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Conformational equilibria in carboxylic acid bimolecules: a rotational study of acrylic acid-formic acid

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Supplementary Information

<u>Content</u>:

1) Completion of one Reference [24]
2) 5 Tables of observed transitions
3) 2 Tables with MP2 optimized geometries

Completion of the Reference:

[24] GAUSSIAN03, Revision B.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Pittsburgh PA, **2003**.

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Table S1. Observed transitions of several isotopomers of the *cis* conformer of AA⋯FA.

Transitions		normal		DCOOH		HCOOD		Acylic-COOD		2-D		Error
		Observed /MHz	*δ* /kHz	Observed /MHz	*δ* /kHz	Observed /MHz	*δ* /kHz	Observed /MHz	*δ* /kHz	Observed /MHz	*δ* /kHz	
5_{05}	4_{04}	8786.0409	0	8571.2809	-2	8739.3062	2	8755.7755	3	8710.3266	2	0.005
5_{15}	4_{14}	8467.5169	0	8265.0285	-2	8421.0640	-4	8436.0935	-2	8390.8857	-7	0.005
5_{14}	4_{13}	9236.6011	0	8996.5796	4	9192.2071	4	9212.3915	2	9169.5238	4	0.005
5_{24}	4_{23}	8861.3001	1	8639.1151	0							0.005
5_{23}	4_{22}	8946.0915	0	8715.5378	0							0.005
5_{33}	4_{32}	8884.7869	-1									0.005
5_{32}	4_{31}	8886.3521	-1									0.005
6_{06}	5_{05}	10498.3971	0	10244.9499	-3	10441.4838	2	10460.5100	2	10405.0779	1	0.005
6_{16}	5_{15}	10150.3222	0	9908.3515	0	10094.3827	0	10112.2407	0	10057.7840	-1	0.005
6_{15}	5_{14}	11070.9274	0	10784.2538	-1	11017.3702	0	11041.3512	-1	10989.6007	2	0.005
7_{07}	6_{06}	12189.1018	0	11898.7802	-3	12121.7015	3	12142.9863	1	12077.2506	3	0.005
7_{17}	6_{16}	11827.9256	0	11546.9335	3	11762.4145	5	11783.0231	3	11719.2207	0	0.005
7_{16}	6_{15}	12897.4692	0	12564.9860	-7	12834.5652	-8	12862.1916	-8	12801.3603	-5	0.005
8_{08}	7_{07}	13857.8437	-1	13532.2044	-3	13779.7433	2	13803.0572	3	10405.0779	1	0.005
8_{18}	7_{17}	13499.9518	-1	13180.4127	9							0.005
9_{09}	8_{08}	15506.1885	-1									0.005
9_{19}	8_{18}	15166.2183	1									0.005
9_{18}	8_{17}	16519.4657	-1									0.005
6_{25}	5_{24}	10625.6812	0	10359.8486	2							0.005
6_{24}	5_{23}	10772.2304	0	10492.0981	1							0.005
6_{34}	5_{33}	10666.5005	0									0.005
6_{33}	5_{32}	10670.6658	0									0.005
7_{26}	6_{25}	12385.7870	0	12076.7285	4							0.005
7_{25}	6_{24}	12615.6700	-1	12284.5802	-4							0.005
7_{35}	6_{34}	12450.1732	0									0.005
7_{34}	6_{33}	12459.5168	1									0.005
9_{28}	8_{27}	15890.4488	1									0.005
9_{27}	8_{26}	16350.7374	1									0.005
10_{010}	9_{09}	17137.3769	0									0.005
10_{110}	9_{19}	16826.7174	1									0.005
4_{04}	3_{03}	7053.9904	0	6879.7263	-1							0.005
4_{13}	3_{12}	7396.1398	0	7203.4165	4							0.005
4_{23}	3_{22}	7093.3408	1									0.005
4_{22}	3_{21}	7136.0361	1									0.005
4_{32}	3_{31}	7105.0234	1									0.005
4_{31}	3_{30}	7105.4707	1									0.005
2_{12}	1_{01}	7469.6731	1	7411.1576	6							0.005
3_{13}	2_{02}	9014.2881	0	8922.3129	5	8925.3867	11	8918.0438	14	8830.4078	2	0.005
4_{14}	3_{03}	10488.9644	-1			10390.3821	3	10384.6967	-6			0.005
5_{15}	4_{04}	11902.4916	0	11751.8810	7	11794.3523	8	11790.0948	-8	11683.6240	2	0.005
2_{21}	1_{10}	15928.8103	0	15901.5627	4							0.005
2_{20}	1_{11}	16087.2338	0									0.005
3_{22}	2_{11}	17548.8428	1	17484.5165	2							0.005
3_{21}	2_{12}	18032.6646	-2									0.005
3_{22}	3_{13}	12922.5620	0									0.005
3_{21}	3_{12}	12019.2693	1	12097.7465	4							0.005

Table S2. Observed transitions of several isotopomers of the *trans* conformer of AA⋯FA.

Transitions		normal		DCOOH		HCOOD		Acylic-COOD		2-D		Error
		Observed /MHz	δ /kHz	Obs /MHz	δ /kHz	Observed /MHz	δ /kHz	Observed /MHz	δ /kHz	Observed /MHz	δ /kHz	
5_{05}	4_{04}	8697.2412	0	8486.2833	-1	8640.8222	2	8671.8140	1	8616.8234	1	0.005
5_{15}	4_{14}	8396.4872	-1	8197.3155	1	8340.9397	-2	8370.2119	-3	8316.0104	-3	0.005
5_{14}	4_{13}	9100.3721	1	8868.0237	4	9044.2347	0	9078.4319	4	9023.9438	1	0.005
5_{24}	4_{23}	8755.5617	0	8539.1204	2							0.005
5_{23}	4_{22}	8821.2430	0	8598.6234	2							0.005
6_{06}	5_{05}	10401.5518	-1	10151.6225	-2	10333.4721	-1	10370.1718	0	10303.7648	0	0.005
6_{16}	5_{15}	10067.3909	0	9829.1454	0	10000.6395	-3	10035.6529	-2	9970.5163	0	0.005
6_{15}	5_{14}	10910.5502	0	10632.7064	0	10843.0709	4	10883.9496	0	10818.4297	1	0.005
7_{07}	6_{06}	12088.3070	1	11800.8779	-2	12008.4210	3	12050.6008	2	11972.6125	1	0.005
7_{17}	6_{16}	11734.1353	2	11457.1759	3	11656.1479	4	11696.8454	5	11620.7235	2	0.005
7_{16}	6_{15}	12714.8788	0	12392.1298	-2	12635.9654	-6	12683.4462	-5	12606.8051	-4	0.005
8_{08}	7_{07}	13756.5480	0	13433.0141	0							0.005
8_{18}	7_{17}	13396.3498	-2	13081.0559	7							0.005
9_{09}	8_{08}	15406.5994	1									0.005
9_{19}	8_{18}	15053.8146	1									0.005
9_{18}	8_{17}	16300.4037	1									0.005
5_{33}	4_{32}	8773.7910	0									0.005
5_{32}	4_{31}	8774.8099	-1									0.005
6_{25}	5_{24}	10500.5857	1	10241.4340	2							0.005
6_{24}	5_{23}	10614.4993	-0	10344.7206	0							0.005
6_{34}	5_{33}	10532.3453	-1									0.005
6_{33}	5_{32}	10535.0630	0									0.005
7_{26}	6_{25}	12242.2984	0	11940.7497	1							0.005
7_{25}	6_{24}	12421.9559	-1	12103.8649	-4							0.005
7_{35}	6_{34}	12292.5545	0									0.005
7_{34}	6_{33}	12298.6516	-2									0.005
8_{27}	7_{26}	13980.1627	-1									0.005
8_{36}	7_{35}	14054.3615	1									0.005
8_{35}	7_{34}	14066.5167	1									0.005
9_{28}	8_{27}	15713.6596	-1									0.005
9_{27}	8_{26}	16079.6789	0									0.005
10_{010}	9_{09}	17040.1100	2									0.005
10_{110}	9_{19}	16706.4200	-1									0.005
4_{04}	3_{03}	6977.3476	0	6806.7590	3							0.005
4_{13}	3_{12}	7285.5450	-1	7099.1561	5							0.005
4_{23}	3_{22}	7007.7736	1									0.005
4_{22}	3_{21}	7040.7779	-1									0.005
4_{32}	3_{31}	7016.8232	3									0.005
4_{31}	3_{30}	7017.1153	3									0.005
2_{12}	1_{01}	7794.1587	1									0.005
3_{13}	2_{02}	9336.5376	1	9238.6072	-1	9244.9562	4	9259.4422	8	9168.5706	6	0.005
4_{14}	3_{03}	10813.9073	0	10685.2316	-6	10711.4941	-4	10730.4829	-8	10628.9756	-6	0.005
5_{15}	4_{04}	12233.0449	-2	12075.7922	-4							0.005
2_{21}	1_{10}	16936.0031	0	16889.9519	4							0.005
2_{20}	1_{11}	17080.2993	1									0.005
2_{20}	1_{11}	17080.2993	1									0.005
3_{22}	3_{13}	13926.3004	-1									0.005
3_{21}	3_{12}	13096.9973	0									0.005

Table S3. Observed transitions of the ^{13}C species of *cis*-AA⋯FA.

transitions		C10 Observed /MHz	C10 δ /kHz	C1 Observed /MHz	C1 δ /kHz	C2 Observed /MHz	C2 δ /kHz	C3 Observed /MHz	C3 δ /kHz	Error
5_{05}	4_{04}	8674.7922	-1	8769.3947	-1	8690.1282	-3	8619.0926	-2	0.005
5_{15}	4_{14}	8362.6289	-4	8451.7385	-5	8376.8424	-6	8309.2958	-4	0.005
5_{14}	4_{13}	9112.0802	2	9218.2236	5	9130.0203	2	9052.4207	2	0.005
6_{06}	5_{05}	10367.1612	-1	10478.7036	-2	10385.0829	-2	10300.8523	-3	0.005
6_{16}	5_{15}	10024.9960	0	10131.4580	1	10041.9401	1	9961.1202	-2	0.005
6_{15}	5_{14}	10922.2240	-1	11048.9621	0	10943.5971	0	10850.7971	1	0.005
7_{07}	6_{06}	12038.8354	2	12166.4838	2	12059.1412	2	11962.1537	0	0.005
7_{17}	6_{16}	11682.4053	7	11806.0003	3	11702.0229	5	11608.0516	8	0.005
7_{16}	6_{15}	12725.0321	-5	12871.9734	-6	12749.7426	-4	12641.9362	-2	0.005
4_{04}	3_{03}	6963.6861	-1	7040.5091	-2	6976.2358	-1	6918.8236	-3	0.005
4_{13}	3_{12}	7296.1489	4	7381.3903	6	7310.5827	6	7248.3336	2	0.005
2_{12}	1_{01}	7440.3371	7	7462.9729	4	7437.4586	3			0.005
3_{13}	2_{02}	8967.6487	0	9004.9190	-4	8966.9233	-3	8920.6760	3	0.005
4_{14}	3_{03}	10426.6144	-7					10370.7310	-3	0.005

Table S4. Observed transitions of the ^{13}C species of *trans*-AA⋯FA.

transitions		C10 Observed /MHz	C10 δ /kHz	C1 Observed /MHz	C1 δ /kHz	C2 Observed /MHz	C2 δ /kHz	C3 Observed /MHz	C3 δ /kHz	Error
5_{05}	4_{04}	8587.7387	-1	8681.1692	-1	8604.2575	-3	8528.5410	-2	0.005
5_{15}	4_{14}	8293.1259	-6	8381.1972	-4	8308.2963	-4	8236.9730	-6	0.005
5_{14}	4_{13}	8979.5952	3	9082.9514	3	8998.9131	3	8915.0823	4	0.005
6_{06}	5_{05}	10271.8641	-1	10382.4549	-2	10291.2097	0	10201.5871	-4	0.005
6_{16}	5_{15}	9943.7632	-2	10049.0863	-1	9961.8542	0	9876.5618	-2	0.005
6_{15}	5_{14}	10766.1422	3	10889.7027	-1	10789.1745	1	10688.9477	-2	0.005
7_{07}	6_{06}	11939.2136	0	12066.2717	1	11961.1647	1	11858.2160	2	0.005
7_{17}	6_{16}	11590.4337	6	11712.8369	5	11611.3848	3	11512.2672	7	0.005
7_{16}	6_{15}	12547.1500	-4			12573.8115	-3			0.005

Table S5. Observed transitions of ^{13}C/deuterated species of *cis* AA⋯FA.

D6&D13

transitions		C10 Observed /MHz	C10 δ /kHz	C1 Observed /MHz	C1 δ /kHz	C2 Observed /MHz	C2 δ /kHz	C3 Observed /MHz	C3 δ /kHz	Error
5_{05}	4_{04}	8601.7703	1	8693.4344	2	8614.8114	2	8544.7913	1	0.005
5_{15}	4_{14}	8288.5245	-5	8374.8818	-2	8300.5962	-5	8234.0042	-2	0.005
5_{14}	4_{13}	9047.5527	1	9150.7857	1	9062.9558	3	8986.3263	5	0.005
6_{06}	5_{05}	10277.1609	-1	10385.1124	-4	10292.3562	0	10209.3794	0	0.005
6_{16}	5_{15}	9935.5156	6	10038.6482	2	9949.8859	-1	9870.2210	-2	0.005
6_{15}	5_{14}	10843.9970	-1	10967.2174	1	10862.3321	1	10770.7037	-4	0.005
7_{07}	6_{06}	11930.9381	0	12054.3487	2	11948.1016	-1	11852.6129	0	0.005
7_{17}	6_{16}	11577.2831	-2			11593.9228	4	11501.3041	3	0.005
7_{16}	6_{15}		-4	12775.3950	-2	12653.7744	-4			0.005

D13

transitions		C10 Observed /MHz	C10 δ /kHz	C1 Observed /MHz	C1 δ /kHz	C2 Observed /MHz	C2 δ /kHz	C3 Observed /MHz	C3 δ /kHz	Error
5_{05}	4_{04}	8629.7858	0	8722.4414	2	8643.4693	1	8573.2734	-3	0.005
5_{15}	4_{14}	8317.8119	2	8405.0735	-4	8330.4614	-6	8263.7160	-4	0.005
5_{14}	4_{13}	9069.4351	1	9173.5710	4	9085.5617	8	9008.8083	8	0.005
6_{06}	5_{05}	10312.3492	0			10328.2982	-4	10245.0942	-1	0.005
6_{16}	5_{15}			10075.2658	1	9986.0948	-1	9906.2408	0	0.005
6_{15}	5_{14}	10870.7780	-7	10995.0962	-4	10889.9726	0	10798.1903	0	0.005
7_{07}	6_{06}	11973.9087	0	12098.7959	-1	11991.9401	3	11896.1579	2	0.005
7_{17}	6_{16}	11619.1953	-2	11740.1971	2	11636.6362	5	11543.7848	3	0.005
7_{16}	6_{15}	12664.6362	5			12686.7836	-6	12580.1736	-5	0.005

D6

transitions		C10 Observed /MHz	C10 δ /kHz	C1 Observed /MHz	C1 δ /kHz	C2 Observed /MHz	C2 δ /kHz	C3 Observed /MHz	C3 δ /kHz	Error
5_{05}	4_{04}	8645.5217	-2			8660.1749	-3	8589.3390	0	0.005
5_{15}	4_{14}	8332.1308	-3			8345.7303	-2	8278.3532	-4	0.005
5_{14}	4_{13}	9088.7329	6			9105.8956	5	9028.4377	8	0.005
6_{06}	5_{05}	10330.5310	1			10347.6496	4	10263.6691	-3	0.005
6_{16}	5_{15}	9988.0363	-3			10004.2465	0	9923.6418	4	0.005
6_{15}	5_{14}	10893.7019	-1			10914.1447	-4	10821.5123	-6	0.005
7_{07}	6_{06}	11994.2438	0			12013.6271	-1	11916.9622	2	0.005
7_{17}	6_{16}	11638.8310	5			11657.5972	2	11563.8624	0	0.005
7_{16}	6_{15}	12691.0247	-3							0.005

Table S6. MP2/6-311++G(d, p) geometry of *cis*-AA⋯FA.

bond lengths/Å		angles/°		dihedral angel/°	
C2C1	1.4837				
C3C2	1.3412	C3C2C1	120.8		
O4C1	1.2287	O4C1C2	123.5	O4C1C2C3	0.0
O5C1	1.3275	O5C1C2	112.2	O5C1C2C3	180.0
H6O5	0.9891	H6O5C1	108.9	H6O5C1C2	180.0
H7C2	1.0848	H7C2C1	116.8	H7C2C1O4	180.0
H8C3	1.0845	H8C3C2	121.1	H8C3C2C1	180.0
H8C3	1.0855	H8C3C2	120.3	H8C3C2C1	0.0
C10C1	3.8496	C10C1C3	152.1	C10C1C3C2	180.0
O11C10	1.2218	O11C10C1	58.5	O11C10C1C3	180.0
O12C10	1.3176	O12C10O11	126.2	O12C10O11C1	0.0
H13O12	0.9934	H13O12C10	108.6	H13O12C10O11	0.0
H14C10	1.0956	H14C10O11	122.3	H14C10O11O12	180.0

Table S7. MP2/6-311++G(d, p) geometry of *trans*-AA⋯FA

bond lengths/Å		angles/°		dihedral angel/°	
C2C1	1.4807				
C3C2	1.3420	C3C2C1	123.2		
O4C1	1.2304	O4C1C2	121.2	O4C1C2C3	180.0
O5C1	1.3268	O5C1C2	114.6	O5C1C2C3	0.0
H6O5	0.9886	H6O5C1	108.7	H6O5C1C2	180.0
H7C2	1.0849	H7C2C1	114.6	H7C2C1O5	180.0
H8C3	1.0850	H8C3C2	120.7	H8C3C2C1	180.0
H8C3	1.0846	H8C3C2	121.0	H8C3C2C1	0.0
C10C1	3.8498	C10C1C3	155.4	C10C1C3C2	180.0
O11C10	1.2219	O11C10C1	58.4	O11C10C1C3	0.0
O12C10	1.3174	O12C10O11	126.3	O12C10O11C1	0.0
H13O12	0.9934	H13O12C10	108.6	H13O12C10O11	0.0
H14C10	1.0955	H14C10O11	122.3	H14C10O11O12	180.0