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**Competitive and Cooperative between $n \rightarrow \pi^*$ and $n \rightarrow \sigma^*$ Interactions in
Benzaldehyde-Formaldehyde: Rotational Characterization**

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Table S1. The binding composition of noncovalent interactions of complexes of formaldehyde (FA).

	Prior	Secondary	Refs.
FA-HF	$n \rightarrow \sigma^*$ HB	-	[1]
FA-HCl	$n \rightarrow \sigma^*$ HB	-	[2]
FA-CIF	$n \rightarrow \sigma^*$ HaB	-	[2]
FA-H ₂ O	$n \rightarrow \sigma^*$ HB	-	[3]
FA-CO ₂	$n \rightarrow \pi^*$ TB	$n \rightarrow \sigma^*$ HB	[4]
FA-CF ₂ H ₂	$n \rightarrow \sigma^*$ HB	$n \rightarrow \sigma^*$ HB	[5]
FA-CFCIH ₂	$n \rightarrow \sigma^*$ HB	$n \rightarrow \sigma^*$ HB	[6]
FA-CF ₃ Cl	$n \rightarrow \sigma^*$ HaB	-	[7]
FA-acetylene	$\pi \rightarrow \sigma^*$ HB	$n \rightarrow \sigma^*$ HB	[8]
FA-dimer	$n \rightarrow \pi^*$ TB	$n \rightarrow \sigma^*$ HB	[9]
FA-formic acid	$n \rightarrow \sigma^*$ HB	-	[10]
FA-pyridine	$n \rightarrow \pi^*$ TB	$n \rightarrow \sigma^*$ HB	[11]
FA-BA	$n \rightarrow \pi^*$ TB	$n \rightarrow \sigma^*$ HB	This work

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Table S2. The calculated spectroscopic parameters and relative energies of the four isomers of the BA-FA complex at different levels of theory.

		<i>A/B/C</i> MHz	Largest discrepancy (%)	$\Delta E_0/\text{cm}^{-1}$	$\Delta E_{0,\text{BSE}}/\text{cm}^{-1}$	
MP2	6-311++G(d,p)	I	3843/550/483	0.7%	0	0
		II	2304/734/560	0.8%	31	28
		III	2045/736/541	-	51	48
		IV	3527/516/451	-	195	191
	aug-cc-pVTZ	I	3858/567/496	3.7%	0	0
		II	2341/752/571	3.2%	35	33
		III	2043/730/535	-	65	60
		IV	3516/530/460	-	187	183
B3LYP-D3(BJ)	6-311++G(d,p)	I	3906/561/493	2.8%	0	0
		II	2351/747/569	2.5%	84	81
		III	2095/751/553	-	135	114
		IV	3581/526/458	-	306	278
	aug-cc-pVTZ	I	3907/564/495	3.3%	0	0
		II	2344/750/570	2.9%	101	99
		III	2079/755/554	-	160	148
		IV	3582/526/458	-	306	299
M06-2X	6-311++G(d,p)	I	3942/564/495	3.2%	0	0
		II	2400/747/572	4.5%	154	159
		III	2099/752/554	-	337	309
		IV	3562/524/463	-	337	309
	aug-cc-pVTZ	I	3929/568/498	3.9%	0	0
		II	2391/752/574	4.1%	185	181
		III	2090/758/549	-	316	300
		IV	3563/533/458	-	320	301

Table S3. Experimental transition frequencies ν_{obs} of the parent species of isomer I with quantum numbers and difference to calculated frequencies $\Delta\nu$ in the least squares fit

J'	K_a'	K_c'	J''	K_a''	K_c''	$\nu_{\text{obs}}/\text{MHz}$	$\Delta\nu_{\text{obs-calc}}/\text{kHz}$
5	0	5	4	0	4	5111.7436	-0.5
5	1	4	4	1	3	5292.9344	-0.3
5	1	5	4	1	4	4961.4883	-2.5
5	2	3	4	2	2	5149.1745	-1.1
5	2	4	4	2	3	5129.3575	-0.9
5	3	2	4	3	1	5135.0864	-4.9
5	3	3	4	3	2	5314.8969	1.1
6	0	6	5	0	5	6123.3030	1.4
6	1	5	5	1	4	6348.6205	0.1
6	1	6	5	1	5	5951.1770	-2.8
6	2	4	5	2	3	6187.9393	-0.6
6	2	5	5	2	4	6153.3900	1.0
6	3	3	5	3	2	6163.5988	-3.5
6	3	4	5	3	3	6163.0805	-0.7
6	4	2	5	4	1	6161.2635	-1.5
6	4	3	5	4	2	6161.2635	1.1
7	0	7	6	0	6	7129.1808	-0.7
7	1	6	6	1	5	7402.6386	0.5
7	1	7	6	1	6	6939.5270	-0.8
7	2	5	6	2	4	7231.3637	-0.6
7	2	6	6	2	5	7176.4160	-0.6
7	3	4	6	3	3	7193.0134	-0.3
7	3	5	6	3	4	7191.8442	1.7
7	4	3	6	4	2	7189.1245	0.5
7	4	4	6	4	3	7189.1147	-1.1
7	5	2	6	5	1	7187.7205	3.3
7	5	3	6	5	2	7187.7205	3.4
8	0	8	7	0	7	8128.7096	-2.2
8	1	7	7	1	6	8454.6365	0.1
8	1	8	7	1	7	7926.3775	-0.1
8	2	6	7	2	5	8279.9512	2.1
8	2	7	7	2	6	8198.2796	3.3
8	3	5	7	3	4	8223.5476	-1.4
8	3	6	7	3	5	8221.2086	-0.7
9	0	9	8	0	8	9121.4318	-2.0
9	1	8	8	1	7	9504.2316	0.3
9	1	9	8	1	8	8911.5970	3.5
9	2	7	8	2	6	9333.9788	0.2
9	2	8	8	2	7	9218.8068	2.4
9	3	6	8	3	5	9255.4654	2.1
9	3	7	8	3	6	9251.1825	-0.2

10	0	10	9	0	9	10107.1640	0.5
10	1	9	9	1	8	10551.0005	-0.4
10	1	10	9	1	9	9895.0940	-4.0
10	2	8	9	2	7	10393.4562	-2.7
10	2	9	9	2	8	10237.8421	2.1
10	3	7	9	3	6	10289.0500	-0.7
10	3	8	9	3	7	10281.7357	1.9
11	0	11	10	0	10	11086.0301	-3.4
11	1	10	10	1	9	11594.4799	-2.9
11	1	11	10	1	10	10876.8044	0.7
11	2	9	10	2	8	11458.0731	-1.5
11	2	10	10	2	9	11255.2286	2.7
11	3	8	10	3	7	11324.6459	0.7
11	3	9	10	3	8	11312.8002	-1.5
12	0	12	11	0	11	12058.5004	0.4
12	1	11	11	1	10	12634.1705	-2.5
12	1	12	11	1	11	11856.6799	-2.3
12	2	10	11	2	9	12527.1818	1.4
12	2	11	11	2	10	12270.8131	3.5
12	3	9	11	3	8	12362.6186	-3.1
12	3	10	11	3	9	12344.3018	7.9
13	0	13	12	0	12	13025.3040	0.1
13	1	13	12	1	12	12834.7306	0.8
2	2	0	1	1	1	12041.8189	0.4
2	2	1	1	1	0	11974.4942	-0.4
3	1	3	2	0	2	6198.7000	9.3
3	2	1	2	1	2	13138.4492	8.5
3	2	2	2	1	1	12934.4739	-8.3
3	3	0	2	2	1	19671.0536	4.3
3	3	1	2	2	0	19670.0426	-3.1
4	2	2	3	1	3	14274.0238	4.2
5	1	5	4	0	4	7960.5253	6.6
5	2	4	4	1	3	14754.6113	0.3
6	1	6	5	0	5	8799.9594	5.0
6	2	5	5	1	4	15615.0656	5.1
7	1	7	6	0	6	9616.1843	3.7
7	2	6	6	1	5	16442.8548	-6.8
8	1	8	7	0	7	10413.3863	9.6
8	2	7	7	1	6	17238.4888	-8.9

Table S4. Experimental transition frequencies ν_{obs} of the parent species of isomer I I with quantum numbers and difference to calculated frequencies $\Delta\nu$ in the least squares fit.

J'	K_a'	K_c'	J''	K_a''	K_c''	$\nu_{\text{obs}}/\text{MHz}$	$\Delta\nu_{\text{obs-calc}}/\text{kHz}$
4	0	4	3	0	3	5007.0557	3.2
4	1	4	3	1	3	4766.6363	3.6
4	1	3	3	1	2	5454.3145	0.1
4	2	3	3	2	2	5127.1059	1.9
4	2	2	3	2	1	5257.6543	-0.7
5	0	5	4	0	4	6173.2901	-0.2
5	1	4	4	1	3	6787.8593	-0.9
5	1	5	4	1	4	5937.0934	0.9
5	2	3	4	2	2	6640.4540	-1.6
5	2	4	4	2	3	6391.9660	0.2
5	3	2	4	3	1	6475.7197	1.1
5	3	3	4	3	2	6461.9490	1.1
5	4	2	4	4	1	6452.0886	-1.9
5	4	1	4	4	0	6452.3054	-0.6
6	0	6	5	0	5	7303.3459	0.3
6	1	5	5	1	4	8097.7862	-0.9
6	1	6	5	1	5	7096.5292	0.4
6	2	4	5	2	3	8047.7631	-1.4
6	2	5	5	2	4	7645.7432	0.1
6	3	3	5	3	2	7799.7100	-1.6
6	3	4	5	3	3	7763.5665	-0.0
6	4	2	5	4	1	7753.0495	-1.4
7	0	7	6	0	6	8409.4420	1.3
7	1	6	6	1	5	9376.3583	-0.7
7	1	7	6	1	6	8245.3141	0.1
7	2	5	6	2	4	9464.5586	-1.3
7	2	6	6	2	5	8886.5584	-0.6
7	3	4	6	3	3	9144.7817	0.7
7	3	5	6	3	4	9065.6129	1.2
7	4	3	6	4	2	9060.0323	0.1
7	4	4	6	4	3	9056.8385	-0.2
7	5	3	6	5	2	9038.8749	1.3
7	5	2	6	5	1	9038.9192	-8.7
8	0	8	7	0	7	9504.8540	0.6
8	1	7	7	1	6	10615.7634	-1.2
8	1	8	7	1	7	9384.5696	1.7
8	2	6	7	2	5	10874.2526	-0.5
8	2	7	7	2	6	10112.8857	-1.1
8	3	5	7	3	4	10516.9636	-0.3
8	3	6	7	3	5	10365.2755	0.8

8	4	5	7	4	4	10366.5076	1.4
8	4	4	7	4	3	10375.1836	1.2
8	5	4	7	5	3	10341.3132	-2.0
8	5	3	7	5	2	10341.5320	0.4
9	0	9	8	0	8	10598.8055	-0.5
9	1	8	8	1	7	11810.4107	-1.5
9	1	9	8	1	8	10515.8611	0.2
9	2	7	8	2	6	12263.5465	-0.5
9	2	8	8	2	7	11323.7024	0.1
9	3	6	8	3	5	11919.9920	-0.2
9	3	7	8	3	6	11659.3301	-0.0
9	4	6	8	4	5	11680.7382	1.7
9	4	5	8	4	4	11701.1898	0.0
9	5	5	8	5	4	11648.1660	1.4
9	5	4	8	5	3	11648.8628	0.4
10	0	10	9	0	9	11695.5693	-2.1
10	1	9	9	1	8	12960.1263	-1.6
10	1	10	9	1	9	11640.9029	-1.0
10	2	8	9	2	7	13623.0924	-0.4
10	2	9	9	2	8	12518.6182	-0.2
10	3	7	9	3	6	13352.0222	0.6
10	3	8	9	3	7	12944.4886	1.5
10	4	7	9	4	6	12998.5358	0.3
10	4	6	9	4	5	13041.7314	4.7
10	5	6	9	5	5	12959.8521	0.1
10	5	5	9	5	4	12961.7880	2.6
11	0	11	10	0	10	12796.1464	0.1
11	1	10	10	1	9	14072.2069	0.2
11	1	11	10	1	10	12761.3038	1.4
11	2	9	10	2	8	14945.7455	-0.8
11	2	10	10	2	9	13697.9646	0.3
11	3	8	10	3	7	14803.4703	1.0
11	3	9	10	3	8	14217.6988	-0.1
11	4	8	10	4	7	14318.1884	-0.5
11	4	7	10	4	6	14401.5044	-2.9
12	0	12	11	0	11	13900.0638	-1.4
12	1	11	11	1	10	15159.7865	-0.8
12	1	12	11	1	11	13878.4087	-0.7
12	2	11	11	2	10	14862.7700	0.2
13	0	13	12	0	12	15006.4757	-0.2
13	1	13	12	1	12	14993.2777	1.1
2	2	0	1	1	1	7630.9731	-0.8
2	2	1	1	1	0	7444.5236	0.0
3	2	2	2	1	1	8556.0160	-0.2

3	2	1	2	1	2	9141.8818	1.2
3	3	0	2	2	1	12132.1414	0.0
3	3	1	2	2	0	12117.9465	-0.8
4	1	4	3	0	3	5960.9048	-0.4
4	2	3	3	1	2	9579.3155	1.7
4	2	2	3	1	3	10813.8186	5.1
4	3	2	3	2	1	13373.9485	-1.0
4	3	1	3	2	2	13445.6879	-0.6
4	4	1	3	3	0	16717.1412	-3.7
4	4	0	3	3	1	16717.8370	0.9
5	0	5	4	1	4	5219.4366	-1.0
5	1	5	4	0	4	6890.9481	2.9
5	2	4	4	1	3	10516.9617	-3.3
5	2	3	4	1	4	12687.6398	3.4
5	3	3	4	2	2	14578.2403	-2.0
5	3	2	4	2	3	14794.3031	-0.0
5	4	2	4	3	1	18002.4378	0.0
5	4	1	4	3	2	18007.3155	2.7
5	3	3	5	2	4	8383.9350	0.7
5	3	2	5	2	3	7956.1898	-0.1
5	4	2	5	3	3	11545.1225	0.2
5	4	1	5	3	2	11526.9621	0.2
6	0	6	5	1	5	6585.6907	-0.0
6	1	6	5	0	5	7814.1818	-1.8
6	2	5	5	1	4	11374.8479	-0.0
6	3	4	5	2	3	15701.3541	0.7
6	3	3	5	2	4	16202.0450	-0.4
6	3	4	6	2	5	8501.7549	-2.7
6	3	3	6	2	4	7708.1394	2.4
6	4	3	6	3	4	11533.6400	-1.1
6	4	2	6	3	3	11480.3040	2.9
7	0	7	6	1	6	9616.1843	-6.8
7	1	7	6	0	6	8756.1533	1.3
7	2	6	6	1	5	12163.6187	-1.1
7	3	5	7	2	6	8680.8100	-0.2
8	0	8	7	1	7	9158.1441	2.0
8	1	8	7	0	7	9731.2791	-0.0
8	2	7	7	1	6	12900.1494	1.6
9	0	9	8	1	8	10372.3802	-0.0
9	1	9	8	0	8	10742.2870	0.3

Table S5. Experimental transition frequencies ν_{obs} of the $^{18}\text{O}(\text{BA})$ isotopologue of isomer I with quantum numbers and difference to calculated frequencies $\Delta\nu$ in the least squares fit

J'	K_a'	K_c'	J''	K_a''	K_c''	$\nu_{\text{obs}}/\text{MHz}$	$\Delta\nu_{\text{obs-calc}}/\text{kHz}$
5	1	5	4	1	4	4931.4275	-2.7
5	0	5	4	0	4	5082.6263	-1.6
5	2	3	4	2	2	5121.6423	1.5
5	1	4	4	1	3	5266.0668	-2.9
6	1	6	5	1	5	5914.9989	-3.1
6	0	6	5	0	5	6087.9123	-1.7
6	1	5	5	1	4	6316.2512	-3.3
6	2	5	5	2	4	6119.2636	2.9
6	2	4	5	2	3	6155.2697	1.2
7	1	7	6	1	6	6897.1806	-1.1
7	0	7	6	0	6	7087.3001	-1.0
7	2	6	6	2	5	7136.4966	3.1
7	1	6	6	1	5	7364.6908	-3.2
8	0	8	7	0	7	8080.1107	1.7
8	2	7	7	2	6	8152.5150	5.8

Table S6. Experimental transition frequencies ν_{obs} of the $^{18}\text{O}(\text{FA})$ isotopologue of isomer I with quantum numbers and difference to calculated frequencies $\Delta\nu$ in the least squares fit

J'	K_a'	K_c'	J''	K_a''	K_c''	$\nu_{\text{obs}}/\text{MHz}$	$\Delta\nu_{\text{obs-calc}}/\text{kHz}$
5	0	5	4	0	4	4958.8342	3.2
6	1	6	5	1	5	5775.5403	1.5
6	0	6	5	0	5	5940.6589	3.7
6	1	5	5	1	4	6154.7685	0.4
7	1	7	6	1	6	6734.8841	0.6
7	0	7	6	0	6	6917.2372	1.9
7	1	6	6	1	5	7176.8127	-4.3
8	1	8	7	1	7	7692.8364	-4.4
8	0	8	7	0	7	7887.9367	3.6
9	1	9	8	1	8	8649.2902	1.4
9	0	9	8	0	8	8852.2968	0.7
10	1	10	9	1	9	9604.1324	0.3
10	0	10	9	0	9	9810.1088	-4.0
11	1	11	10	1	10	10557.3023	-1.8
11	0	11	10	0	10	10761.4569	2.3
12	0	12	11	0	11	11706.6846	-1.6

Table S7. Experimental transition frequencies ν_{obs} of the $^{18}\text{O}(\text{BA})$ isotopologue of isomer I I with quantum numbers and difference to calculated frequencies $\Delta\nu$ in the least squares fit

J'	K_a'	K_c'	J''	K_a''	K_c''	$\nu_{\text{obs}}/\text{MHz}$	$\Delta\nu_{\text{obs-calc}}/\text{kHz}$
4	1	3	3	1	2	5413.3477	0.4
4	0	4	3	0	3	4959.3141	1.1
4	1	4	3	1	3	4720.8581	-2.4
5	1	5	4	1	4	5879.0675	3.9
5	0	5	4	0	4	6110.7830	-3.1
5	1	4	4	1	3	6735.0932	-0.1
6	1	6	5	1	5	7025.9405	0.2
6	0	6	5	0	5	7226.0730	-1.1
6	1	5	5	1	4	8031.8957	0.1
7	1	7	6	1	6	8161.9732	-0.1
7	0	7	6	0	6	8318.3748	1.9
8	1	8	7	1	7	9288.4090	-1.6
8	0	8	7	0	7	9401.2351	0.7

Table S8. Experimental transition frequencies ν_{obs} of the $^{18}\text{O}(\text{FA})$ isotopologue of isomer I I with quantum numbers and difference to calculated frequencies $\Delta\nu$ in the least squares fit

J'	K_a'	K_c'	J''	K_a''	K_c''	$\nu_{\text{obs}}/\text{MHz}$	$\Delta\nu_{\text{obs-calc}}/\text{kHz}$
4	0	4	3	0	3	4875.2076	-6.7
5	1	5	4	1	4	5781.6289	4.2
5	0	5	4	0	4	6012.9653	1.2
5	1	4	4	1	3	6601.9464	-1.6
6	1	6	5	1	5	6911.4443	2.0
6	0	6	5	0	5	7115.7400	-0.3
7	1	7	6	1	6	8031.0734	0.9
7	0	7	6	0	6	8194.7683	-1.3
7	1	6	6	1	5	9124.2138	0.4
8	1	8	7	1	7	9141.5234	0.2
8	0	8	7	0	7	9262.6971	0.8

Table S9. Experimental (r_0) and ab initio (r_e) coordinates of the O atoms of isomer I . ^a

Atom		a/ Å	b/ Å	c/ Å
O8	r_0	-1.5021(8)	-1.166(2)	0.000
	r_e	-1.514	-1.150	0.063
O10	r_0	-3.87(1)	0.9753(7)	0.000
	r_e	-3.858	0.973	0.054

^a Constrain's errors expressed in parentheses in units of the last digit.

Table S10. Experimental (r_0) and ab initio (r_e) coordinates of the O atoms for isomer II . ^a

Atom		a/ Å	b/ Å	c/ Å
O8	r_0	1.5119(8)	1.647(2)	0.000
	r_e	1.526	1.637	0.007
O10	r_0	3.18(2)	-1.430(3)	0.000
	r_e	3.152	-1.421	0.147

^a Constrain's errors expressed in parentheses in units of the last digit.

Table S11. Partial r_0 and MP2/6-311++G(d,p) calculated geometries of isomer I .

Bond lengths (Å)		Valence angles (°)		Dihedral angles (°)	
C1C2	1.395				
C2C3	1.403	C1C2C3	120.1		
C3C4	1.400	C2C3C4	120.2	C1C2C3C4	0.0
C4C5	1.399	C3C4C5	119.7	C2C3C4C5	0.0
C5C6	1.404	C4C5C6	119.6	C3C4C5C6	0.0
C4C7	1.482	C3C4C7	120.8	C2C3C4C7	-180.0
C7O8	1.221	C4C7O8	124.3(1)	C3C4C7O8	-0.0
C8C9	2.75(1)^a	C7O8C9	100.49(7)	C4C7O8C9	-180.0
C9O10	1.216	O8C9O10	100.0(9)	C7O8C9O10	0.0
C2H11	1.108	C3C2H11	120.3	C4C3C2H11	0.0
C3H12	1.088	C2C3H12	119.5	C1C2C3H12	0.0
C5H13	1.086	C4C5H13	120.1	C3C4C5H13	-180.0
C6H14	1.086	C5C6H14	119.9	C4C5C6H14	180.0
C1H15	1.086	C2C1H15	120.0	C3C2C1H15	-180.0
C7H16	1.086	C4C7H16	119.0	C3C4C7H16	0.0
C9H17	1.103	O8C9H17	90.0	C7O8C9H17	120.0
C9H18	1.103	O8C9H18	90.0	C7O8C9H18	-120.0

^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 2.722 Å, 101.0° and 99.8°, respectively.

Table S12. Partial r_0 and MP2/6-311++G(d,p) calculated geometries of isomer I I.

Bond lengths (Å)		Valence angles (°)		Dihedral angles (°)	
C1C2	1.403				
C2C3	1.395	C1C2C3	120.3		
C3C4	1.405	C2C3C4	119.4	C1C2C3C4	0.0
C4C5	1.403	C3C4C5	120.3	C2C3C4C5	-0.0
C5C6	1.399	C4C5C6	120.0	C3C4C5C6	0.0
C4C7	1.482	C3C4C7	120.9	C2C3C4C7	-180.0
C7O8	1.220	C4C7O8	124.9	C3C4C7O8	-0.0
C8C9	2.86(2)^a	C7O8C9	144.65(9)	C4C7O8C9	0.0
C9O10	1.215	O8C9O10	113.1(9)	C7O8C9O10	-0.0
C2H11	1.086	C3C2H11	119.7	C4C3C2H11	-180.0
C3H12	1.086	C2C3H12	120.9	C1C2C3H12	-180.0
C5H13	1.088	C4C5H13	119.6	C3C4C5H13	-180.0
C6H14	1.086	C5C6H14	120.1	C4C5C6H14	180.0
C1H15	1.086	C2C1H15	119.9	C3C2C1H15	180.0
C7H16	1.110	C4C7H16	114.8	C3C4C7H16	180.0
C9H17	1.103	O8C9H17	90.0	C7O8C9H17	-120.0
C9H18	1.103	O8C9H18	90.0	C7O8C9H18	120.0

^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 2.85 Å, 144.3° and 110.2°, respectively

Table S13. Measured intensities (in arbitrary units) of the two observed isomers for several μ_a -type selected transitions.

Transitions	Isomer	Frequencies	Intensities
$6_{06} \leftarrow 5_{05}$	I	6123.3025	0.0543
	II	7303.3412	0.0264
$6_{16} \leftarrow 5_{15}$	I	5951.1718	0.0204
	II	7096.5221	0.0211
$7_{07} \leftarrow 6_{06}$	I	7129.1845	0.0472
	II	8409.4478	0.0104
$7_{17} \leftarrow 6_{16}$	I	6939.5246	0.0193
	II	8245.3145	0.0132
$8_{08} \leftarrow 7_{07}$	I	8128.7189	0.0229
	II	9504.8578	0.0114
$8_{18} \leftarrow 7_{17}$	I	7926.3752	0.0174
	II	9384.5687	0.0095
$9_{09} \leftarrow 8_{08}$	I	9121.4342	0.0262
	II	10598.8012	0.0041
$9_{19} \leftarrow 8_{18}$	I	8911.6012	0.0109
	II	10515.8678	0.0079
$10_{010} \leftarrow 9_{09}$	I	10107.1612	0.0147
	II	11695.5748	0.0050
$10_{110} \leftarrow 9_{19}$	I	9895.0978	0.0177
	II	11640.9045	0.0049

Table S14. Stabilization energy contributions ($> 0.2 \text{ kJ mol}^{-1}$) in isomer I of BA-FA.

Donor NBO	Acceptor NBO	E (kJ mol ⁻¹)
From benzaldehyde to HCHO		
$\sigma(1)$ C12 - H13	$\pi^*(1)$ C15 - O18	0.25
$\sigma(1)$ C12 - H13	$\pi^*(2)$ C15 - O18	0.38
$\pi(1)$ C12 - O14	$\pi^*(2)$ C15 - O18	0.38
n(1) O14	$\pi^*(2)$ C15 - O18	4.14
n(2) O14	$\sigma^*(1)$ C15 - H16	0.25
n(2) O14	$\sigma^*(1)$ C15 - H17	0.25
n(2) O14	$\pi^*(1)$ C15 - O18	1.21
n(2) O14	$\pi^*(2)$ C15 - O18	11.25
From HCHO to benzaldehyde		
$\pi(2)$ C15 - O18	$\sigma^*(1)$ C3 - C12	1.17
$\pi(2)$ C15 - O18	$\sigma^*(1)$ C12 - H13	1.25
$\pi(2)$ C15 - O18	$\pi^*(1)$ C12 - O14	0.54
n(2) O18	$\sigma^*(1)$ C12 - H13	1.92

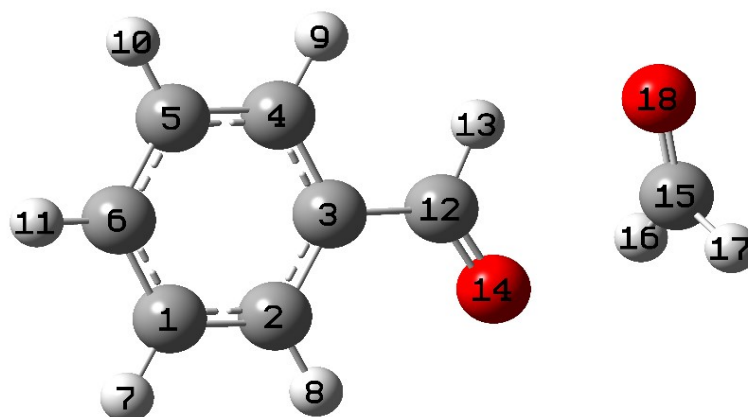


Table S15. Stabilization energy contributions ($> 0.2 \text{ kJ mol}^{-1}$) in isomer II of BA-FA.

Donor NBO	Acceptor NBO	E (kJ mol ⁻¹)
From benzaldehyde to HCHO		
n(1) O14	$\pi^*(2)$ C15 - O18	5.82
n(2) O14	$\pi^*(2)$ C15 - O18	3.84
From HCHO to benzaldehyde		
$\pi(2)$ C15 - O18	$\sigma^*(1)$ C2 - H8	1.51
$\pi(2)$ C15 - O18	$\pi^*(1)$ C12 - O14	0.25
n(1) O18	$\sigma^*(1)$ C2 - H8	1.17
n(2) O18	$\sigma^*(1)$ C2 - H8	0.50

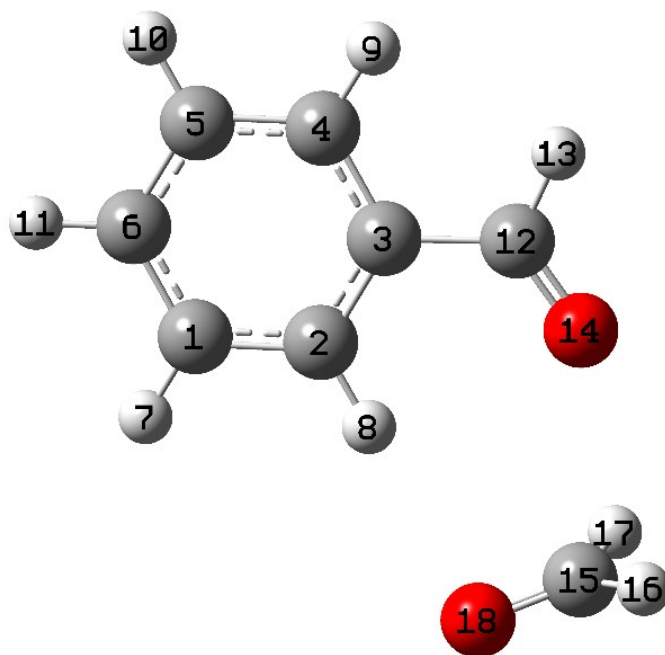


Table S16. Stabilization energy contributions ($> 0.2 \text{ kJ mol}^{-1}$) in isomer III of BA-FA.

Donor NBO	Acceptor NBO	E (kJ mol^{-1})
From benzaldehyde to HCHO		
$\sigma(1) \text{ C12} - \text{H13}$	$\sigma^*(1) \text{ C15} - \text{H16}$	0.21
$n(1) \text{ O14}$	$\sigma^*(1) \text{ C15} - \text{H16}$	0.66
$n(2) \text{ O14}$	$\sigma^*(1) \text{ C15} - \text{H16}$	4.96
From HCHO to benzaldehyde		
$\sigma(1) \text{ C15} - \text{H16}$	$\pi^*(1) \text{ C12} - \text{O14}$	0.25
$n(1) \text{ O18}$	$\sigma^*(1) \text{ C2} - \text{H8}$	1.55
$n(2) \text{ O18}$	$\sigma^*(1) \text{ C2} - \text{H8}$	4.73

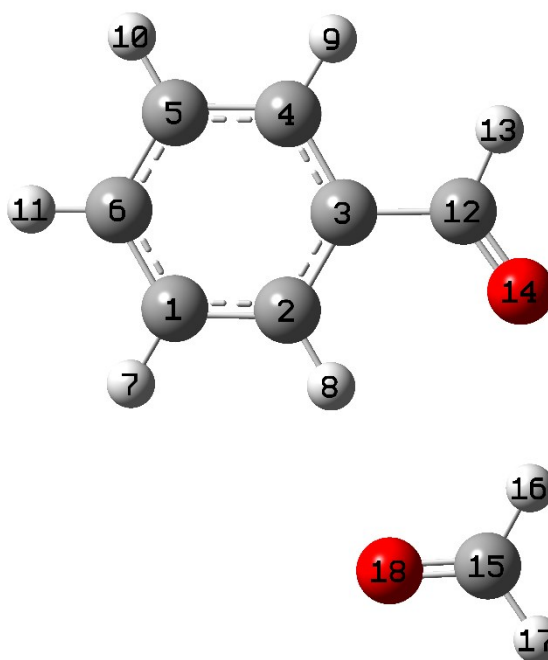


Table S17. Stabilization energy contributions ($> 0.2 \text{ kJ mol}^{-1}$) in isomer IV of BA-FA

Donor NBO	Acceptor NBO	E (kJ mol ⁻¹)
From benzaldehyde to HCHO		
n(1) O14	$\sigma^*(1) \text{ C15} - \text{H17}$	0.75
n(2) O14	$\sigma^*(1) \text{ C15} - \text{H16}$	0.25
n(2) O14	$\sigma^*(1) \text{ C15} - \text{H17}$	2.22
From HCHO to benzaldehyde		
n(1) O18	$\sigma^*(1) \text{ C12} - \text{H13}$	0.96
n(2) O18	$\sigma^*(1) \text{ C2} - \text{C12}$	0.38
n(2) O18	$\sigma^*(1) \text{ C12} - \text{H13}$	1.88

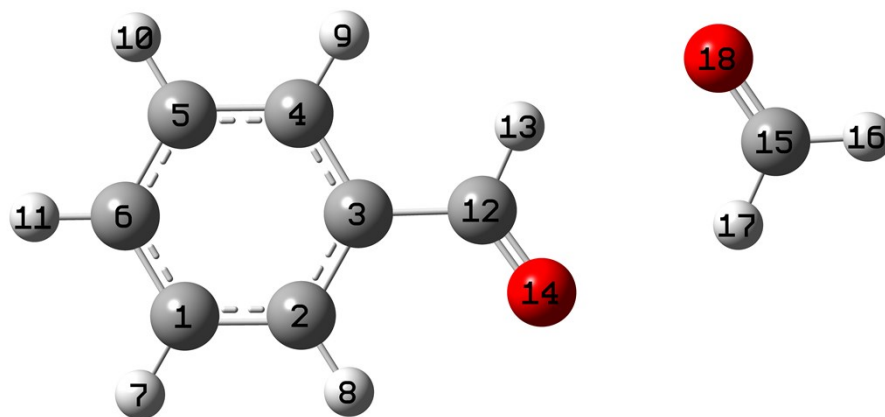


Table S18. Stabilization energy contributions ($> 0.2 \text{ kJ mol}^{-1}$) in the FA homodimer.

Donor NBO	Acceptor NBO	E (kJ mol ⁻¹)
From HCHO to HCHO		
$\pi(2) \text{ C1} - \text{O4}$	$\sigma^*(1) \text{ C5} - \text{H6}$	0.67
$\pi(2) \text{ C1} - \text{O4}$	$\sigma^*(1) \text{ C5} - \text{H7}$	1.59
$\pi(2) \text{ C1} - \text{O4}$	$\pi^*(2) \text{ C5} - \text{O8}$	0.75
$n(1) \text{ O4}$	$\sigma^*(1) \text{ C5} - \text{H7}$	1.39
From HCHO to HCHO		
$\sigma(1) \text{ C5} - \text{H6}$	$\pi^*(2) \text{ C1} - \text{O4}$	0.21
$\sigma(1) \text{ C5} - \text{H7}$	$\pi^*(2) \text{ C1} - \text{O4}$	0.42
$\pi(2) \text{ C5} - \text{O8}$	$\pi^*(2) \text{ C1} - \text{O4}$	0.33
$n(1) \text{ O8}$	$\pi^*(2) \text{ C1} - \text{O4}$	3.51
$n(2) \text{ O8}$	$\sigma^*(1) \text{ C1} - \text{H2}$	0.38
$n(2) \text{ O8}$	$\sigma^*(1) \text{ C1} - \text{H3}$	0.38
$n(2) \text{ O8}$	$\pi^*(1) \text{ C1} - \text{O4}$	1.09
$n(2) \text{ O8}$	$\pi^*(2) \text{ C1} - \text{O4}$	11.26

