4
6 1 6	5 1 5	5285.4426	0.8
6 1 5	5 1 4	5775.5132	-0.5
6 2 4	5 2 3	5621.8333	0.5
6 2 5	5 2 4	5539.0510	-0.1
6 3 4	5 3 3	5562.1686	-1.7
6 3 3	5 3 2	5564.6811	1.0
7 0 7	6 0 6	6345.2585	-0.2
7 1 7	6 1 6	6158.4027	-0.9
7 1 6	6 1 5	6727.4386	0.6
7 2 5	6 2 4	6585.5987	0.1
7 2 6	6 2 5	6456.0615	2.2
7 3 4	6 3 3	6498.0788	0.0
7 3 5	6 3 4	6492.4503	-2.0
7 4 3	6 4 2	6487.2249	0.2
7 4 4	6 4 3	6487.1424	0.4
8 0 8	7 0 7	7211.4172	-0.2
8 1 8	7 1 7	7028.2606	0.0
8 1 7	7 1 6	7673.8018	0.0
8 2 7	7 2 6	7370.248	-0.3
8 2 6	7 2 5	7558.4062	-0.1
8 3 6	7 3 5	7423.6745	0.4
8 3 5	7 3 4	7434.8644	0.4
8 4 5	7 4 4	7416.9997	-0.7
8 4 4	7 4 3	7417.2270	-0.5
8 5 4	7 5 3	7412.0393	3.0
8 5 3	7 5 2	7412.0393	0.9
9 0 9	8 0 8	8066.7358	0.7
9 1 9	8 1 8	7894.9308	-0.2
9 1 8	8 1 7	8613.3740	0.1
9 2 8	8 2 7	8281.2464	-0.2
9 2 7	8 2 6	8538.6692	1.5
9 3 7	8 3 6	8355.6105	2.1
9 3 6	8 3 5	8375.9554	1.0
9 4 6	8 4 5	8348.0550	-2.4
9 4 5	8 4 4	8348.5997	-1.4
9 5 5	8 5 4	8341.0452	-2.8

9 5 4	8 5 3	8341.0573	2.5
10 0 10	9 0 9	8913.2442	0.5
10 1 10	9 1 9	8758.4392	0.9
10 1 9	9 1 8	9544.7937	-0.4
10 2 9	9 2 8	9188.7053	-0.6
10 2 8	9 2 7	9523.8565	-1.6
10 3 8	9 3 7	9287.9235	0.5
10 3 7	9 3 6	9322.3947	-1.5
10 4 7	9 4 6	9280.4135	1.4
10 4 6	9 4 5	9281.5855	-0.4
11 0 11	10 0 10	9753.4465	-0.8
11 1 11	10 1 10	9618.8992	-0.8
11 1 10	10 1 9	10466.6194	0.9
11 2 10	10 2 9	10092.3100	0.1
11 2 9	10 2 8	10510.9346	-0.1
11 3 9	10 3 8	10220.1901	-2.6
11 3 8	10 3 7	10275.3146	-0.9
12 0 12	11 0 11	10589.816	0.7
12 1 12	11 1 11	10476.5108	-0.5
12 1 11	11 1 10	11377.4141	-0.2
12 2 11	11 2 10	10991.7828	-1.0
12 2 10	11 2 9	11496.8291	0.8
12 3 10	11 3 9	11151.9168	0.6
12 3 9	11 3 8	11235.8205	-1.5
13 0 13	12 0 12	11424.3955	0.9
13 1 13	12 1 12	11331.5253	0.9
13 1 12	12 1 11	12275.9160	0.4
13 2 12	12 2 11	11886.9055	0.6
13 2 11	12 2 10	12478.8149	1.8
13 3 11	12 3 10	12082.5426	3.9
13 3 10	12 3 9	12204.851	1.4
14 0 14	13 0 13	12258.6383	-0.4
14 1 14	13 1 13	12184.2267	-0.4
14 1 13	13 1 12	13161.2364	-1.3
14 2 13	13 2 12	12777.5120	-0.6
14 2 12	13 2 11	13454.6579	-2.2
15 0 15	14 0 14	13093.4292	1.5
15 1 15	14 1 14	13034.9200	-1.7