

## **Sulfur-Arene Interactions: The S $\cdots\pi$ and S-H $\cdots\pi$ Interactions in the Dimers of Benzofuran $\cdots$ Sulfur Dioxide and Benzofuran $\cdots$ Hydrogen Sulfide**

### ELECTRONIC SUPPORTING INFORMATION

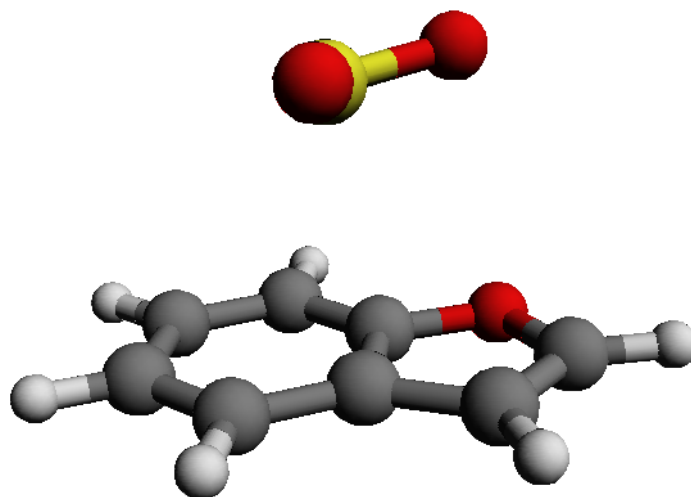
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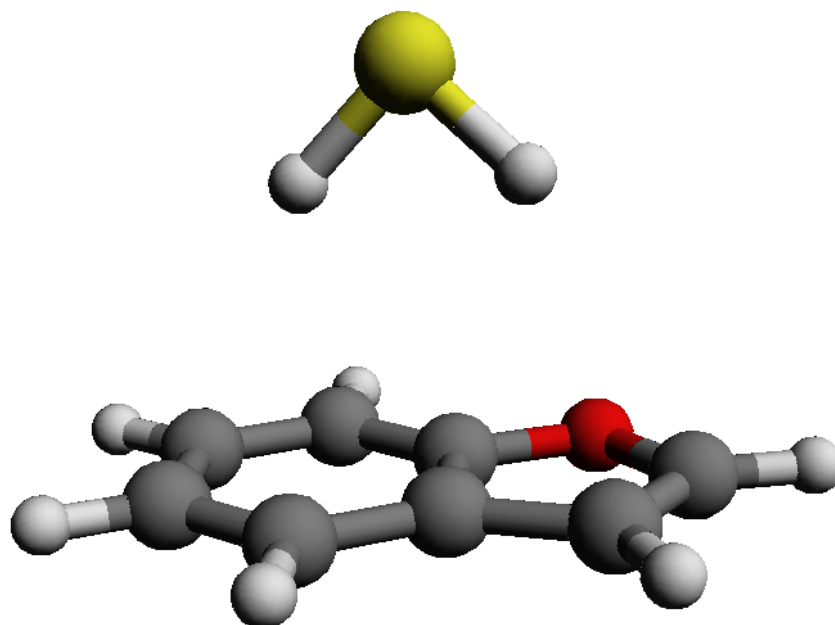
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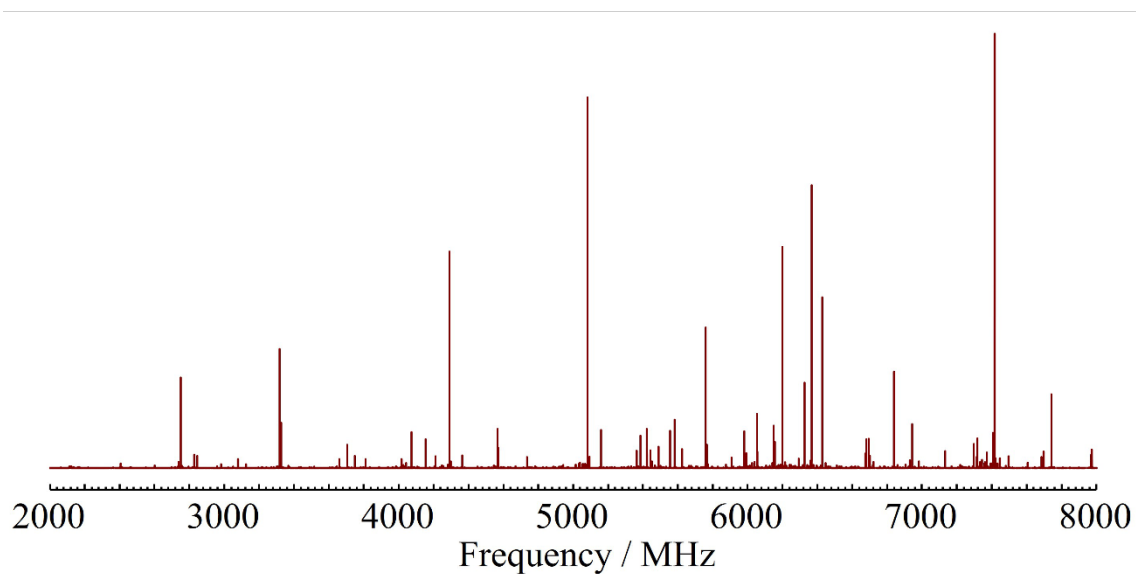
**Figure S1.** Rotatable 3D figure of the global minimum of the dimer benzofuran...sulfur dioxide according to the B2PLYP-D3(BJ)/def2-TZVP calculations of Table 1.



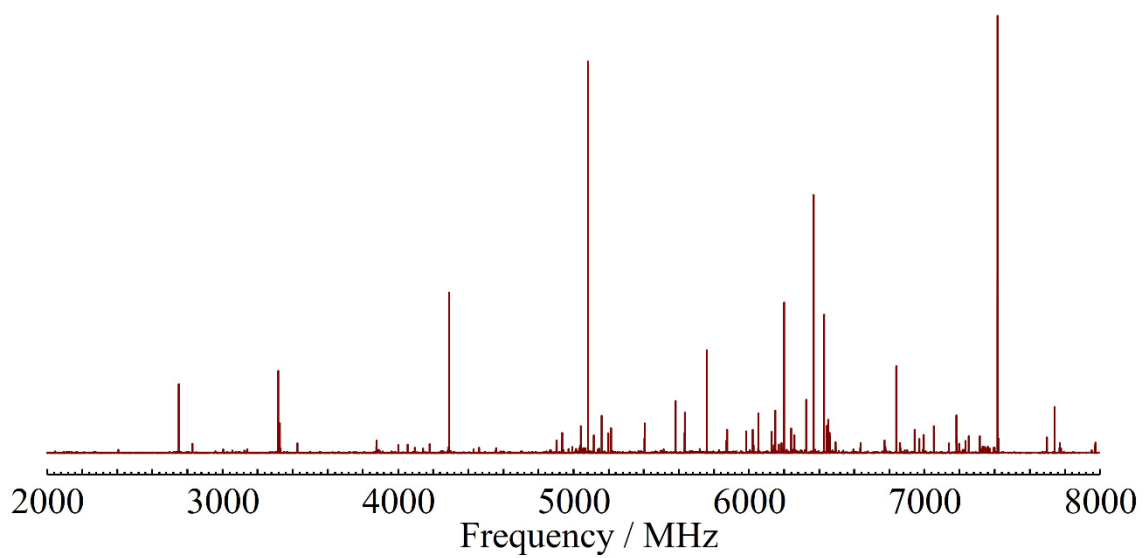
**Figure S2.** Rotatable 3D figure of the global minimum of the dimer benzofuran...hydrogen sulfide according to the B2PLYP-D3(BJ)/def2-TZVP calculations of Table 2.



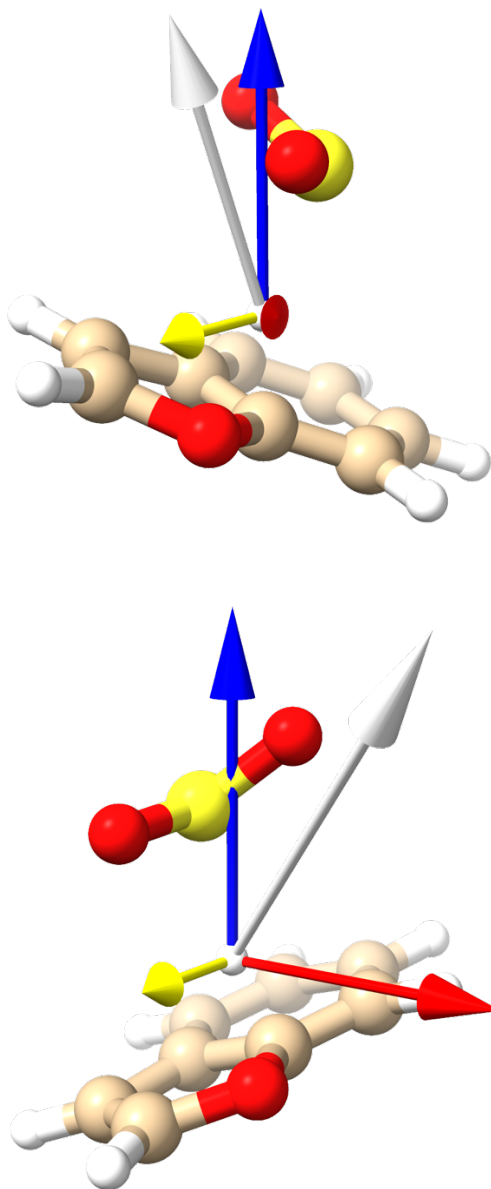
**Figure S3.** Microwave spectrum of the dimer benzofuran...sulfur dioxide (1 M averages were collected for the time-domain spectrum, followed by a Fourier transformation with a Kaiser-Bessel window).



**Figure S4.** Microwave spectrum of the dimer benzofuran...hydrogen sulfide (1 M averages were collected for the time-domain spectrum, followed by a Fourier transformation with a Kaiser-Bessel window).



**Figure S5.** A comparison between the two most stable structures of the dimer benzofuran...sulfur dioxide (upper panel: isomer I, lower panel: isomer II), showing the electric dipole moment components in the principal inertial axes (blue, yellow, red and grey vectors represent respectively  $\mu_a$ ,  $\mu_b$ ,  $\mu_c$  and  $\mu_{Total}$ ). The absence of  $\mu_c$  transitions in the spectrum confirmed the assignment of isomer I.



**Table S1.** Theoretical spectroscopic parameters of the first four stable isomers of the benzofuran...sulfur dioxide dimer using the B3LYP-D3(BJ) method and the def2-TZVP, jun-cc-pVTZ and cc-pVTZ basis sets.

	B3LYP-D3(BJ)											
	def2-TZVP				jun-cc-pVTZ				cc-pVTZ			
	I	II	III	IV	I	II	III	IV	I	II	III	IV
$A / \text{MHz}^a$	1074.3[1.7%] <sup>c</sup>	1062.9[0.6%]	1260.1	1365	1069.9[1.3%]	1062.6[0.6%]	1249.1	1373.9	1073.1[1.6%]	1062.1[0.6%]	1254.5	1360.9
$B / \text{MHz}$	833.4[2.6%]	839.4[3.4%]	664.4	598	829.4[2.1%]	833.1[2.6%]	668.8	589.0	833.4[2.6%]	839.4[3.4%]	665.8	597.8
$C / \text{MHz}$	659.1[2.6%]	639.6[-0.4%]	554.7	529	652.8[1.6%]	636.5[-0.9%]	548.9	519.6	659.5[2.7%]	636.2[-0.9%]	553.5	528.3
$D_J / \text{kHz}$	0.47	0.25	0.55	0.40	0.42	0.27	1.3	0.40	0.49	0.25	0.52	0.38
$D_{JK} / \text{kHz}$	-0.17	2.6	-2.0	-1.3	0.38	2.3	-5.2	-1.3	-0.18	2.8	-1.9	-1.2
$D_K / \text{kHz}$	-0.14	-2.6	3.1	3.2	-0.62	-2.4	7.1	3.3	-0.15	-2.8	2.9	3.0
$\delta_J / \text{kHz}$	0.003	-0.06	0.19	0.07	-0.004	-0.05	0.52	0.06	0.01	-0.07	0.18	0.06
$\delta_K / \text{kHz}$	0.44	3.7	0.82	0.63	1.0	3.3	1.4	0.61	0.48	4.1	0.67	0.58
$ \mu_a  / \text{D}$	1.8	2.1	2.4	2.2	2.0	2.3	2.5	2.4	1.8	2.1	2.5	2.3
$ \mu_b  / \text{D}$	0.8	0.6	0.3	0.4	0.8	0.6	0.5	0.5	0.8	0.6	0.4	0.4
$ \mu_c  / \text{D}$	0.2	1.4	0.0	0.1	0.2	1.4	0.0	0.1	0.1	1.5	0.0	0.1
$\Delta E / \text{kJ mol}^{-1b}$	0.0	2.3	2.4	5.2	0.0	2.0	2.1	4.9	0.0	2.1	2.2	5.0
$\Delta E_0 / \text{kJ mol}^{-1}$	0.0	1.9	2.0	4.7	0.0	1.7	1.8	4.5	0.0	1.8	1.9	4.6
$\Delta G / \text{kJ mol}^{-1}$	1.5	1.2	0.0	2.4	3.1	3.2	0.0	4.0	1.4	1.1	0.0	2.6
$\Delta E_c / \text{kJ mol}^{-1}$	-25.77	-23.56	-23.77	-21.05	-25.73	-23.64	-23.68	-20.96	-25.36	-23.18	-23.43	-20.71

<sup>a</sup>Rotational constants ( $A, B, C$ ), Watson's A-reduction centrifugal distortion constants ( $D_J, D_{JK}, D_K, d_J, d_K$ ) and electric dipole moments ( $\mu_\alpha, \alpha = a, b, c$ ). <sup>b</sup>Relative energies uncorrected ( $\Delta E$ ) and corrected with the zero-point energy ( $\Delta E_0$ ), Gibbs energy ( $\Delta G, 298 \text{ K}, 1 \text{ atm}$ ) and complexation energy ( $\Delta E_c$ , including BSSE corrections). <sup>c</sup>Relative deviations respect to the experimental values in Table 1 in square brackets, defined as (theory-experiment)/experiment.

**Table S2.** Theoretical spectroscopic parameters of the first four stable isomers of the benzofuran···sulfur dioxide dimer using the B2PLYP-D3(BJ) method and the def2-TZVP, jun-cc-pVTZ and cc-pVTZ basis sets.

	B2PLYP-D3(BJ)										
	def2-TZVP			jun-cc-pVTZ				cc-pVTZ			
	I	II	III	I	II	III	IV	I	II	III	IV
$A / \text{MHz}^a$	1070.1[1.3%]	1066.0[0.9%]	1244.1	1065.3[0.9%]	1060.2[0.4%]	1243.0	1300.2	1068.1[1.1%]	1067.0[1.0%]	1239.8	1301.2
$B / \text{MHz}$	830.5[2.3%]	830.1[2.2%]	666.0	828.9[2.1%]	829.6[2.2%]	660.2	615.0	829.5[2.2%]	827.6[1.9%]	665.4	617.1
$C / \text{MHz}$	658.9[2.6%]	629.4[-2.0%]	559.1	653.8[1.8%]	631.4[-1.7%]	552.8	540.8	658.8[2.6%]	625.3[-2.6%]	557.1	545.3
$D_J / \text{kHz}$	0.53	0.62	0.53	0.46	0.30	0.73	0.65	0.57	0.73	0.47	0.55
$D_{JK} / \text{kHz}$	-0.16	2.0	-1.9	0.41	3.0	-2.7	-2.4	-0.18	1.3	-1.6	-2.0
$D_K / \text{kHz}$	-0.19	-2.3	2.9	-0.67	-3.0	3.8	6.2	-0.21	1.7	2.5	4.8
$\delta_J / \text{kHz}$	0.003	-0.04	0.18	-0.007	-0.008	0.27	0.15	0.01	-0.04	0.15	0.13
$\delta_K / \text{kHz}$	0.54	3.7	0.90	1.1	4.2	1.4	0.008	0.61	2.9	0.63	0.67
$ \mu_a  / \text{D}$	1.5	1.8	2.2	1.7	2.0	2.3	2.0	1.5	1.8	2.3	1.9
$ \mu_b  / \text{D}$	0.8	0.7	0.2	0.8	0.7	0.3	0.3	0.8	0.7	0.2	0.3
$ \mu_c  / \text{D}$	0.1	1.5	0.1	0.1	1.5	0.0	0.1	0.1	1.5	0.1	0.0
$\Delta E / \text{kJ mol}^{-1}$	0.0	1.9	0.2	0.1	1.7	0.0	2.2	0.0	1.7	0.1	2.4
$\Delta E_0 / \text{kJ mol}^{-1}$	0.0	1.7	2.1	0.0	1.6	2.0	4.6	0.0	1.6	1.9	4.5
$\Delta G / \text{kJ mol}^{-1}$	1.5	0.3	0.0	2.2	1.7	0.0	1.3	1.0	0.1	0.0	0.9
$\Delta E_c / \text{kJ mol}^{-1}$	-21.30	-19.25	-19.41	-22.22	-20.33	-20.17	-17.32	-20.54	-18.58	-18.83	-16.11

<sup>a</sup>Parameter definition as in Table S1.



**Table S3.** Theoretical spectroscopic parameters of the first two stable isomers of the benzofuran...hydrogen sulfide dimer using the B3LYP-D3(BJ) method and the def2-TZVP, jun-cc-pVTZ and cc-pVTZ basis sets.

Parameters	B3LYP-D3(BJ)					
	def2-TZVP		jun-cc-pVTZ		cc-pVTZ	
	I	II	I	II	I	II
$A / \text{MHz}^a$	1169.9[-0.3%] <sup>b</sup>	1207.1[2.8%]	1171.3[-0.2%]	1202.7[2.5%]	1170.6[-0.3%]	1212.7[3.3%]
$B / \text{MHz}$	1086.6[4.7%]	1105.6[6.6%]	1076.6[3.8%]	1104.7[6.5%]	1082.6[4.3%]	1090.7[5.1%]
$C / \text{MHz}$	787.6[3.1%]	811.8[6.3%]	783.0[2.5%]	809.1[5.9%]	786.0[2.9%]	806.5[5.6%]
$D_J / \text{kHz}$	2.0	2.4	2.1	2.5	2.2	2.9
$D_{JK} / \text{kHz}$	-3.6	-6.5	-4.0	-7.0	-4.5	-8.7
$D_K / \text{kHz}$	1.9	4.5	2.2	5.0	2.5	6.2
$\delta_J / \text{kHz}$	-0.14	-0.23	-0.13	-0.24	-0.13	-0.34
$\delta_K / \text{kHz}$	-3.0	-10.6	-3.6	-12.2	-4.8	-12.3
$ \mu_a  / \text{D}$	1.4	0.2	1.4	0.1	1.5	0.1
$ \mu_b  / \text{D}$	0.1	0.5	0.0	0.5	0.0	0.5
$ \mu_c  / \text{D}$	0.9	0.3	0.9	0.3	0.9	0.2
$\Delta E / \text{kJ mol}^{-1}$	0.0	1.8	0.0	1.0	0.0	1.4
$\Delta E_0 / \text{kJ mol}^{-1}$	0.0	1.6	0.0	1.0	0.0	1.2
$\Delta G / \text{kJ mol}^{-1}$	0.0	1.8	0.0	1.3	0.0	0.8
$\Delta E_c / \text{kJ mol}^{-1}$	-16.02	-14.98	-16.02	-14.98	-16.28	-15.10

<sup>a</sup>Parameter definition as in Table S1. <sup>b</sup>Relative deviations respect to the experimental values in Table 2 in square brackets, defined as (theory-experiment)/experiment.

**Table S4.** Theoretical spectroscopic parameters of the first two stable isomers of the benzofuran...hydrogen sulfide dimer using the B2PLYP-D3(BJ) method and the def2-TZVP, jun-cc-pVTZ and cc-pVTZ basis sets.

Parameters	B2PLYP-D3(BJ)					
	def2-TZVP		jun-cc-pVTZ		cc-pVTZ	
	I	II	I	II	I	II
$A / \text{MHz}$	1167.9[-0.5%]	1197.7[2.0%]	1167.8[-0.5%]	1191.8[1.5%]	1169.2[-0.4%]	1202.1[2.4%]
$B / \text{MHz}$	1087.7[4.8%]	1112.7[7.2%]	1083.0[4.4%]	1118.2[7.8%]	1083.1[4.4%]	1100.1[6.0%]
$C / \text{MHz}$	788.6[3.2%]	812.4[6.3%]	786.1[2.9%]	812.8[6.4%]	786.8[3.0%]	807.9[5.8%]
$D_J / \text{kHz}$	0.64	2.5	0.89	2.4	1.9	2.8
$D_{JK} / \text{kHz}$	4.1	-6.9	2.6	-6.3	-2.9	-8.1
$D_K / \text{kHz}$	-4.5	4.8	-3.3	4.4	1.3	5.7
$\delta_J / \text{kHz}$	-0.20	-0.28	-0.2	-0.25	-0.16	-0.34
$\delta_K / \text{kHz}$	18.2	-13.0	13.3	-13.6	-1.2	-13.2
$ \mu_a  / \text{D}$	1.4	0.1	1.4	0.1	1.5	0.1
$ \mu_b  / \text{D}$	0.2	0.5	0.1	0.5	0.1	0.5
$ \mu_c  / \text{D}$	0.9	0.2	0.9	0.3	0.8	0.2
$\Delta E / \text{kJ mol}^{-1}$	0.0	1.3	0.0	0.8	0.0	0.9
$\Delta E_0 / \text{kJ mol}^{-1}$	0.0	1.5	0.0	0.9	0.0	1.3
$\Delta G / \text{kJ mol}^{-1}$	0.0	1.0	0.0	1.1	0.0	1.0
$\Delta E_c / \text{kJ mol}^{-1}$	-14.02	-13.10	-14.81	-13.89	-14.35	-13.26

<sup>a</sup>Parameter definition as in Table S3.

**Table S5.** Experimental transition frequencies for the parent species of the benzofuran...(<sup>32</sup>S)-sulfur dioxide dimer (quantum numbers  $J, K_a, K_c$ ).

$J'$	$K_a'$	$K_c'$	$J''$	$K_a''$	$K_c''$	$\nu_{\text{obs.}}/\text{MHz}$	$\Delta\nu/\text{MHz}$
2	1	2	1	1	1	2738.5625	0.0063
2	0	2	1	0	1	2845.6145	0.0057
2	1	1	1	1	0	3078.0462	0.0068
3	1	3	2	1	2	4073.7992	0.0054
3	0	3	2	0	2	4152.9848	-0.0033
3	2	2	2	2	1	4362.3915	0.0099
3	1	2	2	1	1	4567.3209	0.0095
3	2	1	2	2	0	4571.8566	0.0159
4	1	4	3	1	3	5385.2652	-0.0020
4	0	4	3	0	3	5422.9739	-0.0014
4	2	3	3	2	2	5766.0614	0.0065
4	3	2	3	3	1	5908.1656	0.0016
4	1	3	3	1	2	5979.8782	-0.0042
4	3	1	3	3	0	5992.5122	-0.0030
4	2	2	3	2	1	6156.4107	-0.0062
5	1	5	4	1	4	6681.3286	0.0057
5	0	5	4	0	4	6695.1843	-0.0031
5	2	4	4	2	3	7132.9470	0.0080
5	1	4	4	1	3	7296.5123	-0.0055
5	3	3	4	3	2	7373.0300	0.0044
5	2	3	4	2	2	7684.2779	-0.0256
6	1	6	5	1	5	7969.8582	0.0073
6	0	6	5	0	5	7974.2982	0.0040
6	1	6	5	0	5	7976.1196	0.0052
5	3	3	5	2	4	2061.0194	0.0031
5	2	4	5	1	5	2362.4727	0.0072
5	2	4	5	0	5	2368.7347	0.0057
2	0	2	1	1	1	2601.5311	0.0054
2	1	2	1	0	1	2982.6314	-0.0079
2	2	1	1	1	0	3810.2785	-0.0100
3	1	2	2	2	1	3835.0655	0.0033
3	0	3	2	1	2	4015.9664	0.0088
2	2	0	1	1	1	4042.7290	-0.0011
3	1	3	2	0	2	4210.8185	-0.0057
3	2	2	2	1	1	5094.6215	-0.0092
4	0	4	3	1	3	5365.1385	-0.0007
4	1	4	3	0	3	5443.0988	-0.0046
4	1	3	3	2	2	5452.5699	0.0068
3	2	1	2	1	2	5876.0245	0.0098
3	3	1	2	2	0	5978.4929	-0.0091
3	2	1	2	0	2	6013.0569	0.0117
3	3	0	2	2	1	6056.9134	0.0041
4	2	3	3	1	2	6293.3657	-0.0085

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5	2	3	4	3	2	6525.8748	-0.0203
5	0	5	4	1	4	6675.0593	0.0000
5	1	5	4	0	4	6701.4565	0.0055
5	1	4	4	2	3	6983.0237	-0.0023
4	3	2	3	2	1	7314.8174	-0.0080
5	4	1	4	4	0	7431.9355	-0.0085
5	2	4	4	1	3	7446.4302	-0.0005
4	3	1	3	2	2	7687.0347	-0.0083
4	2	2	3	1	3	7958.6430	0.0051
6	0	6	5	1	5	7968.0400	0.0093

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**Table S6.** Experimental transition frequencies for the  $^{34}\text{S}$  isotopologue of the benzofuran...sulfur dioxide dimer (quantum numbers  $J, K_a, K_c$ ).

$J'$	$K_a'$	$K_c'$	$J''$	$K_a''$	$K_c''$	$\nu_{\text{obs.}}/\text{MHz}$	$\Delta\nu/\text{MHz}$
3	1	3	2	1	2	4032.8700	0.0044
3	0	3	2	0	2	4114.8360	-0.0076
3	2	2	2	2	1	4314.1075	0.0138
3	2	1	2	2	0	4513.4118	0.0027
3	1	2	2	1	1	4517.0092	0.0094
4	1	4	3	1	3	5332.6858	-0.0005
4	0	4	3	0	3	5373.3958	-0.0055
4	2	3	3	2	2	5704.7782	0.0132
4	1	3	3	1	2	5920.4109	-0.0049
4	2	2	3	2	1	6080.7659	-0.0021
5	1	5	4	1	4	6617.0730	-0.0021
5	0	5	4	0	4	6632.6614	-0.0115
5	2	4	4	2	3	7060.4558	0.0034
5	1	4	4	1	3	7231.4724	0.0087
5	2	3	4	2	2	7597.0721	-0.0177
6	1	6	5	1	5	7893.6258	-0.0013
6	0	6	5	0	5	7898.8302	0.0058

**Table S7.** Experimental transition frequencies for the parent species of the benzofuran...(<sup>32</sup>S)-hydrogen sulfide dimer (quantum numbers  $J, K_a, K_c$ ).

$J'$	$K_a'$	$K_c'$	$v'$	$J''$	$K_a''$	$K_c''$	$v''$	$\nu_{\text{obs.}}/\text{MHz}$	$\Delta\nu/\text{MHz}$
1	1	0	0	0	0	0	0	2211.6737	-0.0024
2	1	2	0	1	1	1	0	3329.0151	0.0012
2	0	2	0	1	0	1	0	3426.0253	-0.0011
2	1	1	0	1	1	0	0	3875.8767	-0.0022
2	1	1	0	1	0	1	0	4286.3104	-0.0024
2	2	0	0	1	1	0	0	4463.2979	0.0048
2	2	1	0	1	1	1	0	4560.3066	0.0001
2	2	0	0	1	0	1	0	4873.7283	0.0013
3	1	3	0	2	1	2	0	4903.0701	0.0000
3	0	3	0	2	0	2	0	4935.3800	0.0018
3	2	2	0	2	2	1	0	5403.5634	0.0086
3	1	2	0	2	1	1	0	5632.9067	-0.0042
3	2	1	0	2	2	0	0	5871.7954	0.0046
4	1	4	0	3	1	3	0	6443.4540	-0.0012
4	0	4	0	3	0	3	0	6449.9174	0.0020
3	2	1	0	2	1	1	0	6459.2170	0.0122
3	1	2	0	2	0	2	0	6493.1842	-0.0131
3	2	2	0	2	1	2	0	6634.8507	0.0033
3	3	0	0	2	2	0	0	6776.5255	-0.0043
3	3	1	0	2	2	1	0	6862.5526	-0.0041
4	2	3	0	3	2	2	0	7052.4148	-0.0091
4	1	3	0	3	1	2	0	7183.2178	-0.0023
3	2	1	0	2	0	2	0	7319.4937	0.0025
3	3	0	0	2	1	1	0	7363.9455	0.0016
4	3	2	0	3	3	1	0	7418.9459	0.0031
4	2	2	0	3	2	1	0	7768.4635	0.0021
4	3	1	0	3	3	0	0	7772.7316	-0.0041
5	1	5	0	4	1	4	0	7973.5707	0.0038
5	0	5	0	4	0	4	0	7974.6030	-0.0018
1	1	0	1	0	0	0	1	2211.2558	0.0018
4	1	3	1	4	1	4	1	2289.6117	0.0046
2	1	2	1	1	1	1	1	3329.7212	0.0000
2	0	2	1	1	0	1	1	3426.1735	-0.0025
2	1	1	1	1	1	0	1	3877.1574	-0.0003
2	1	1	1	1	0	1	1	4286.6732	0.0002
2	2	0	1	1	1	0	1	4461.8018	-0.0003
2	2	1	1	1	1	1	1	4558.2554	-0.0024
2	2	0	1	1	0	1	1	4871.3148	-0.0025
3	1	3	1	2	1	2	1	4903.7322	0.0020
3	0	3	1	2	0	2	1	4935.5800	0.0024
3	1	2	1	2	2	0	1	5048.8676	0.0042
3	2	2	1	2	2	1	1	5405.0445	0.0002
3	1	2	1	2	1	1	1	5633.5015	-0.0062

3	2	1	1	2	0	0	1	5874.5716	0.0012
4	1	4	1	3	1	3	1	6444.1628	0.0012
4	0	4	1	3	0	3	1	6450.4727	-0.0018
3	1	2	1	2	0	2	1	6494.0066	0.0020
3	2	2	1	2	1	2	1	6633.5748	-0.0061
3	3	0	1	2	2	0	1	6773.1923	0.0025
3	3	1	1	2	2	1	1	6859.1410	0.0012
4	2	3	1	3	2	2	1	7053.5597	-0.0025
4	1	3	1	3	1	2	1	7182.8323	0.0068
3	2	1	1	2	0	2	1	7319.7128	0.0011
3	3	0	1	2	1	1	1	7357.8330	-0.0011
4	3	2	1	3	3	1	1	7421.6364	-0.0007
4	2	2	1	3	2	1	1	7770.4036	0.0041
4	3	1	1	3	3	0	1	7777.6680	-0.0058
5	1	5	1	4	1	4	1	7974.4305	-0.0008
5	0	5	1	4	0	4	1	7975.4381	0.0008

**Table S8.** Experimental transition frequencies for the  $^{34}\text{S}$  isotopologue of the benzofuran...hydrogen sulfide dimer (quantum numbers  $J, K_a, K_c$ ).

$J'$	$K_a'$	$K_c'$	$v'$	$J''$	$K_a''$	$K_c''$	$v''$	$\nu_{\text{obs.}}/\text{MHz}$	$\Delta\nu/\text{MHz}$
2	1	1	0	1	1	0	0	3759.4382	0.0041
3	1	3	0	2	1	2	0	4783.3880	0.0040
3	0	3	0	2	0	2	0	4828.5380	0.0007
3	2	2	0	2	2	1	0	5250.0754	-0.0040
3	1	2	0	2	1	1	0	5494.9004	0.0059
3	2	1	0	2	2	0	0	5671.6879	-0.0208
4	1	4	0	3	1	3	0	6291.2003	0.0030
4	0	4	0	3	0	3	0	6302.4753	-0.0097
4	2	3	0	3	2	2	0	6872.9002	0.0188
4	2	2	0	3	2	1	0	7546.3376	0.0111
5	0	5	0	4	0	4	0	7788.2125	-0.0084
3	2	1	0	2	1	1	0	6326.4128	-0.0011
3	2	2	0	2	1	2	0	6532.3127	-0.0024
3	3	0	0	2	2	0	0	6732.7502	0.0088
3	3	1	0	2	2	1	0	6816.7752	-0.0107
2	1	1	1	1	1	0	1	3760.5882	-0.0107
3	1	3	1	2	1	2	1	4784.0755	0.0095
3	0	3	1	2	0	2	1	4828.7505	-0.0086
3	2	2	1	2	2	1	1	5251.4504	-0.0031
3	1	2	1	2	1	1	1	5495.7254	0.0152
3	2	1	1	2	2	0	1	5674.2254	-0.0097
4	1	4	1	3	1	3	1	6291.9253	-0.0066
4	0	4	1	3	0	3	1	6303.0253	-0.0057
4	2	3	1	1	2	2	1	6874.0877	0.0144
4	3	2	1	3	3	1	1	7192.6501	0.0087
4	3	1	1	2	3	0	1	7480.4001	-0.0177
4	2	2	1	3	2	1	1	7548.4751	0.0171
5	1	5	1	1	1	4	1	7786.8500	-0.0046
5	0	5	1	0	0	4	1	7789.0500	0.0005
3	2	1	1	0	1	1	1	6326.2128	0.0061
3	2	2	1	1	1	2	1	6531.0377	0.0035
3	3	0	1	1	2	0	1	6729.3377	0.0060
3	3	1	1	0	2	1	1	6813.4127	-0.0188



**Table S9.** Substitution coordinates according to the Kraitchman equations for the position of the sulfur atom in the benzofuran...sulfur dioxide dimer (principal inertial axis system).

Atom: S	<i>a</i>	<i>b</i>	<i>c</i>
Substitution coordinates	±1.9365(8)	±0.384(4)	±0.352(5)
Isomer 1			
B2PLYP-D3(BJ)/cc-pVTZ	1.8236	-0.5933	0.3875
B2PLYP-D3(BJ)/jun-cc-pVTZ	1.8390	-0.5256	0.3899
Isomer 2			
B2PLYP-D3(BJ)/cc-pVTZ	1.9272	0.0647	-0.4332
B2PLYP-D3(BJ)/jun-cc-pVTZ	1.9202	-0.1309	-0.4282

**Table S10.** Substitution coordinates according to the Kraitchman equations for the position of the sulfur atom in the benzofuran...hydrogen sulfide dimer (principal inertial axis system).

Atom: S	<i>a</i>	<i>b</i>	<i>c</i>
Substitution coordinates	$\pm 2.8224(5)$	$\pm 0.610(3)$	imaginary
Isomer 1			
B2PLYP-D3(BJ)/cc-pVTZ	2.7972	-0.3826	-0.0631
B2PLYP-D3(BJ)/jun-cc-pVTZ	2.8110	-0.2752	-0.0658
Isomer 2			
B2PLYP-D3(BJ)/cc-pVTZ	2.2929	-1.4020	-0.1261
B2PLYP-D3(BJ)/jun-cc-pVTZ	2.2833	-1.3816	-0.1290

**Table S11.** Near-equilibrium atomic coordinates ( $r_e$ ) according to density-functional theory (B2PLYLP-D3(BJ)/cc-pVTZ) for the global minimum (isomer I) of the benzofuran...sulfur dioxide dimer and comparison with the effective structure ( $r_o$ ) coordinates of Table 3 (principal inertial axis system).

Atom	Isomer I					
	$r_e$			$r_o$		
	$a^a$	$b$	$c$	$a$	$b$	$c$
O	-0.9883	1.8504	0.7083	-1.4823	1.6102	0.7466
C	-0.4861	2.3954	-0.4454	-1.1364	2.2955	-0.3903
C	-0.4030	1.4907	-1.4477	-0.7862	1.4675	-1.4082
C	-0.8805	0.2487	-0.8998	-0.9159	0.1268	-0.8869
C	-1.0300	-1.0626	-1.3688	-0.7180	-1.1669	-1.3897
C	-1.5086	-2.0238	-0.4921	-0.9593	-2.2447	-0.5442
C	-1.8412	-1.7037	0.8342	-1.3913	-2.0539	0.7844
C	-1.7052	-0.4107	1.3223	-1.5936	-0.7789	1.3024
C	-1.2237	0.5359	0.4323	-1.3466	0.2828	0.4402
H	-0.2340	3.4377	-0.3862	-1.1919	3.3651	-0.3114
H	-0.0350	1.6751	-2.4406	-0.4778	1.7641	-2.3944
H	-0.7658	-1.3210	-2.3837	-0.3872	-1.3205	-2.4063
H	-1.6264	-3.0423	-0.8319	-0.8136	-3.2505	-0.9098
H	-2.2094	-2.4797	1.4890	-1.5685	-2.9152	1.4114
H	-1.9513	-0.1508	2.3403	-1.9239	-0.6161	2.3166
O	2.5343	-0.8240	-0.8648	2.6775	-0.3056	-0.8724
S	1.8236	-0.5933	0.3875	1.9591	-0.2607	0.3641
O	2.0495	0.6757	1.0706	1.9274	0.9583	1.1123

<sup>a</sup>Principal inertial axes denoted  $a$ ,  $b$ ,  $c$ .

**Table S12.** Predicted near-equilibrium atomic coordinates (principal inertial axis system) for isomers II, III and IV of the benzofuran···sulfur dioxide dimer (B2PLYP-D3(BJ)/cc-PVTZ).

Atom	Isomer II			Isomer III			Isomer IV		
	<i>a</i> <sup>a</sup>	<i>b</i>	<i>c</i>	<i>a</i>	<i>b</i>	<i>c</i>	<i>a</i>	<i>b</i>	<i>c</i>
O	-1.0762	1.2991	1.2846	-2.3595	-0.4079	-1.1392	-0.3859	-1.9085	-0.4433
C	-1.5237	2.1231	0.2831	-2.6181	-1.4443	-0.2773	0.2977	-1.9770	0.7426
C	-1.7555	1.4534	-0.8684	-1.9565	-1.3142	0.8949	-0.0310	-0.9653	1.5817
C	-1.4243	0.0796	-0.6020	-1.2053	-0.0915	0.7922	-1.0107	-0.1721	0.8856
C	-1.4047	-1.1086	-1.3395	-0.3206	0.6122	1.6167	-1.7297	0.9957	1.1602
C	-0.9810	-2.2698	-0.7094	0.2366	1.7889	1.1339	-2.5971	1.4748	0.1910
C	-0.5814	-2.2687	0.6358	-0.0725	2.2720	-0.1477	-2.7570	0.8159	-1.0383
C	-0.5911	-1.1018	1.3902	-0.9471	1.5897	-0.9837	-2.0498	-0.3415	-1.3360
C	-1.0138	0.0484	0.7414	-1.4924	0.4183	-0.4831	-1.1879	-0.8025	-0.3545
H	-1.6174	3.1587	0.5522	-3.2924	-2.1921	-0.6516	0.9827	-2.7999	0.8306
H	-2.1024	1.8814	-1.7913	-1.9916	-1.9984	1.7232	0.3732	-0.8010	2.5645
H	-1.7086	-1.1225	-2.3762	-0.0698	0.2456	2.6015	-1.6088	1.5131	2.1005
H	-0.9567	-3.1970	-1.2630	0.9269	2.3440	1.7517	-3.1626	2.3752	0.3811
H	-0.2532	-3.1903	1.0928	0.3848	3.1873	-0.4922	-3.4428	1.2187	-1.7691
H	-0.2757	-1.0821	2.4221	-1.1917	1.9466	-1.9724	-2.1591	-0.8568	-2.2778
O	1.7886	1.5095	-0.5804	3.1065	0.2663	-0.5114	2.1558	1.6757	0.5267
S	1.9272	0.0647	-0.4332	1.9240	-0.5813	-0.4173	1.9868	0.5971	-0.4388
O	2.8298	-0.4301	0.5994	2.0210	-1.7932	0.3882	3.1286	-0.2724	-0.6963

<sup>a</sup>Principal inertial axes denoted *a*, *b*, *c*.

**Table S13.** Near-equilibrium atomic coordinates ( $r_e$ ) according to density-functional theory (B2PLYLP-D3(BJ)/cc-pVTZ) for the global minimum (isomer I) of the benzofuran...hydrogen sulfide dimer and comparison with the effective structure ( $r_0$ ) coordinates of Table 3 (principal inertial axis system).

Atom	Isomer I					
	$r_e$			$r_0$		
	$a^a$	$b$	$c$	$a$	$b$	$c$
O	-1.0754	-1.3908	-1.0745	-1.3254	-1.2493	-1.0568
C	-1.1256	-2.1913	0.0369	-1.4155	-2.0583	0.0474
C	-0.9695	-1.4886	1.1832	-1.0956	-1.4065	1.1950
C	-0.8021	-0.1149	0.7868	-0.7691	-0.0556	0.8021
C	-0.5713	1.0956	1.4479	-0.3652	1.1110	1.4666
C	-0.4202	2.2432	0.6843	-0.1403	2.2551	0.7082
C	-0.4977	2.2043	-0.7175	-0.3106	2.2538	-0.6915
C	-0.7289	1.0143	-1.3956	-0.7106	1.1072	-1.3698
C	-0.8742	-0.1197	-0.6144	-0.9295	-0.0238	-0.5923
H	-1.2819	-3.2362	-0.1584	-1.7197	-3.0687	-0.1525
H	-0.9734	-1.8922	2.1797	-1.0910	-1.8239	2.1857
H	-0.5019	1.1354	2.5252	-0.2328	1.1192	2.5384
H	-0.2369	3.1885	1.1739	0.1714	3.1654	1.1985
H	-0.3732	3.1179	-1.2799	-0.1266	3.1615	-1.2471
H	-0.7811	0.9668	-2.4723	-0.8453	1.0899	-2.4402
H	1.9707	0.6736	-0.0571	2.0958	0.4700	-0.0989
S	2.7972	-0.3826	-0.0631	2.8151	-0.6554	-0.1304
H	1.8237	-1.2141	0.3346	1.7801	-1.3929	0.2815

<sup>a</sup>Principal inertial axes denoted  $a$ ,  $b$ ,  $c$ .

**Table S14.** Predicted near-equilibrium atomic coordinates (principal inertial axis system) for isomer II of the benzofuran...hydrogen sulfide dimer (B2PLYP-D3(BJ)/cc-PVTZ).

	Isomer II		
	<i>a</i>	<i>b</i>	<i>c</i>
O	-1.6401	-0.7841	-1.0463
C	-1.9468	-1.5480	0.0505
C	-1.4231	-1.0437	1.1908
C	-0.7123	0.1474	0.8075
C	0.0516	1.1135	1.4698
C	0.6150	2.1354	0.7199
C	0.4279	2.2104	-0.6699
C	-0.3307	1.2646	-1.3488
C	-0.8821	0.2522	-0.5820
H	-2.5442	-2.4177	-0.1511
H	-1.5220	-1.4649	2.1749
H	0.2087	1.0605	2.5372
H	1.2123	2.8896	1.2111
H	0.8819	3.0201	-1.2223
H	-0.4787	1.3056	-2.4169
H	2.0787	-0.0850	-0.2588
S	2.2929	-1.4020	-0.1261
H	3.4687	-1.3457	-0.7678

<sup>a</sup>Principal inertial axes denoted *a*, *b*, *c*.

**Table S15.** Effective structure fit of the six observed rotational constants of the dimer benzofuran...sulfur dioxide to the three parameters in Table 3. The two monomers were fixed to the effective structures of refs. 46 and 51. The initial orientation between the two monomers was taken from the ab initio calculation B2PLYP-D3(BJ)/cc-pVTZ.

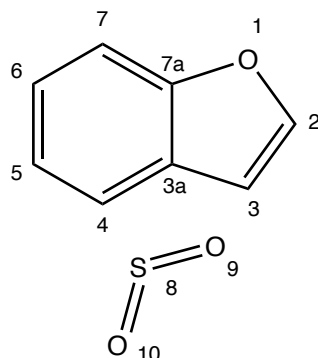
Isotope	Name	Axis	Rotational constant	Residual (exp.-calc.)
1	Parent	A / MHz	1056.0360	0.1229
		B / MHz	811.9498	0.0776
		C / MHz	642.2082	-0.0077
2	<sup>34</sup> S	A / MHz	1054.9000	0.4789
		B / MHz	802.0770	-0.1957
		C / MHz	635.9850	-0.0219
rms / MHz				0.2048

**Table S16.** Effective structure ( $r_0$ ) fit of the six observed rotational constants of the dimer benzofuran...hydrogen sulfide to the three parameters in Table 3. The two monomers were fixed to the effective structures of refs. 46 and 51. The initial orientation between the two monomers was taken from the DFT calculation B2PLYP-D3(BJ)/cc-pVTZ.

Isotope	Name	Axis	Rotational constant	Residual (exp.-calc.)
1	Parent	A / MHz	1173.9314	0.0009
		B / MHz	1037.5461	-0.0004
		C / MHz	763.9491	-0.0120
2	<sup>34</sup> S	A / MHz	1172.4240	-0.3778
		B / MHz	1004.8820	0.0064
		C / MHz	745.4430	-0.0520
rms / MHz				0.1558



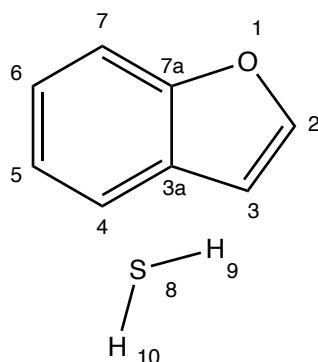
**Table S17.** Natural-bond-orbital analysis (stabilization energy contributions  $\geq 0.2$  kJ mol<sup>-1</sup>) for the benzofuran-sulfur dioxide complex using the B3LYP-D3(BJ) / aug-cc-pVTZ level.



Interactions	Donor NBO	Acceptor NBO	E / kJ mol <sup>-1</sup>
S... $\pi$	BD(2)C3a-C4	BD*(1)S8-O10	2.7
	BD(2)C3a-C4	BD*(2)S8-O10	1.0
	BD(2)C3a-C4	BD*(1)S8-O9	1.3
	BD(2)C3a-C4	RY*(5)S8	0.5
	BD(1)C3a-C4	RY*(34)S8	0.2
	BD(1)C3a-C4	RY*(16)S8	0.3
	BD(2)C7a-C7	BD*(1)S8-O9	0.4
	BD(2)C7a-C7	BD*(1)S8-O10	0.8
	BD(1)C7a-C3a	RY*(16)S8	0.2
	BD(1)C7a-C3a	RY*(13)S8	0.4
	BD(1)C3a-C3	RY*(13)S8	0.2
	BD(1)C3-C2	BD*(1)S8-O9	0.2
	C3... $\pi$	BD(1)S8-O10	RY*(1)C3a
BD(1)S8-O10		RY*(6)C3a	0.6
BD(1)S8-O10		RY*(11)C3a	0.5
BD(2)S8-O10		RY*(2)C3a	0.3
BD(2)S8-O10		RY*(3)C3a	1.2
BD(2)S8-O10		RY*(11)C3a	0.3
BD(1)S8-O9		RY*(3)C3a	0.6
BD(1)S8-O9		RY*(10)C3a	0.2
BD(2)S8-O9		RY*(1)C3a	0.7
BD(2)S8-O9		RY*(2)C3a	0.5
BD(2)S8-O9		RY*(4)C3a	0.2
BD(2)S8-O9		RY*(11)C3a	0.2
C2... $\pi$	BD(2)S8-O9	RY*(2)C7a	0.5
	BD(2)S8-O9	RY*(4)C7a	0.2
	BD(2)S8-O9	RY*(6)C7a	0.4
	BD(1)S8-O9	RY*(10)C7a	0.2
S...C3	LP(1)S8	RY*(3)C3a	1.2
	LP(1)S8	RY*(1)C3a	0.7

	LP(1)S8	RY*(2)C3a	0.3
$\pi \cdots \pi^*$	BD(1)S8-O9	BD*(1)C7-C7a	0.7
	BD(1)S8-O9	BD*(1)C3a-C4	0.6
$n \cdots \pi^*$	LP(1)S10	BD*(1)C4-C3a	0.5

**Table S18.** The NBO analysis (stabilization energy contributions  $\geq 0.2$  kJ mol<sup>-1</sup>) for the benzofuran–hydrogen sulfide complex using the B3LYP-D3(BJ) / aug-cc-pVTZ level.



Interactions	Donor NBO	Acceptor NBO	E / kJ mol <sup>-1</sup>
SH9... $\pi$	BD(2)C7-C6	BD*(1)S8-H9	0.6
	BD(2)C5-C4	BD*(1)S8-H9	1.4
	BD(1)C6-C5	RY*(3)H9	0.3
	BD(1)C5-C4	RY*(3)H9	0.3
	BD(1)C3a-C4	RY*(1)H9	0.2
	BD(1)C3a-C4	RY*(15)H9	0.4
	BD(1)C7a-C3a	RY*(9)H9	0.4
SH10... $\pi$	BD(2)C3-C2	BD*(1)S8-H10	1.7
	BD(2)C7a-C3a	BD*(1)S8-H10	0.3
	BD(1)C4-C3a	RY*(7)H10	0.4
	BD(2)C7a-C3a	RY*(7)H10	0.2
n... $\pi^*$	LP(2)S8	BD*(2)C7a-C3a	0.4
<b>Total</b>			<b>6.4</b>