Electronic Supplementary Information

Three non-bonding interaction typologies of the thiazole-formaldehyde complex observed by rotational spectroscopy

Wenqin Li,[a, b, #] Yugao Xu,[a, #] Yan Jin,[a] Xiaolong Li,[a] Walther Caminati[c] and Gang Feng[a,*]

[a] School of Chemistry and Chemical Engineering, Chongqing University, Daxuecheng South Rd. 55, 401331, Chongqing, China. * E-mail: fengg@cqu.edu.cn

[b] Departamento de Química Física y Química Inorganica, Facultad de Ciencias, Universidad de Valladolid, E-47011 Valladolid, Spain.

[c] Dipartimento di Chimica "G. Ciamician", Università di Bologna, Via Selmi 2, I-40126 Bologna, Italy.

Content

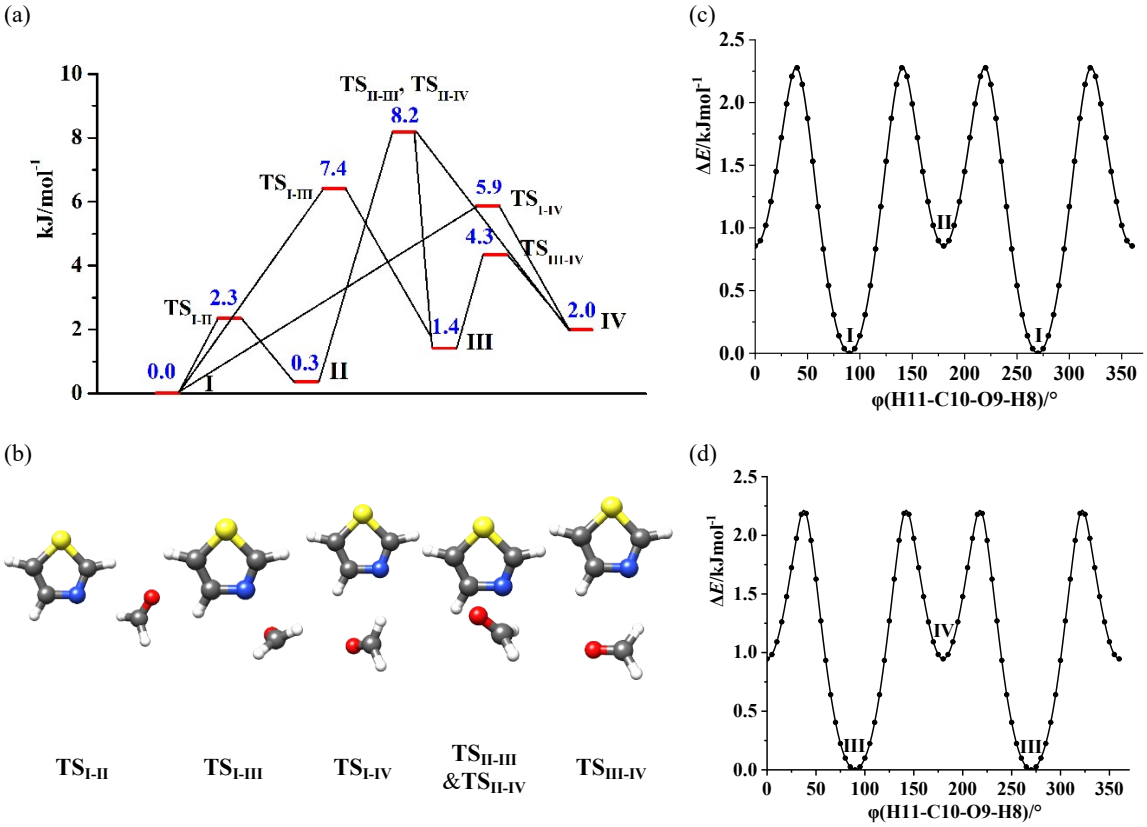


Figure S1. (a) Isomerization pathways between isomers **I-IV** and (b) the relative transition states as well as potential energy curve connecting the isomerization of **I** and **II** (c) and **III** and **IV** (d). The structures of the TSs were obtained at the B3LYP-D3(BJ)/def2-TZVP level of theory. The relative zero-point energies of the TSs and minima are calculated at the CCSD/6–311++G(2d,p) level.

Table S1. Energy minima of the thiazole-formaldehyde complex obtained at the B3LYP-D3(BJ)/def2-TZVP level of theory.

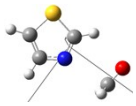
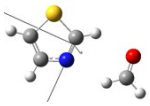
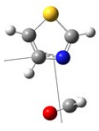
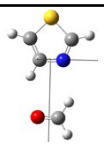
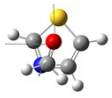
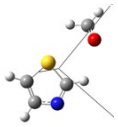
Isomer	**I**	**II**	**III**	**IV**	**V**	**VI**	**VII**
							
A/MHz	5299	5120	6887	6998	3190	5751	3434
B/MHz	1124	1000	1005	879	1649	1101	1384
C/MHz	933	837	882	781	1468	958	1220
μ_a/D	−2.4	1.2	−2.5	−1.4	−0.5	1.9	2.3
μ_b/D	1.8	1.5	−1.4	1.3	−0.8	−2.9	0.7
μ_c/D	0	0	0	0	−0.4	1.3	−1.6
$1.5\chi_{aa}$/MHz	−5.10	−3.87	−4.80	−3.77	3.06	1.39	2.31
$0.25(\chi_{bb}-\chi_{cc})$/MHz	−0.52	−0.78	−0.62	−0.83	−0.592	−1.68	−0.42
ΔE_0/kJmol^{-1}	0	1.1	1.6	3.0	5.7	5.6	5.9
D_0/kJmol^{-1}	-22.0	-20.1	-20.2	-18.1	-14.3	-14.0	-14.2
$D_{0,\mathrm{BSSE}}$/kJmol^{-1}	-20.8	-18.5	-18.9	-16.5	-13.4	-13.3	-12.9

Table S2. Rotational parameters obtained at the B3LYP–D3(BJ)/def2–TZVP (1), B3LYP–D3(BJ)/6–311++G(d,p) (2), B3LYP–D3(BJ)/6–311++G(2d,p) (3), B3LYP–D3(BJ)/aug-cc-pVDZ (4), CCSD/aug-cc-pVDZ (5), CCSD/6–311++G(d,p) (6), and CCSD/6–311++G(2d,p) (7) level of theories, as well as the ground vibrational state rotational constants calculated at the B3LYP–D3(BJ)/def2–TZVP level of theory (8). Experimental rotational constants and ^{14}N quadrupole coupling constants are included for comparison.

Parameters	Exp.	1	2	3	4	5	6	7	8
Isomer **I**									
A/MHz	5213.62	5299	5250	5265	5214	5113	5198	5201	5258
B/MHz	1076.60	1124	1122	1122	1122	1082	1068	1077	1084
C/MHz	897.98	933	931	931	929	899	891	898	905
$1.5\chi_{aa}$/MHz	−4.50	−5.10	−5.07	−5.02	−4.61	−4.29	−4.85	−4.80	
$0.25(\chi_{bb}-\chi_{cc})$/MHz	−0.49	−0.52	−0.42	−0.46	−0.37	−0.40	−0.46	−0.50	
Isomer **II**									
A/MHz	5102.02	5120	5068	5075	5007	4929	5049	5042	5114
B/MHz	989.97	1000	1004	1001	1002	928	970	977	981
C/MHz	829.68	837	838	836	834	819	814	818	823
$1.5\chi_{aa}$/MHz	−4.21	−3.87	−3.78	−3.65	−3.31	−2.92	−4.57	−3.44	
$0.25(\chi_{bb}-\chi_{cc})$/MHz	−0.56	−0.78	−0.68	−0.74	−0.64	−0.65	−0.54	−0.75	
Isomer **III**									
A/MHz	6862.08	6887	6840	6860	6800	6758	6855	6849	6836
B/MHz	955.20	1005	1004	1003	1003	961	948	957	968
C/MHz	843.90	882	881	881	879	847	838	844	854
$1.5\chi_{aa}$/MHz	−4.21	−4.80	−4.74	−4.76	−4.20	−3.95	−3.55	−4.62	
$0.25(\chi_{bb}-\chi_{cc})$/MHz	−0.56	−0.62	−0.52	−0.54	−0.48	−0.49	−0.69	−0.57	
Isomer **IV**									
A/MHz		6998	6948	6963	6891	6828	6951	6938	6947
B/MHz		879	881	878	874	855	848	854	863
C/MHz		781	782	780	776	760	756	760	768
$1.5\chi_{aa}$/MHz		−3.77	−3.69	−3.63	−3.06	−2.77	−3.41	−3.47	
$0.25(\chi_{bb}-\chi_{cc})$/MHz		−0.83	−0.74	−0.78	−0.71	−0.71	−0.75	−0.76	

Table S3. r_0 (isomers **I**, **II** and **III**) and r_e (isomer **IV**) structural coordinates in the principal axe system.

Isomer	Atom	*a*/Å	*b*/Å	*c*/Å
I	S	-1.744	-0.934	0.000
	C	-0.057	-0.526	0.000
	N	0.208	0.746	0.000
	C	-0.965	1.481	0.000
	C	-2.116	0.756	0.000
	H	-3.133	1.118	0.000
	H	-0.911	2.562	0.000
	H	0.707	-1.292	0.000
	O	3.151	-0.719	0.000
	C	3.104	0.486	0.000
	H	3.085	1.067	-0.937
	H	3.078	1.067	0.937
II	S	-1.670	-1.014	0.000
	C	-0.044	-0.384	0.000
	N	0.036	0.915	0.000
	C	-1.216	1.486	0.000
	C	-2.262	0.612	0.000
	H	-3.319	0.824	0.000
	H	-1.306	2.564	0.000
	H	0.817	-1.040	0.000
	O	3.215	-0.708	0.000
	C	3.382	0.488	0.000
	H	2.529	1.189	0.000
	H	4.401	0.923	0.000
III	S	-2.313	-0.127	0.000
	C	-0.905	-1.152	0.000
	N	0.230	-0.519	0.000
	C	0.039	0.844	0.000
	C	-1.262	1.250	0.000
	H	-1.654	2.254	0.000
	H	0.904	1.492	0.000
	H	-1.004	-2.228	0.000
	O	3.428	0.531	0.000
	C	3.106	-0.631	0.000
	H	2.949	-1.197	-0.936
	H	2.949	-1.197	0.936
IV	N	0.026	0.800	0.000
	C	0.086	-0.586	0.000
	C	-1.116	-1.223	0.000
	S	-2.403	-0.065	0.000
	C	-1.210	1.197	0.000
	O	3.494	-0.625	0.000
	C	3.510	0.584	0.000
	H	-1.305	-2.285	0.000
	H	1.055	-1.068	0.000
	H	-1.503	2.239	0.000
	H	4.464	1.141	0.000
	H	2.578	1.173	0.000

Table S4. Observed rotational transitions and residuals (in MHz) for isomer **I** of the thiazole-formaldehyde complex.

J'	K_a'	K_c'	F'	v'	J''	K_a''	K_c''	F''	v'	Obs.	Obs.−Cal.
3	0	3	4	1	2	0	2	3	1	5901.8964	0.0008
3	0	3	3	1	2	0	2	2	1	5901.8335	−0.0064
3	0	3	2	1	2	0	2	1	1	5901.7160	0.0016
3	1	3	4	1	2	1	2	3	1	5653.1583	−0.0020
3	1	3	3	1	2	1	2	2	1	5652.8732	−0.0039
3	1	3	2	1	2	1	2	1	1	5653.0937	−0.0022
3	1	2	4	1	2	1	1	3	1	6188.7988	−0.0038
3	1	2	3	1	2	1	1	2	1	6188.5399	−0.0025
3	1	2	2	1	2	1	1	1	1	6188.8581	−0.0007
3	2	2	4	1	2	2	1	3	1	5924.6186	0.0004
3	2	2	3	1	2	2	1	2	1	5923.6517	−0.0033
3	2	2	2	1	2	2	1	1	1	5925.1527	-0.0007
3	2	2	3	1	2	2	1	3	1	5924.6186	0.0003
3	2	2	2	1	2	2	1	2	1	5923.6517	−0.0035
4	0	4	5	1	3	0	3	4	1	7842.9927	−0.0030
4	0	4	4	1	3	0	3	3	1	7842.9438	−0.0022
4	0	4	3	1	3	0	3	2	1	7842.9055	−0.0072
4	1	4	5	1	3	1	3	4	1	7531.0793	−0.0031
4	1	4	4	1	3	1	3	3	1	7530.9470	−0.0027
4	1	4	3	1	3	1	3	2	1	7531.0163	−0.0001
4	1	3	5	1	3	1	2	4	1	8244.7452	0.0000
4	1	3	4	1	3	1	2	3	1	8244.6268	0.0001
4	1	3	3	1	3	1	2	2	1	8244.7301	−0.0057
4	2	3	5	1	3	2	2	4	1	7894.8534	−0.0012
4	2	3	4	1	3	2	2	3	1	7894.4402	−0.0026
4	2	3	3	1	3	2	2	2	1	7894.9581	−0.0023
4	2	2	5	1	3	2	1	4	1	7951.0790	−0.0021
4	2	2	4	1	3	2	1	3	1	7950.6925	−0.0038
4	2	2	3	1	3	2	1	2	1	7951.1759	−0.0071
5	0	5	6	1	4	0	4	5	1	9762.4593	−0.0024
5	0	5	5	1	4	0	4	4	1	9762.4113	−0.0013
5	0	5	4	1	4	0	4	3	1	9762.4113	−0.0026
5	1	5	6	1	4	1	4	5	1	9403.8690	−0.0039
5	1	5	5	1	4	1	4	4	1	9403.7953	0.0004
5	1	5	4	1	4	1	4	3	1	9403.8266	0.0024
5	1	4	6	1	4	1	3	5	1	10294.4076	−0.0104
5	1	4	5	1	4	1	3	4	1	10294.3462	−0.0024
5	1	4	4	1	4	1	3	3	1	10294.4076	0.0047
5	2	4	6	1	4	2	3	5	1	9861.3322	0.0000
5	2	4	5	1	4	2	3	4	1	9861.1102	−0.0032
5	2	4	4	1	4	2	3	3	1	9861.3547	0.0000
5	2	3	6	1	4	2	2	5	1	9972.7736	0.0007
5	2	3	5	1	4	2	2	4	1	9972.5872	−0.0002
5	2	3	4	1	4	2	2	3	1	9972.7899	−0.0018
5	3	3	6	1	4	3	2	5	1	9892.1557	0.0015
5	3	3	5	1	4	3	2	4	1	9891.6985	0.0003
5	3	3	4	1	4	3	2	3	1	9892.2671	0.0004
5	3	2	6	1	4	3	1	5	1	9894.5032	0.0009
5	3	2	5	1	4	3	1	4	1	9894.0491	0.0015
5	3	2	4	1	4	3	1	3	1	9894.6138	−0.0007
6	0	6	7	1	5	0	5	6	1	11656.5500	−0.0013
6	0	6	6	1	5	0	5	5	1	11656.4998	−0.0013
6	0	6	5	1	5	0	5	4	1	11656.5128	−0.0076
6	0	6	6	1	5	0	5	6	1	11655.3662	−0.0047
6	1	6	7	1	5	1	5	6	1	11270.6256	−0.0010

6	1	6	6	1	5	1	5	5	1	11270.5739	0.0005
6	1	6	5	1	5	1	5	4	1	11270.5862	−0.0044
6	1	5	7	1	5	1	4	6	1	12335.8053	−0.0029
6	1	5	6	1	5	1	4	5	1	12335.7573	−0.0026
6	1	5	5	1	5	1	4	4	1	12335.8026	0.0077
6	2	5	7	1	5	2	4	6	1	11823.0724	0.0020
6	2	5	6	1	5	2	4	5	1	11822.9351	−0.0019
6	2	5	5	1	5	2	4	4	1	11823.0724	0.0015
6	2	4	7	1	5	2	3	6	1	12014.9960	−0.0025
6	2	4	6	1	5	2	3	5	1	12014.9034	−0.0004
6	2	4	5	1	5	2	3	4	1	12014.9960	0.0002
6	3	4	7	1	5	3	3	6	1	11876.4784	0.0006
6	3	4	6	1	5	3	3	5	1	11876.2112	−0.0006
6	3	4	5	1	5	3	3	4	1	11876.5189	−0.0006
6	3	3	7	1	5	3	2	6	1	11882.7246	0.0010
6	3	3	6	1	5	3	2	5	1	11882.4641	0.0038
6	3	3	5	1	5	3	2	4	1	11882.7647	−0.0003
6	4	3	7	1	5	4	2	6	1	11867.5233	0.0039
6	4	3	5	1	5	4	2	4	1	11867.6215	0.0011
6	4	2	7	1	5	4	1	6	1	11867.5866	0.0011
7	0	7	8	1	6	0	6	7	1	13523.4213	0.0001
7	0	7	7	1	6	0	6	6	1	13523.3655	−0.0043
7	0	7	6	1	6	0	6	5	1	13523.4016	0.0021
7	1	7	8	1	6	1	6	7	1	13130.6878	0.0015
7	1	7	7	1	6	1	6	6	1	13130.6514	0.0053
7	1	7	6	1	6	1	6	5	1	13130.6514	−0.0075
7	1	6	8	1	6	1	5	7	1	14366.6232	−0.0015
7	1	6	7	1	6	1	5	6	1	14366.5818	−0.0042
7	1	6	6	1	6	1	5	5	1	14366.6232	0.0092
7	2	6	8	1	6	2	5	7	1	13779.1373	0.0081
7	2	6	7	1	6	2	5	6	1	13779.0395	0.0000
7	2	6	6	1	6	2	5	5	1	13779.1232	−0.0001
7	2	5	8	1	6	2	4	7	1	14078.5881	0.0048
7	2	5	7	1	6	2	4	6	1	14078.5398	0.0039
7	2	5	6	1	6	2	4	5	1	14078.5700	−0.0045
8	0	8	9	1	7	0	7	8	1	15363.7231	−0.0002
8	0	8	8	1	7	0	7	7	1	15363.6732	0.0009
8	0	8	7	1	7	0	7	6	1	15363.7138	0.0066
8	1	8	9	1	7	1	7	8	1	14983.6606	0.0040
8	1	8	8	1	7	1	7	7	1	14983.6295	0.0055
8	1	8	7	1	7	1	7	6	1	14983.6449	0.0095
8	1	7	9	1	7	1	6	8	1	16384.2545	0.0034
8	1	7	8	1	7	1	6	7	1	16384.2114	−0.0051
8	1	7	7	1	7	1	6	6	1	16384.2545	0.0120
9	0	9	10	1	8	0	8	9	1	17180.6900	0.0049
9	0	9	9	1	8	0	8	8	1	17180.6427	0.0069
9	0	9	8	1	8	0	8	7	1	17180.6900	0.0176
2	1	2	2	1	1	0	1	1	1	7908.2098	−0.0053
2	1	2	1	1	1	0	1	0	1	7907.1945	−0.0093
3	1	3	2	1	2	0	2	1	1	9617.0383	−0.0044
3	1	3	4	1	2	0	2	3	1	9617.2059	−0.0018
3	1	3	3	1	2	0	2	2	1	9617.1062	0.0004
3	2	1	4	1	3	1	2	3	1	12175.3035	−0.0109
3	2	1	3	1	3	1	2	2	1	12174.7697	0.0016
3	2	1	4	1	3	1	2	4	1	12174.8856	−0.0002
3	2	1	3	1	3	1	2	3	1	12175.3454	−0.0016
4	1	4	3	1	3	0	3	2	1	11246.3431	−0.0016
4	1	4	4	1	3	0	3	3	1	11246.2142	−0.0013

4	1	4	5	1	3	0	3	4	1	11246.3905	−0.0040
2	2	0	3	1	2	1	1	3	1	12416.4784	−0.0038
2	2	0	2	1	2	1	1	2	1	12417.6235	−0.0029
2	2	0	1	1	2	1	1	1	1	12415.8387	−0.0073
2	2	0	3	1	1	1	1	2	1	16723.3870	−0.0006
2	2	0	2	1	1	1	1	1	1	16724.2020	−0.0043
2	2	1	3	1	1	1	0	2	1	16539.2246	−0.0068
2	2	1	2	1	1	1	0	1	1	16539.4526	−0.0004
2	2	1	1	1	1	1	0	0	1	16539.8012	−0.0075
2	2	1	2	1	2	1	2	2	1	12948.2388	0.0021
2	2	1	1	1	2	1	2	1	1	12945.5056	0.0035
3	2	2	4	1	3	1	3	4	1	13217.9427	0.0092
3	2	2	3	1	3	1	3	3	1	13219.0220	0.0075
3	2	2	2	1	3	1	3	2	1	13217.5690	0.0094
4	2	3	5	1	4	1	4	5	1	13581.7132	0.0043
4	2	3	4	1	4	1	4	4	1	13582.5101	0.0025
4	2	3	3	1	4	1	4	3	1	13581.5095	0.0059
4	2	2	5	1	4	1	3	5	1	11881.2181	−0.0036
4	2	2	4	1	4	1	3	4	1	11881.4204	0.0036
4	2	2	3	1	4	1	3	3	1	11881.1702	−0.0013
5	1	5	5	1	4	0	4	4	1	12807.0634	−0.0008
5	1	5	4	1	4	0	4	3	1	12807.2538	−0.0023
5	1	5	6	1	4	0	4	5	1	12807.2692	−0.0025
5	0	5	4	1	4	1	4	3	1	6358.9858	0.0038
5	0	5	5	1	4	1	4	4	1	6359.1392	−0.0040
5	0	5	6	1	4	1	4	5	1	6359.0532	−0.0097
5	2	4	6	1	5	1	5	6	1	14039.1728	0.0046
5	2	4	5	1	5	1	5	5	1	14039.8299	0.0036
5	2	4	4	1	5	1	5	4	1	14039.0283	−0.0058
5	2	3	6	1	5	1	4	6	1	11559.5726	−0.0039
5	2	3	5	1	5	1	4	5	1	11559.6538	−0.0017
5	2	3	4	1	5	1	4	4	1	11559.5699	0.0094
6	1	6	6	1	5	0	5	5	1	14315.2260	0.0010
6	1	6	5	1	5	0	5	4	1	14315.4338	0.0009
6	1	6	7	1	5	0	5	6	1	14315.4338	−0.0027
6	0	6	5	1	5	1	5	4	1	8611.6711	−0.0071
6	0	6	6	1	5	1	5	5	1	8611.8473	−0.0022
6	0	6	7	1	5	1	5	6	1	8611.7431	0.0016
7	1	7	8	1	6	0	6	7	1	15789.5714	0.0000
7	1	7	7	1	6	0	6	6	1	15789.3716	0.0016
7	1	7	6	1	6	0	6	5	1	15789.5714	0.0000
7	0	7	8	1	6	1	6	7	1	10864.5287	−0.0071
7	0	7	7	1	6	1	6	6	1	10864.6473	0.0013
7	0	7	6	1	6	1	6	5	1	10864.4845	−0.0024
3	0	3	4	0	2	0	2	3	0	5901.1525	0.0044
3	0	3	3	0	2	0	2	2	0	5901.0963	0.0039
3	0	3	2	0	2	0	2	1	0	5900.9705	0.0037
3	1	3	4	0	2	1	2	3	0	5652.3877	−0.0004
3	1	3	3	0	2	1	2	2	0	5652.1076	0.0025
3	1	3	2	0	2	1	2	1	0	5652.3267	0.0028
3	1	2	4	0	2	1	1	3	0	6188.0912	0.0033
3	1	2	3	0	2	1	1	2	0	6187.8327	0.0050
3	1	2	2	0	2	1	1	1	0	6188.1518	0.0077
3	2	2	4	0	2	2	1	3	0	5923.8776	0.0021
3	2	2	3	0	2	2	1	2	0	5922.9134	0.0010
3	2	2	2	0	2	2	1	1	0	5924.4120	0.0012
3	2	2	3	0	2	2	1	3	0	5923.8776	0.0020
3	2	2	2	0	2	2	1	2	0	5922.9134	0.0008

4	0	4	5	0	3	0	3	4	0	7841.9984	0.0049
4	0	4	4	0	3	0	3	3	0	7841.9498	0.0060
4	0	4	3	0	3	0	3	2	0	7841.9116	0.0012
4	1	4	5	0	3	1	3	4	0	7530.0629	0.0113
4	1	4	4	0	3	1	3	3	0	7529.9133	−0.0055
4	1	4	3	0	3	1	3	2	0	7529.9976	0.0120
4	1	3	5	0	3	1	2	4	0	8243.7968	0.0061
4	1	3	4	0	3	1	2	3	0	8243.6768	0.0047
4	1	3	3	0	3	1	2	2	0	8243.7796	−0.0016
4	2	3	5	0	3	2	2	4	0	7893.8714	0.0080
4	2	3	4	0	3	2	2	3	0	7893.4584	0.0067
4	2	3	3	0	3	2	2	2	0	7893.9674	−0.0017
4	2	2	5	0	3	2	1	4	0	7950.1063	0.0043
4	2	2	4	0	3	2	1	3	0	7949.7180	0.0007
4	2	2	3	0	3	2	1	2	0	7950.2015	−0.0023
5	0	5	6	0	4	0	4	5	0	9761.2039	0.0036
5	0	5	5	0	4	0	4	4	0	9761.1537	0.0025
5	0	5	4	0	4	0	4	3	0	9761.1527	0.0002
5	0	5	5	0	4	0	4	5	0	9760.0742	0.0041
5	1	5	6	0	4	1	4	5	0	9402.5852	0.0028
5	1	5	5	0	4	1	4	4	0	9402.5064	0.0022
5	1	5	4	0	4	1	4	3	0	9402.5384	0.0049
5	1	4	6	0	4	1	3	5	0	10293.2227	0.0004
5	1	4	5	0	4	1	3	4	0	10293.1554	0.0024
5	2	4	6	0	4	2	3	5	0	9860.0908	−0.0009
5	2	4	5	0	4	2	3	4	0	9859.8711	−0.0018
5	2	4	4	0	4	2	3	3	0	9860.1149	0.0006
5	2	3	6	0	4	2	2	5	0	9971.5614	0.0054
5	2	3	5	0	4	2	2	4	0	9971.3707	0.0001
5	2	3	4	0	4	2	2	3	0	9971.5746	−0.0002
5	3	3	6	0	4	3	2	5	0	9890.9200	−0.0001
5	3	3	5	0	4	3	2	4	0	9890.4619	−0.0022
5	3	3	4	0	4	3	2	3	0	9891.0346	0.0019
5	3	2	6	0	4	3	1	5	0	9893.2684	−0.0006
5	3	2	5	0	4	3	1	4	0	9892.8176	0.0032
5	3	2	4	0	4	3	1	3	0	9893.3831	0.0018
6	0	6	7	0	5	0	5	6	0	11655.0243	−0.0014
6	0	6	6	0	5	0	5	5	0	11654.9735	−0.0020
6	0	6	5	0	5	0	5	4	0	11654.9921	−0.0027
6	0	6	6	0	5	0	5	6	0	11653.8446	−0.0007
6	1	6	7	0	5	1	5	6	0	11269.0754	0.0003
6	1	6	6	0	5	1	5	5	0	11269.0240	0.0021
6	1	6	5	0	5	1	5	4	0	11269.0381	−0.0010
6	1	5	7	0	5	1	4	6	0	12334.3680	−0.0014
6	1	5	6	0	5	1	4	5	0	12334.3203	−0.0008
6	1	5	5	0	5	1	4	4	0	12334.3642	0.0081
6	2	5	7	0	5	2	4	6	0	11821.5804	0.0009
6	2	5	6	0	5	2	4	5	0	11821.4447	−0.0014
6	2	5	5	0	5	2	4	4	0	11821.5804	0.0004
6	2	4	7	0	5	2	3	6	0	12013.5488	0.0009
6	2	4	6	0	5	2	3	5	0	12013.4536	0.0004
6	2	4	5	0	5	2	3	4	0	12013.5488	0.0037
6	3	4	7	0	5	3	3	6	0	11874.9966	−0.0014
6	3	4	6	0	5	3	3	5	0	11874.7305	−0.0016
6	3	4	5	0	5	3	3	4	0	11875.0390	−0.0008
6	3	3	7	0	5	3	2	6	0	11881.2400	−0.0059
6	3	3	6	0	5	3	2	5	0	11880.9828	0.0002
6	3	3	5	0	5	3	2	4	0	11881.2855	−0.0018

6	4	3	7	0	5	4	2	6	0	11866.0338	−0.0042
6	4	3	5	0	5	4	2	4	0	11866.1303	−0.0087
6	4	2	7	0	5	4	1	6	0	11866.1020	−0.0022
7	0	7	8	0	6	0	6	7	0	13521.6267	−0.0001
7	0	7	7	0	6	0	6	6	0	13521.5740	−0.0016
7	0	7	6	0	6	0	6	5	0	13521.6048	−0.0003
7	1	7	8	0	6	1	6	7	0	13128.8715	−0.0009
7	1	7	7	0	6	1	6	6	0	13128.8354	0.0031
7	1	7	6	0	6	1	6	5	0	13128.8354	−0.0098
7	1	6	8	0	6	1	5	7	0	14364.9410	0.0006
7	1	6	7	0	6	1	5	6	0	14364.8969	−0.0047
7	1	6	6	0	6	1	5	5	0	14364.9261	−0.0034
7	2	6	8	0	6	2	5	7	0	13777.3848	−0.0019
7	2	6	7	0	6	2	5	6	0	13777.2951	−0.0019
7	2	6	6	0	6	2	5	5	0	13777.3848	0.0039
7	2	5	8	0	6	2	4	7	0	14076.9020	0.0000
7	2	5	7	0	6	2	4	6	0	14076.8517	−0.0029
7	2	5	6	0	6	2	4	5	0	14076.9020	0.0087
8	0	8	9	0	7	0	7	8	0	15361.6500	−0.0069
8	0	8	8	0	7	0	7	7	0	15361.6042	−0.0016
8	0	8	7	0	7	0	7	6	0	15361.6392	−0.0016
8	1	8	9	0	7	1	7	8	0	14981.5754	−0.0039
8	1	8	8	0	7	1	7	7	0	14981.5377	−0.0090
8	1	8	7	0	7	1	7	6	0	14981.5541	−0.0040
8	1	7	9	0	7	1	6	8	0	16382.3199	0.0020
8	1	7	8	0	7	1	6	7	0	16382.2749	−0.0085
8	1	7	7	0	7	1	6	6	0	16382.3095	0.0001
9	0	9	10	0	8	0	8	9	0	17178.3318	−0.0128
9	0	9	9	0	8	0	8	8	0	17178.2882	−0.0071
9	0	9	8	0	8	0	8	7	0	17178.3318	−0.0001
2	1	2	2	0	1	0	1	1	0	7907.6832	−0.0012
2	1	2	1	0	1	0	1	0	0	7906.6851	0.0119
3	1	3	2	0	2	0	2	1	0	9616.2413	0.0050
3	1	3	4	0	2	0	2	3	0	9616.4085	0.0072
3	1	3	3	0	2	0	2	2	0	9616.3099	0.0106
3	2	1	4	0	3	1	2	3	0	12175.2411	−0.0022
3	2	1	3	0	3	1	2	2	0	12174.6935	−0.0034
3	2	1	4	0	3	1	2	4	0	12174.8131	−0.0016
3	2	1	3	0	3	1	2	3	0	12175.2753	−0.0006
4	1	4	3	0	3	0	3	2	0	11245.2579	0.0029
4	1	4	4	0	3	0	3	3	0	11245.1302	0.0044
4	1	4	5	0	3	0	3	4	0	11245.3098	0.0050
2	2	0	3	0	2	1	1	3	0	12416.4362	0.0020
2	2	0	2	0	2	1	1	2	0	12417.5807	0.0022
2	2	0	1	0	2	1	1	1	0	12415.7984	0.0004
2	2	0	3	0	1	1	1	2	0	16722.8817	−0.0010
2	2	0	2	0	1	1	1	1	0	16723.7083	0.0069
2	2	1	3	0	1	1	0	2	0	16538.7077	0.0015
2	2	1	2	0	1	1	0	1	0	16538.9295	0.0017
2	2	1	1	0	1	1	0	0	0	16539.2852	0.0017
2	2	1	2	0	2	1	2	2	0	12948.2388	−0.0059
2	2	1	1	0	2	1	2	1	0	12945.5056	−0.0045
3	2	2	4	0	3	1	3	4	0	13217.9755	0.0013
3	2	2	3	0	3	1	3	3	0	13219.0507	−0.0013
3	2	2	2	0	3	1	3	2	0	13217.5942	−0.0028
4	2	3	5	0	4	1	4	5	0	13581.7896	0.0036
4	2	3	4	0	4	1	4	4	0	13582.5894	0.0046
4	2	3	3	0	4	1	4	3	0	13581.5814	0.0007

4	2	2	3	0	4	1	3	3	0	11881.0773	0.0014
5	1	5	5	0	4	0	4	4	0	12805.6893	0.0031
5	1	5	4	0	4	0	4	3	0	12805.8855	0.0073
5	1	5	6	0	4	0	4	5	0	12805.8929	−0.0007
5	0	5	4	0	4	1	4	3	0	6357.8170	0.0091
5	0	5	5	0	4	1	4	4	0	6357.9635	−0.0056
5	0	5	6	0	4	1	4	5	0	6357.8810	−0.0078
5	2	4	6	0	5	1	5	6	0	14039.2921	−0.0033
5	2	4	5	0	5	1	5	5	0	14039.9487	−0.0047
5	2	4	4	0	5	1	5	4	0	14039.1533	−0.0081
5	2	3	6	0	5	1	4	6	0	11559.4566	−0.0031
5	2	3	5	0	5	1	4	5	0	11559.5360	−0.0027
5	2	3	4	0	5	1	4	4	0	11559.4430	−0.0006
6	1	6	6	0	5	0	5	5	0	14313.5556	−0.0013
6	1	6	5	0	5	0	5	4	0	14313.7698	0.0050
6	1	6	7	0	5	0	5	6	0	14313.7698	0.0013
6	0	6	5	0	5	1	5	4	0	8610.2702	0.0010
6	0	6	6	0	5	1	5	5	0	8610.4417	0.0012
6	0	6	7	0	5	1	5	6	0	8610.3332	0.0008
7	1	7	8	0	6	0	6	7	0	15787.6124	−0.0027
7	1	7	7	0	6	0	6	6	0	15787.4128	−0.0008
7	1	7	6	0	6	0	6	5	0	15787.6124	−0.0028
7	0	7	8	0	6	1	6	7	0	10862.8797	−0.0044
7	0	7	7	0	6	1	6	6	0	10862.9950	0.0007
7	0	7	6	0	6	1	6	5	0	10862.8335	−0.0017

Table S5. Observed rotational transitions and residuals (in MHz) for ^{34}S1 isotopologue of isomer **I** of the thiazole-formaldehyde complex.

J'	K_a'	K_c'	F'	v'	J''	K_a''	K_c''	F''	v''	Obs.	Obs.−Cal.
3	0	3	4	1	2	0	2	3	1	5827.2512	−0.0014
3	0	3	3	1	2	0	2	2	1	5827.2043	0.0074
3	0	3	2	1	2	0	2	1	1	5827.0652	−0.0063
4	0	4	5	1	3	0	3	4	1	7743.3515	−0.0057
4	0	4	4	1	3	0	3	3	1	7743.3010	−0.0062
4	0	4	3	1	3	0	3	2	1	7743.2658	−0.0084
4	1	4	5	1	3	1	3	4	1	7434.1682	0.0022
4	1	4	4	1	3	1	3	3	1	7434.0240	−0.0092
4	1	4	3	1	3	1	3	2	1	7434.0993	−0.0006
4	1	3	5	1	3	1	2	4	1	8142.7811	−0.0049
4	1	3	4	1	3	1	2	3	1	8142.6626	−0.0047
4	1	3	3	1	3	1	2	2	1	8142.7811	0.0044
5	0	5	6	1	4	0	4	5	1	9637.7447	−0.0064
5	0	5	5	1	4	0	4	4	1	9637.7002	−0.0014
5	0	5	4	1	4	0	4	3	1	9637.7002	−0.0031
5	1	5	6	1	4	1	4	5	1	9282.6867	−0.0033
5	1	5	5	1	4	1	4	4	1	9282.6073	−0.0045
5	1	5	4	1	4	1	4	3	1	9282.6425	0.0012
5	1	4	6	1	4	1	3	5	1	10166.9059	−0.0009
5	1	4	5	1	4	1	3	4	1	10166.8350	−0.0024
5	1	4	4	1	4	1	3	3	1	10166.8932	0.0015
5	2	4	6	1	4	2	3	5	1	9737.0425	0.0000
5	2	4	5	1	4	2	3	4	1	9736.8219	−0.0018
5	2	4	4	1	4	2	3	3	1	9737.0668	0.0017
5	2	3	6	1	4	2	2	5	1	9848.9631	0.0009
5	2	3	5	1	4	2	2	4	1	9848.7783	0.0012
5	2	3	4	1	4	2	2	3	1	9848.9786	−0.0024
6	0	6	7	1	5	0	5	6	1	11506.7181	0.0017
6	0	6	6	1	5	0	5	5	1	11506.6628	−0.0029
6	0	6	5	1	5	0	5	4	1	11506.6824	−0.0029
6	1	6	7	1	5	1	5	6	1	11125.1630	0.0014
6	1	6	6	1	5	1	5	5	1	11125.1087	0.0004
6	1	6	5	1	5	1	5	4	1	11125.1239	−0.0016
6	1	5	7	1	5	1	4	6	1	12182.6930	−0.0002
6	1	5	6	1	5	1	4	5	1	12182.6473	0.0025
6	1	5	5	1	5	1	4	4	1	12182.6875	0.0076
7	0	7	8	1	6	0	6	7	1	13348.4842	0.0092
7	0	7	7	1	6	0	6	6	1	13348.4310	0.0076
7	0	7	6	1	6	0	6	5	1	13348.4616	0.0083
2	2	0	3	1	2	1	1	3	1	12182.4268	−0.0051
2	2	1	3	1	1	1	0	2	1	16254.2066	0.0022
2	2	1	2	1	1	1	0	1	1	16254.4285	0.0025
3	0	3	4	0	2	0	2	3	0	5826.5422	0.0080
3	0	3	3	0	2	0	2	2	0	5826.4684	−0.0099
4	0	4	5	0	3	0	3	4	0	7742.3935	−0.0003
4	0	4	4	0	3	0	3	3	0	7742.3440	0.0001
4	0	4	3	0	3	0	3	2	0	7742.3064	−0.0044
4	1	4	5	0	3	1	3	4	0	7433.1712	0.0011
4	1	4	4	0	3	1	3	3	0	7433.0378	0.0004
4	1	3	5	0	3	1	2	4	0	8141.8739	0.0000
4	1	3	4	0	3	1	2	3	0	8141.7516	−0.0035
4	1	3	3	0	3	1	2	2	0	8141.8739	0.0094
5	0	5	6	0	4	0	4	5	0	9636.5357	−0.0026
5	0	5	5	0	4	0	4	4	0	9636.4873	−0.0016
5	0	5	4	0	4	0	4	3	0	9636.4873	−0.0033

5	1	5	6	0	4	1	4	5	0	9281.4460	0.0028
5	1	5	5	0	4	1	4	4	0	9281.3661	0.0011
5	1	5	4	0	4	1	4	3	0	9281.3901	−0.0042
5	1	4	6	0	4	1	3	5	0	10165.7625	−0.0016
5	1	4	5	0	4	1	3	4	0	10165.6953	0.0005
6	0	6	7	0	5	0	5	6	0	11505.2500	0.0004
6	0	6	6	0	5	0	5	5	0	11505.2002	0.0012
6	0	6	5	0	5	0	5	4	0	11505.2132	−0.0054
6	1	6	7	0	5	1	5	6	0	11123.6661	0.0035
6	1	6	6	0	5	1	5	5	0	11123.6075	−0.0016
7	0	7	8	0	6	0	6	7	0	13346.7514	0.0018
7	0	7	7	0	6	0	6	6	0	13346.6981	0.0001
7	0	7	6	0	6	0	6	5	0	13346.7310	0.0031

Table S6. Observed rotational transitions and residuals (in MHz) for ^{13}C4 isotopologue of isomer **I** of the thiazole-formaldehyde complex.

J'	K_a'	K_c'	F'	v'	J''	K_a''	K_c''	F''	v''	Obs.	Obs.−Cal.
3	0	3	4	1	2	0	2	3	1	5878.8156	−0.0055
3	0	3	3	1	2	0	2	2	1	5878.7616	−0.0030
4	0	4	5	1	3	0	3	4	1	7810.7249	0.0002
4	0	4	4	1	3	0	3	3	1	7810.6714	−0.0025
4	1	4	5	1	3	1	3	4	1	7495.9317	−0.0077
4	1	4	4	1	3	1	3	3	1	7495.8051	−0.0014
5	0	5	6	1	4	0	4	5	1	9719.8176	−0.0025
5	0	5	5	1	4	0	4	4	1	9719.7705	0.0006
5	0	5	4	1	4	0	4	3	1	9719.7705	−0.0020
5	1	5	6	1	4	1	4	5	1	9359.3950	−0.0029
5	1	5	5	1	4	1	4	4	1	9359.3204	0.0008
5	1	5	4	1	4	1	4	3	1	9359.3513	0.0021
5	1	4	6	1	4	1	3	5	1	10263.4761	0.0037
5	1	4	5	1	4	1	3	4	1	10263.3983	−0.0044
5	1	4	4	1	4	1	3	3	1	10263.4622	0.0049
6	0	6	7	1	5	0	5	6	1	11602.3086	0.0021
6	0	6	6	1	5	0	5	5	1	11602.2540	−0.0009
6	0	6	5	1	5	0	5	4	1	11602.2760	0.0004
6	1	6	7	1	5	1	5	6	1	11216.5202	0.0057
6	1	6	6	1	5	1	5	5	1	11216.4673	0.0063
6	1	6	5	1	5	1	5	4	1	11216.4760	−0.0025

Table S7. Observed rotational transitions and residuals (in MHz) for ^{13}C5 isotopologue of isomer **I** of the thiazole-formaldehyde complex.

J'	K_a'	K_c'	F'	v'	J''	K_a''	K_c''	F''	v''	Obs.	Obs.−Cal.
3	0	3	4	1	2	0	2	3	1	5847.5030	−0.0043
3	0	3	3	1	2	0	2	2	1	5847.4558	0.0039
4	0	4	5	1	3	0	3	4	1	7771.0492	−0.0005
4	0	4	4	1	3	0	3	3	1	7770.9968	−0.0034
4	0	4	3	1	3	0	3	2	1	7770.9660	−0.0006
4	1	4	5	1	3	1	3	4	1	7462.8416	−0.0019
4	1	4	4	1	3	1	3	3	1	7462.7087	−0.0021
5	0	5	6	1	4	0	4	5	1	9673.4207	0.0036
5	0	5	5	1	4	0	4	4	1	9673.3667	−0.0014
5	0	5	4	1	4	0	4	3	1	9673.3667	−0.0025
5	1	5	6	1	4	1	4	5	1	9318.7862	0.0003
5	1	5	5	1	4	1	4	4	1	9318.7119	0.0041
5	1	4	6	1	4	1	3	5	1	10197.6532	0.0080
5	1	4	5	1	4	1	3	4	1	10197.5730	−0.0029
5	1	4	4	1	4	1	3	3	1	10197.6260	−0.0039
6	0	6	7	1	5	0	5	6	1	11550.9247	0.0060
6	0	6	6	1	5	0	5	5	1	11550.8728	0.0041
6	0	6	5	1	5	0	5	4	1	11550.8970	0.0093
6	1	6	7	1	5	1	5	6	1	11168.8212	0.0065
6	1	6	6	1	5	1	5	5	1	11168.7629	0.0014
6	1	6	5	1	5	1	5	4	1	11168.7706	−0.0080

Table S8. Observed rotational transitions and residuals (in MHz) for ^{18}O9 isotopologue of isomer **I** of the thiazole-formaldehyde complex.

J'	K_a'	K_c'	F'	v'	J''	K_a''	K_c''	F''	v''	Obs.	Obs.−Cal.
3	0	3	4	1	2	0	2	3	1	5681.0231	−0.0015
3	0	3	3	1	2	0	2	2	1	5680.9609	−0.0092
3	0	3	2	1	2	0	2	1	1	5680.8397	−0.0034
4	0	4	5	1	3	0	3	4	1	7551.6406	−0.0056
4	0	4	4	1	3	0	3	3	1	7551.5934	−0.0046
4	0	4	3	1	3	0	3	2	1	7551.5561	−0.0068
4	1	4	5	1	3	1	3	4	1	7257.1834	−0.0035
4	1	4	4	1	3	1	3	3	1	7257.0536	−0.0009
4	1	4	3	1	3	1	3	2	1	7257.1159	−0.0049
4	1	3	5	1	3	1	2	4	1	7925.0880	−0.0040
4	1	3	4	1	3	1	2	3	1	7924.9713	−0.0026
4	1	3	3	1	3	1	2	2	1	7925.0880	0.0054
5	0	5	6	1	4	0	4	5	1	9403.1458	−0.0074
5	0	5	5	1	4	0	4	4	1	9403.0959	−0.0100
5	0	5	4	1	4	0	4	3	1	9403.0959	−0.0093
5	1	5	6	1	4	1	4	5	1	9062.6616	−0.0029
5	1	5	5	1	4	1	4	4	1	9062.5851	−0.0017
5	1	5	4	1	4	1	4	3	1	9062.6154	−0.0002
5	1	4	6	1	4	1	3	5	1	9896.2756	−0.0012
5	1	4	5	1	4	1	3	4	1	9896.2040	−0.0041
5	1	4	4	1	4	1	3	3	1	9896.2593	−0.0023
5	2	4	6	1	4	2	3	5	1	9490.1738	0.0027
5	2	4	5	1	4	2	3	4	1	9489.9585	0.0059
5	2	4	4	1	4	2	3	3	1	9490.1961	0.0026
5	2	3	6	1	4	2	2	5	1	9588.2420	0.0080
5	2	3	5	1	4	2	2	4	1	9588.0557	0.0086
5	2	3	4	1	4	2	2	3	1	9588.2616	0.0086
6	0	6	7	1	5	0	5	6	1	11232.0632	−0.0090
6	0	6	6	1	5	0	5	5	1	11232.0142	−0.0096
6	0	6	5	1	5	0	5	4	1	11232.0326	−0.0084
6	1	6	7	1	5	1	5	6	1	10862.7793	0.0009
6	1	6	6	1	5	1	5	5	1	10862.7279	0.0023
6	1	6	5	1	5	1	5	4	1	10862.7433	0.0009
6	1	5	7	1	5	1	4	6	1	11860.2404	0.0001
6	1	5	6	1	5	1	4	5	1	11860.1868	−0.0059
6	2	5	7	1	5	2	4	6	1	11378.9436	0.0094
6	2	5	6	1	5	2	4	5	1	11378.8100	0.0088
6	2	5	5	1	5	2	4	4	1	11378.9436	0.0090
6	2	4	7	1	5	2	3	6	1	11548.1188	−0.0102
6	2	4	6	1	5	2	3	5	1	11548.0239	−0.0089
6	2	4	5	1	5	2	3	4	1	11548.1188	−0.0074
7	0	7	8	1	6	0	6	7	1	13036.4399	−0.0090
7	0	7	7	1	6	0	6	6	1	13036.3887	−0.0108
7	0	7	6	1	6	0	6	5	1	13036.4209	−0.0063
7	1	7	8	1	6	1	6	7	1	12656.9208	0.0089
7	1	7	7	1	6	1	6	6	1	12656.8846	0.0124
7	1	7	6	1	6	1	6	5	1	12656.8846	0.0000
7	1	6	8	1	6	1	5	7	1	13815.0208	0.0075
7	1	6	7	1	6	1	5	6	1	13814.9829	0.0073
7	1	6	6	1	6	1	5	5	1	13815.0124	0.0100
8	0	8	9	1	7	0	7	8	1	14816.3851	−0.0021
8	0	8	8	1	7	0	7	7	1	14816.3341	−0.0035
8	0	8	7	1	7	0	7	6	1	14816.3710	0.0000
8	1	8	9	1	7	1	7	8	1	14444.6706	0.0005

9	0	9	0	1	8	0	8	9	1	16574.2318	0.0068
9	0	9	9	1	8	0	8	8	1	16574.1859	0.0092
9	0	9	8	1	8	0	8	7	1	16574.2223	0.0099
3	0	3	4	0	2	0	2	3	0	5680.3311	0.0009
3	0	3	3	0	2	0	2	2	0	5680.2687	−0.0069
4	0	4	5	0	3	0	3	4	0	7550.7095	−0.0044
4	0	4	4	0	3	0	3	3	0	7550.6610	−0.0047
4	0	4	3	0	3	0	3	2	0	7550.6250	−0.0056
4	1	4	5	0	3	1	3	4	0	7256.2283	−0.0009
4	1	4	4	0	3	1	3	3	0	7256.0914	−0.0055
4	1	4	3	0	3	1	3	2	0	7256.1589	−0.0043
4	1	3	5	0	3	1	2	4	0	7924.2049	−0.0020
4	1	3	4	0	3	1	2	3	0	7924.0893	0.0005
4	1	3	3	0	3	1	2	2	0	7924.2049	0.0075
5	0	5	6	0	4	0	4	5	0	9401.9761	−0.0020
5	0	5	5	0	4	0	4	4	0	9401.9271	−0.0037
5	0	5	4	0	4	0	4	3	0	9401.9271	−0.0031
5	1	5	6	0	4	1	4	5	0	9061.4654	0.0002
5	1	5	5	0	4	1	4	4	0	9061.3886	0.0011
5	1	5	4	0	4	1	4	3	0	9061.4163	0.0000
5	1	4	6	0	4	1	3	5	0	9895.1650	−0.0025
5	1	4	5	0	4	1	3	4	0	9895.1004	0.0016
6	0	6	7	0	5	0	5	6	0	11230.6511	0.0022
6	0	6	6	0	5	0	5	5	0	11230.5993	−0.0011
6	0	6	5	0	5	0	5	4	0	11230.6128	−0.0048
6	1	6	7	0	5	1	5	6	0	10861.3420	0.0061
6	1	6	6	0	5	1	5	5	0	10861.2851	0.0019
6	1	6	5	0	5	1	5	4	0	10861.3051	0.0052
6	1	5	7	0	5	1	4	6	0	11858.9070	0.0023
6	1	5	6	0	5	1	4	5	0	11858.8589	0.0018
7	0	7	8	0	6	0	6	7	0	13034.7740	0.0019
7	0	7	7	0	6	0	6	6	0	13034.7221	−0.0005
7	0	7	6	0	6	0	6	5	0	13034.7545	0.0042

Table S9. Observed rotational transitions and residuals (in MHz) for ^{13}C10 isotopologue of isomer **I** of the thiazole-formaldehyde complex.

J'	K_a'	K_c'	F'	v'	J''	K_a''	K_c''	F''	v''	Obs.	Obs.−Cal.
4	0	4	5	1	3	0	3	4	1	7700.5684	−0.0054
4	0	4	4	1	3	0	3	3	1	7700.5192	−0.0058
4	0	4	3	1	3	0	3	2	1	7700.4915	0.0008
5	0	5	6	1	4	0	4	5	1	9587.1674	0.0020
5	0	5	5	1	4	0	4	4	1	9587.1149	−0.0024
5	0	5	4	1	4	0	4	3	1	9587.1149	−0.0026
5	1	5	6	1	4	1	4	5	1	9237.8575	−0.0025
5	1	5	5	1	4	1	4	4	1	9237.7834	0.0012
5	1	5	4	1	4	1	4	3	1	9237.8173	0.0061
5	1	4	6	1	4	1	3	5	1	10098.2219	0.0014
5	1	4	5	1	4	1	3	4	1	10098.1494	−0.0020
5	1	4	4	1	4	1	3	3	1	10098.2085	0.0033
6	0	6	7	1	5	0	5	6	1	11449.9278	−0.0015
6	0	6	6	1	5	0	5	5	1	11449.8812	0.0010
6	0	6	5	1	5	0	5	4	1	11449.9016	0.0033
6	1	6	7	1	5	1	5	6	1	11072.3035	−0.0024
6	1	6	6	1	5	1	5	5	1	11072.2621	0.0091
6	1	6	5	1	5	1	5	4	1	11072.2621	−0.0078

Table S10. Observed rotational transitions and residuals (in MHz) for isomer **II** of the thiazole-formaldehyde complex.

J'	K_a'	K_c'	F'	J''	K_a''	K_c''	F''	Obs.	Obs.−Cal.
4	0	4	5	3	0	3	4	7232.8103	0.0007
4	0	4	4	3	0	3	3	7232.7594	0.0019
4	0	4	3	3	0	3	2	7232.7559	0.0087
4	1	3	5	3	1	2	4	7589.5992	0.0016
4	1	3	4	3	1	2	3	7589.5086	0.0018
4	1	3	3	3	1	2	2	7589.5992	−0.0085
4	2	3	5	3	2	2	4	7274.8242	−0.0002
4	2	3	4	3	2	2	3	7274.5027	−0.0011
4	2	2	5	3	2	1	4	7320.5289	0.0007
4	2	2	4	3	2	1	3	7320.2448	0.0028
5	0	5	6	4	0	4	5	9007.3200	0.0000
5	0	5	5	4	0	4	4	9007.2662	0.0011
5	0	5	4	4	0	4	3	9007.2801	−0.0047
5	1	5	6	4	1	4	5	8678.0996	0.0007
5	1	5	5	4	1	4	4	8678.0332	0.0019
5	1	5	4	4	1	4	3	8678.0525	0.0009
5	1	4	6	4	1	3	5	9477.7287	−0.0004
5	1	4	5	4	1	3	4	9477.6732	−0.0007
5	1	4	4	4	1	3	3	9477.7287	0.0007
5	2	4	6	4	2	3	5	9087.6778	0.0038
5	2	4	5	4	2	3	4	9087.4991	−0.0028
5	2	4	4	4	2	3	3	9087.6881	−0.0037
5	2	3	6	4	2	2	5	9178.4123	0.0031
5	2	3	5	4	2	2	4	9178.2809	0.0010
6	0	6	7	5	0	5	6	10760.8172	−0.0005
6	0	6	6	5	0	5	5	10760.7568	−0.0020
6	0	6	5	5	0	5	4	10760.7968	0.0012
6	1	6	7	5	1	5	6	10402.2271	0.0025
6	1	6	6	5	1	5	5	10402.1831	0.0067
6	1	6	5	5	1	5	4	10402.1831	−0.0073
6	1	5	7	5	1	4	6	11359.2346	−0.0001
6	1	5	6	5	1	4	5	11359.1964	0.0025
6	1	5	5	5	1	4	4	11359.2346	0.0030
6	2	5	7	5	2	4	6	10896.6845	0.0022
6	2	5	6	5	2	4	5	10896.5729	−0.0027
6	2	5	5	5	2	4	4	10896.6845	0.0014
6	2	4	7	5	2	3	6	11053.3895	−0.0034
6	2	4	6	5	2	3	5	11053.3310	−0.0052
6	2	4	5	5	2	3	4	11053.3895	0.0000
7	0	7	8	6	0	6	7	12491.3248	−0.0033
7	0	7	7	6	0	6	6	12491.2693	0.0033
7	0	7	6	6	0	6	5	12491.3137	0.0007
7	1	7	8	6	1	6	7	12120.7912	0.0025
7	1	7	7	6	1	6	6	12120.7483	−0.0022
7	1	7	6	6	1	6	5	12120.7655	0.0022
7	1	6	8	6	1	5	7	13232.3221	0.0010
7	1	6	7	6	1	5	6	13232.2809	−0.0049
7	1	6	6	6	1	5	5	13232.3221	0.0040
8	0	8	9	7	0	7	8	14198.7029	−0.0008
8	0	8	8	7	0	7	7	14198.6406	0.0005
2	1	2	3	1	0	1	2	7591.0747	−0.0052
2	1	2	2	1	0	1	1	7590.9705	−0.0032
2	1	2	1	1	0	1	0	7590.4779	−0.0030
2	2	1	3	1	1	0	2	16135.5555	0.0017
2	2	1	2	1	1	0	1	16135.5555	0.0046

2	2	0	3	1	1	1	2	16300.3004	0.0043
2	2	0	2	1	1	1	1	16301.1090	−0.0023
3	1	3	4	2	0	2	3	9172.0304	−0.0019
3	1	3	3	2	0	2	2	9171.7597	−0.0039
3	1	3	2	2	0	2	1	9171.9623	−0.0072
3	2	2	2	2	1	1	1	17794.8596	0.0035
3	2	2	4	2	1	1	3	17794.8256	0.0006
3	2	2	3	2	1	1	2	17794.7681	−0.0004
3	2	1	2	2	1	2	1	18297.9609	−0.0012
3	2	1	4	2	1	2	3	18298.4232	0.0006
3	2	1	3	2	1	2	2	18299.2666	−0.0002
4	1	4	3	3	0	3	2	10680.4563	0.0047
4	1	4	4	3	0	3	3	10680.1151	−0.0024
4	1	4	5	3	0	3	4	10680.4407	−0.0028
4	2	3	4	3	1	2	3	19373.0458	0.0033
4	2	3	5	3	1	2	4	19373.2285	0.0057
2	2	0	3	2	1	1	3	12340.4877	0.0007
2	2	0	2	2	1	1	2	12341.1895	−0.0034
2	2	0	1	2	1	1	1	12340.0925	−0.0018
5	1	5	5	4	0	4	4	12125.3891	−0.0022
5	1	5	4	4	0	4	3	12125.7561	0.0001
5	1	5	6	4	0	4	5	12125.7325	−0.0002
5	2	4	6	5	1	5	6	13795.1984	0.0064
5	2	4	5	5	1	5	5	13795.9048	−0.0034
5	2	4	4	5	1	5	4	13795.0375	−0.0085
5	2	3	6	5	1	4	6	11552.9498	0.0054
5	2	3	5	5	1	4	5	11552.8566	0.0000
5	2	3	4	5	1	4	4	11552.9607	−0.0014
6	1	6	6	5	0	5	5	13520.3037	0.0011
6	1	6	5	5	0	5	4	13520.6601	−0.0014
6	1	6	7	5	0	5	6	13520.6399	0.0026
7	1	7	8	6	0	6	7	14880.6089	0.0007
7	1	7	7	6	0	6	6	14880.2919	−0.0023
7	1	7	6	6	0	6	5	14880.6256	−0.0036

Table S11. Observed rotational transitions and residuals (in MHz) for ^{18}O9 isotopologue of isomer **II** of the thiazole-formaldehyde complex.

J'	K_a'	K_c'	F'	J''	K_a''	K_c''	F''	Obs.	Obs.−Cal.
5	0	5	6	4	0	4	5	8687.1768	−0.0031
5	0	5	5	4	0	4	4	8687.1308	0.0036
7	0	7	8	6	0	6	7	12056.1798	0.0049
7	0	7	7	6	0	6	6	12056.1242	0.0094
7	1	7	8	6	1	6	7	11699.0018	−0.0095
7	1	7	7	6	1	6	6	11698.9627	−0.0114
2	2	1	3	1	1	0	2	15965.8640	−0.0174
2	2	1	2	1	1	0	1	15965.8640	−0.0011
2	2	0	3	1	1	1	2	16120.0843	−0.0054
2	2	0	2	1	1	1	1	16120.8974	−0.0009
3	1	3	4	2	0	2	3	8989.2475	0.0078
3	1	3	3	2	0	2	2	8988.9683	0.0061
4	1	4	3	3	0	3	2	10450.3760	−0.0084
4	1	4	4	3	0	3	3	10450.0336	−0.0047
4	1	4	5	3	0	3	4	10450.3760	0.0035
4	2	3	4	3	1	2	3	19096.1275	0.0018
4	2	3	5	3	1	2	4	19096.3287	0.0121
5	1	5	4	4	0	4	3	11851.3836	−0.0015
5	1	5	6	4	0	4	5	11851.3655	0.0064
6	1	6	6	5	0	5	5	13203.1227	0.0019
6	1	6	5	5	0	5	4	13203.4884	−0.0033
6	1	6	7	5	0	5	6	13203.4654	0.0004
3	2	2	3	2	1	1	2	17568.9280	−0.0025
3	2	2	2	2	1	1	2	17568.9280	−0.0026
3	2	2	3	2	1	1	3	17568.9984	−0.0017
3	2	2	4	2	1	1	3	17568.9984	−0.0016
3	2	2	2	2	1	1	1	17569.0372	−0.0012
3	2	1	4	2	1	2	3	18039.9181	−0.0023
3	2	1	3	2	1	2	3	18039.9666	0.0066

Table S12. Observed rotational transitions and residuals (in MHz) for isomer **III** of the thiazole-formaldehyde complex.

J'	K_a'	K_c'	F'	v'	J''	K_a''	K_c''	F''	v''	Obs.	Obs.−Cal.
4	0	4	5	1	3	0	3	4	1	7181.0266	0.0016
4	0	4	4	1	3	0	3	3	1	7180.9840	−0.0054
4	0	4	3	1	3	0	3	2	1	7180.9480	0.0023
4	1	4	5	1	3	1	3	4	1	6970.9490	−0.0006
4	1	4	4	1	3	1	3	3	1	6970.8227	−0.0037
4	1	4	3	1	3	1	3	2	1	6970.8751	−0.0064
4	1	3	5	1	3	1	2	4	1	7416.0047	−0.0092
4	1	3	4	1	3	1	2	3	1	7415.9153	0.0078
4	1	3	3	1	3	1	2	2	1	7416.0047	−0.0057
4	2	3	5	1	3	2	2	4	1	7195.4335	−0.0002
4	2	3	4	1	3	2	2	3	1	7195.0492	−0.0005
4	2	3	3	1	3	2	2	2	1	7195.5287	−0.0036
4	2	2	5	1	3	2	1	4	1	7210.9874	0.0000
4	2	2	4	1	3	2	1	3	1	7210.6208	0.0030
4	2	2	3	1	3	2	1	2	1	7211.0770	−0.0070
5	0	5	6	1	4	0	4	5	1	8964.5623	−0.0023
5	0	5	5	1	4	0	4	4	1	8964.5268	−0.0051
5	0	5	4	1	4	0	4	3	1	8964.5180	−0.0005
5	1	5	6	1	4	1	4	5	1	8710.7449	−0.0010
5	1	5	5	1	4	1	4	4	1	8710.6758	0.0009
5	1	5	4	1	4	1	4	3	1	8710.6962	−0.0002
5	1	4	6	1	4	1	3	5	1	9266.8749	−0.0065
5	1	4	5	1	4	1	3	4	1	9266.8194	−0.0022
5	2	4	6	1	4	2	3	5	1	8992.1874	0.0000
5	2	4	5	1	4	2	3	4	1	8991.9836	−0.0010
5	2	4	4	1	4	2	3	3	1	8992.2030	−0.0050
5	2	3	6	1	4	2	2	5	1	9023.2418	0.0017
5	2	3	5	1	4	2	2	4	1	9023.0572	0.0017
5	2	3	4	1	4	2	2	3	1	9023.2563	−0.0024
5	3	3	6	1	4	3	2	5	1	9000.8865	0.0013
5	3	3	5	1	4	3	2	4	1	9000.4527	−0.0037
5	3	2	6	1	4	3	1	5	1	9001.1697	−0.0012
5	3	2	5	1	4	3	1	4	1	9000.7386	−0.0040
6	0	6	7	1	5	0	5	6	1	10740.4289	0.0001
6	0	6	6	1	5	0	5	5	1	10740.3944	−0.0019
6	0	6	5	1	5	0	5	4	1	10740.3944	−0.0042
6	1	6	7	1	5	1	5	6	1	10448.6867	0.0027
6	1	6	6	1	5	1	5	5	1	10448.6346	−0.0021
6	1	5	7	1	5	1	4	6	1	11115.5999	−0.0030
6	1	5	6	1	5	1	4	5	1	11115.5588	−0.0049
6	1	5	5	1	5	0	3	4	1	11115.5950	0.0028
6	2	5	7	1	5	2	4	6	1	10787.6025	−0.0021
6	2	5	6	1	5	2	4	5	1	10787.4809	−0.0016
6	2	5	5	1	5	2	4	4	1	10787.6025	−0.0022
6	2	4	7	1	5	2	3	6	1	10841.7686	−0.0015
6	2	4	6	1	5	2	3	5	1	10841.6725	0.0027
6	2	4	5	1	5	2	3	4	1	10841.7686	0.0002
6	3	4	7	1	5	3	3	6	1	10802.7972	0.0007
6	3	4	6	1	5	3	3	5	1	10802.5447	−0.0012

Table S13. Observed rotational transitions and residuals (in MHz) for ^{18}O9 isotopologue of isomer **III** of the thiazole-formaldehyde complex.

J'	K_a'	K_c'	F'	v'	J''	K_a''	K_c''	F''	v''	Obs.	Obs.−Cal.
4	0	4	5	0	3	0	3	4	0	6902.3250	−0.0041
4	0	4	3	0	3	0	3	2	0	6902.2487	0.0022
5	0	5	6	0	4	0	4	5	0	8617.6893	−0.0012
5	0	5	5	0	4	0	4	4	0	8617.6667	0.0052
5	0	5	4	0	4	0	4	3	0	8617.6438	0.0015
5	1	4	6	0	4	1	3	5	0	8897.9007	−0.0034
5	1	4	5	0	4	1	3	4	0	8897.8360	−0.0062
5	1	4	4	0	4	1	3	3	0	8897.8818	−0.0065
6	0	6	7	0	5	0	5	6	0	10326.3465	0.0021
6	0	6	6	0	5	0	5	5	0	10326.3127	−0.0037
6	0	6	5	0	5	0	5	4	0	10326.3127	0.0000
6	1	5	7	0	5	1	4	6	0	10673.4254	0.0018
6	1	5	6	0	5	1	4	5	0	10673.3850	0.0014
6	1	5	5	0	5	1	4	4	0	10673.4125	0.0030
7	0	7	8	0	6	0	6	7	0	12027.1110	0.0051
7	0	7	7	0	6	0	6	6	0	12027.0669	−0.0110
7	0	7	6	0	6	0	6	5	0	12027.0864	0.0028
7	1	6	8	0	6	1	5	7	0	12446.6401	0.0051
7	1	6	7	0	6	1	5	6	0	12446.6078	0.0016
7	1	6	6	0	6	1	5	5	0	12446.6228	−0.0007
4	0	4	5	1	3	0	3	4	1	6902.6039	−0.0107
4	0	4	4	1	3	0	3	3	1	6902.5694	−0.0122
4	0	4	3	1	3	0	3	2	1	6902.5264	−0.0054
5	0	5	6	1	4	0	4	5	1	8618.0366	−0.0105
5	0	5	5	1	4	0	4	4	1	8618.0117	−0.0062
5	0	5	4	1	4	0	4	3	1	8617.9966	−0.0021
5	1	5	6	1	4	1	4	5	1	8380.1016	−0.0064
5	1	5	5	1	4	1	4	4	1	8380.0281	−0.0085
5	1	5	4	1	4	1	4	3	1	8380.0538	−0.0066
5	1	4	6	1	4	1	3	5	1	8898.2286	−0.0015
5	1	4	5	1	4	1	3	4	1	8898.1653	−0.0028
5	1	4	4	1	4	1	3	3	1	8898.2125	−0.0017
6	0	6	7	1	5	0	5	6	1	10326.7670	−0.0048
6	0	6	6	1	5	0	5	5	1	10326.7310	−0.0129
6	0	6	5	1	5	0	5	4	1	10326.7310	−0.0091
6	1	6	7	1	5	1	5	6	1	10052.4355	0.0011
6	1	6	6	1	5	1	5	5	1	10052.3891	0.0013
6	1	6	5	1	5	1	5	4	1	10052.4071	0.0078
6	1	5	7	1	5	1	4	6	1	10673.8157	0.0012
6	1	5	6	1	5	1	4	5	1	10673.7787	0.0042
6	1	5	5	1	5	1	4	4	1	10673.8003	−0.0001
7	0	7	8	1	6	0	6	7	1	12027.5963	−0.0079
7	0	7	7	1	6	0	6	6	1	12027.5720	−0.0042
7	1	7	8	1	6	1	6	7	1	11722.8672	0.0105
7	1	7	7	1	6	1	6	6	1	11722.8376	0.0145
7	1	6	8	1	6	1	5	7	1	12447.0970	0.0061
7	1	6	7	1	6	1	5	6	1	12447.0724	0.0103
7	1	6	6	1	6	1	5	5	1	12447.0813	0.0018
8	0	8	9	1	7	0	7	8	1	13719.5264	0.0059
8	0	8	8	1	7	0	7	7	1	13719.5023	0.0103

Table S14. r_s, r_0, and r_e coordinates for isomers **I** - **III**.

	a/Å			*b*/Å			*c*/Å		
	r_e	r_0	r_s	r_e	r_0	r_s	r_e	r_0	r_s
I									
^{34}S1	1.735	1.744(1)	±1.7105(9)	0.943	0.9344(9)	±0.944(2)	0	0	0
^{13}C4	0.979	0.965(1)	±0.953(2)	−1.481	−1.4809(2)	±1.475(1)	0	0	0
^{13}C5	2.122	2.1156(8)	±2.1153(8)	−0.744	−0.756(1)	±0.713(2)	0	0	0
^{18}O9	−3.180	−3.151(5)	±3.1429(5)	0.712	0.719(1)	±0.719(2)	0	0	0
^{13}C10	−3.077	−3.104(5)	±3.0729(6)	−0.491	−0.4863(7)	±0.487(4)	0	0	0
II									
^{18}O9	−3.254	−3.21(2)	±3.2152(5)	0.699	0.7078(8)	±0.702(2)	0	0	0
III									
^{18}O9	3.403	3.43(2)	±3.3748(7)	−0.551	−0.531(8)	±0.548(4)	0	0	0

[a] In parentheses are the Costain's error in units of the last digit.

Table S15. The result of NBO analysis for isomer **I**.

From thiazole to formaldehyde			From formaldehyde to thiazole		
Donor NBO[a]	Acceptor NBO[b]	$E^{(2)}$/kcal/mol	Donor NBO	Acceptor NBO	$E^{(2)}$/kcal/mol
BD(1)C2-N3	RY*(1)C10	0.07	BD(1)C10-O9	RY*(2)C2	0.11
BD(1)C2-N3	RY*(6)C10	0.06	BD(1)C10-O9	RY*(3)H8	0.05
BD(1)C2-N3	BD*(2)C10-O9	0.07	BD(2)C10-O9	RY*(3)H8	0.05
BD(1)C2-H8	RY*(5)C10	0.10	BD(2)C10-O9	BD*(1)C2-S1	0.27
BD(1)C2-H8	RY*(4)O9	0.06	BD(2)C10-O9	BD*(1)C2-H8	0.23
BD(1)N3-C4	RY*(3)C10	0.22	BD(2)C10-O9	BD*(1)N3-C4	0.16
BD(1)N3-C4	RY*(4)C10	0.11	LP(2)O9	RY*(8)C2	0.05
BD(1)N3-C4	RY*(6)C10	0.05	LP(2)O9	BD*(1)C2-H8	0.20
LP(1)N3	RY*(4)C10	0.06			
LP(1)N3	RY*(1)H11	0.16			
LP(1)N3	RY*(2)H11	0.09			
LP(1)N3	RY*(1)H12	0.16			
LP(1)N3	RY*(2)H12	0.09			
LP(1)N3	BD*(2)C10-O9	2.51			

[a]BD for 2-center bond, LP for 1-center valence lone pair the unstarred and starred labels corresponding to Lewis and non-Lewis NBOs, respectively.

[b]RY* for 1-center Rydberg, and BD* for 2-center antibond, the unstarred and starred labels corresponding to Lewis and non-Lewis NBOs, respectively.

Table S16. The result of NBO analysis for isomer **II**.

From thiazole to formaldehyde			From formaldehyde to thiazole		
Donor NBO[a]	Acceptor NBO[b]	$E^{(2)}$/kcal/mol	Donor NBO	Acceptor NBO	$E^{(2)}$/kcal/mol
BD(1)C2-N3	RY*(3)C10	0.20	BD(1)C10-O9	RY*(2)C4	0.10
BD(1)C2-N3	RY*(4)C10	0.13	BD(1)C10-O9	RY*(2)H7	0.12
BD(1)N3-C4	RY*(1)C10	0.06	BD(2)C10-O9	RY*(2)H7	0.08
BD(1)N3-C4	BD*(2)C10-O9	0.05	BD(2)C10-O9	BD*(1)C2-N3	0.13
BD(1)C4-H7	RY*(5)C10	0.06	BD(2)C10-O9	BD*(1)C4-C5	0.17
LP(1)N3	RY*(4)C10	0.06	BD(2)C10-O9	BD*(1)C4-H7	0.22
LP(1)N3	RY*(1)H11	0.15	LP(1)O9	BD*(1)C4-H7	0.14
LP(1)N3	RY*(2)H11	0.09			
LP(1)N3	RY*(1)H11	0.15			
LP(1)N3	RY*(2)H11	0.09			
LP(1)N3	BD*(2)C10-O9	2.29			

[a]BD for 2-center bond, LP for 1-center valence lone pair the unstarred and starred labels corresponding to Lewis and non-Lewis NBOs, respectively.

[b]RY* for 1-center Rydberg, and BD* for 2-center antibond, the unstarred and starred labels corresponding to Lewis and non-Lewis NBOs, respectively.

Table S17. The result of NBO analysis for isomer **III**.

From thiazole to formaldehyde			From formaldehyde to thiazole		
Donor NBO[a]	Acceptor NBO[b]	$E^{(2)}$/kcal/mol	Donor NBO	Acceptor NBO	$E^{(2)}$/kcal/mol
BD(1)C2-H8	RY*(4)C10	0.07	BD(2)O9-C10	RY*(2)C2	0.06
BD(1)C2-H8	RY*(4)H11	0.10	BD(1)C10-H11	BD*(1)N3-C4	0.09
BD(1)N3-C4	RY*(2)H11	0.12	BD(1)C10-H12	RY*(2)H8	0.05
BD(1)N3-C4	RY*(4)H11	0.06	LP(1)O9	BD*(1)C2-H8	0.40
BD(1)C4-H7	RY*(1)H11	0.09	LP(2)O9	RY*(1)H8	0.08
LP(1)N3	RY*(4)C10	0.05	LP(2)O9	RY*(2)H8	0.06
LP(1)N3	RY*(1)H11	0.39	LP(2)O9	BD*(1)C2-S1	0.18
LP(1)N3	RY*(2)H11	0.15	LP(2)O9	BD*(1)C2-H8	1.11
LP(1)N3	BD*(1)C10-H11	0.98			

[a]BD for 2-center bond, LP for 1-center valence lone pair the unstarred and starred labels corresponding to Lewis and non-Lewis NBOs, respectively.
[b]RY* for 1-center Rydberg, and BD* for 2-center antibond, the unstarred and starred labels corresponding to Lewis and non-Lewis NBOs, respectively.

Table S18. The result of NBO analysis for isomer **IV**.

From thiazole to formaldehyde			From formaldehyde to thiazole		
Donor NBO[a]	Acceptor NBO[b]	$E^{(2)}$/kcal/mol	Donor NBO	Acceptor NBO	$E^{(2)}$/kcal/mol
BD(1)C2-N3	RY*(2)H11	0.13	BD(2)O9-C10	RY*(2)C4	0.05
BD(1)C2-N3	RY*(3)H11	0.06	BD(2)O9-C10	RY*(1)H7	0.13
BD(1)C4-H7	RY*(4)C10	0.07	BD(1)C10-H12	RY*(1)H7	0.06
BD(1)C4-H7	RY*(3)H11	0.09	BD(1)C10-H11	BD*(1)C2-N3	0.06
LP(1)N3	RY*(3)C10	0.06	LP(1)O9	BD*(1)C4-H7	0.28
LP(1)N3	RY*(1)H11	0.35	LP(2)O9	RY*(1)H7	0.13
LP(1)N3	RY*(2)H11	0.15	LP(2)O9	BD*(1)C4-C5	0.07
LP(1)N3	BD*(1)C10-H11	1.02	LP(2)O9	BD*(1)C4-H7	0.94

[a]BD for 2-center bond, LP for 1-center valence lone pair the unstarred and starred labels corresponding to Lewis and non-Lewis NBOs, respectively.
[b]RY* for 1-center Rydberg, and BD* for 2-center antibond, the unstarred and starred labels corresponding to Lewis and non-Lewis NBOs, respectively.