Table S-1: Coefficients of the one-dimensional Fourier expansion for the potential energy curves of 2AT given in Figure 2 calculated at the MP2 and B3LYP-D3BJ/6-311++G(d,p) levels of theory. The potential is expanded as $V(\varphi) = \sum_{i=0}^{12} a_i f_i$ for MP2 and $V(\varphi) = \sum_{i=0}^{9} a_i f_i$ for B3LYP-D3BJ.

		MP2		**B3LYP-D3BJ**	
i	**f*ᵢ***	**a_i / Hartree**	**a_i / cm^{-1}**	**a_i / Hartree**	**a_i / cm^{-1}**
0	1	–704.3291215		–705.7867039	
1	cos 1α	–0.0006664	–146.3	–0.0002781	–61.0
2	cos 2α	–0.0054717	–1200.9	–0.0066204	–1453.0
3	cos 3α	–0.0001464	–32.1	–0.0002363	–51.9
4	cos 4α	0.0006446	141.5	0.0004726	103.7
5	cos 5α	–0.0001127	–24.7	–0.0000770	–16.9
6	cos 6α	–0.0000269	–5.9	–0.0000661	–14.5
7	cos 8α	0.0000738	16.2	/	/

Table S-2a: Nuclear Coordinates in the principal axis system of *anti*-2AT and *syn*-2AT optimized at the B3LYP-D3BJ/6-311++G(d,p) level of theory (for atom numbering see Figure 1).

	***syn*-2AT**			***anti*-2AT**		
	***a* / Å**	***b* / Å**	***c* / Å**	***a* / Å**	***b* / Å**	***c* / Å**
S1	–0.953154	–1.129718	–0.000215	–0.883991	–1.162249	–0.000024
C3	0.167446	0.208248	–0.000055	0.156924	0.243875	0.000000
C2	–0.500266	1.413605	–0.000303	–0.589429	1.399795	0.000003
C4	–1.910718	1.267983	0.000078	–1.986519	1.164361	0.000022
C5	–2.295419	–0.048616	0.000469	–2.295633	–0.171521	0.000016
C6	1.613275	–0.061779	–0.000076	1.632782	0.166132	–0.000011
O7	2.040571	–1.203321	0.000210	2.299415	1.185138	–0.000023
C8	2.542995	1.135780	0.000104	2.274785	–1.205666	0.000041
H9	–3.300923	–0.441775	0.000841	–3.272775	–0.629977	0.000029
H10	–2.607974	2.094603	0.000147	–2.734473	1.945419	0.000043
H11	0.005232	2.369704	–0.000514	–0.121776	2.374482	0.000003
H12	2.370369	1.757297	–0.882759	1.966055	–1.774429	0.882130
H13	3.572239	0.781490	0.000323	3.357407	–1.093684	–0.000211
H14	2.370000	1.757344	0.882861	1.965661	–1.774741	–0.881706

Table S-2b: Nuclear coordinates in the principal axis system of *anti*-2AT and *syn*-2AT optimized at the MP2/6-311++G(d,p) level of theory (for atom numbering see Figure 1).

	***syn*-2AT**			***anti*-2AT**		
	***a* / Å**	***b* / Å**	***c* / Å**	***a* / Å**	***b* / Å**	***c* / Å**
S1	–0.942077	–1.123837	0.000802	0.873736	–1.151212	0.064566
C3	0.160303	0.199028	0.001549	–0.149529	0.236593	0.027211
C2	–0.512946	1.418873	–0.000335	0.600702	1.405593	–0.054691
C4	–1.917553	1.262818	–0.000953	1.990838	1.159925	–0.071778
C5	–2.288941	–0.072805	–0.000715	2.286967	–0.193672	–0.014957
C6	1.614564	–0.058733	–0.000037	–1.631514	0.163058	0.015487
O7	2.051400	–1.204246	–0.001820	–2.298952	1.185481	0.099831
C8	2.526106	1.151338	0.000785	–2.267258	–1.202681	–0.140547
H9	–3.292389	–0.479872	–0.000466	3.261640	–0.664715	–0.001659
H10	–2.630328	2.079818	–0.002002	2.753283	1.928904	–0.126708
H11	–0.004221	2.376749	–0.000395	0.129588	2.381304	–0.095835
H12	2.337220	1.767558	–0.883436	–2.064223	–1.590888	–1.144173
H13	3.562394	0.812270	–0.000693	–3.344780	–1.115302	0.002607
H14	2.339015	1.765316	0.886921	–1.852833	–1.912527	0.582119

Table S-3a: Equilibrium rotational constants, X_e (X = A, B, C) of *syn*-2AT calculated at various levels of theory. The deviations ΔX between the calculated and the ground state experimental values X_0 are given in MHz. The relative deviations of the semi-experimental equilibrium structures with respect to X_e^BO are given in %. The relative energy difference (in kJ/mol) is $E_{anti\text{-}2AT} - E_{syn\text{-}2AT}$.

	***A* /**	**Δ*A* /**	***B* /**	**Δ*B* /**	***C* /**	**Δ*C* /**	**Δ*E* /**
Method/Basis Set	**MHz**	**MHz**	**MHz**	**MHz**	**MHz**	**MHz**	**kJ/mol**
MP2/6-31G(d,p)	3561.3	–26.8	1418.8	2.9	1021.0	–1.1	5.5
MP2/6-31+G(d,p)	3552.2	–35.9	1414.5	–1.4	1018.1	–4.0	5.1
MP2/6-31++G(d,p)	3552.2	–35.9	1414.5	–1.4	1018.0	–4.1	4.8
MP2/6-311G(d,p)	3560.2	–27.9	1416.8	0.9	1019.9	–2.2	6.2
MP2/6-311+G(d,p)	3555.0	–33.1	1414.5	–1.4	1018.3	–3.8	5.1
MP2/6-311++G(d,p)	3554.6	–33.5	1414.5	–1.4	1018.3	–3.8	5.7
MP2/6-311G(df,pd)	3585.9	–2.2	1425.0	9.1	1026.3	4.2	5.4
MP2/6-311+G(df,pd)	3580.6	–7.5	1422.2	6.3	1024.4	2.3	4.1
MP2/6-311++G(df,pd)	3580.3	–7.8	1422.3	6.4	1024.4	2.3	3.8
MP2/6-311G(2d,2p)	3565.5	–22.6	1421.7	5.8	1022.8	0.7	4.8
MP2/6-311+G(2d,2p)	3561.5	–26.6	1420.4	4.5	1021.8	–0.3	3.8
MP2/6-311++G(2d,2p)	3561.4	–26.7	1420.4	4.5	1021.8	–0.3	3.7
MP2/6-311G(2df,2pd)	3589.8	1.8	1430.2	14.3	1029.2	7.1	4.9
MP2/6-311+G(2df,2pd)	3584.9	–3.2	1428.2	12.3	1027.8	5.7	3.5
MP2/6-311++G(2df,2pd)	3584.7	–3.4	1428.1	12.2	1027.7	5.6	3.5
MP2/6-311G(3df,3pd)	3596.6	8.5	1429.4	13.5	1029.4	7.3	3.7
MP2/6-311+G(3df,3pd)	3591.2	3.1	1428.6	12.7	1028.6	6.5	3.0
MP2/6-311++G(3df,3pd)	3591.1	3.0	1428.6	12.7	1028.5	6.4	3.0
MP2/cc-pVDZ	3521.0	–67.1	1405.3	–10.6	1010.8	–11.3	3.7
MP2/cc-pVTZ	3578.8	–9.3	1426.0	10.1	1026.1	4.0	3.6
MP2/aug-cc-pVDZ	3507.7	–80.4	1401.3	–14.6	1007.7	–14.4	3.7
MP2/aug-cc-pVTZ	3576.6	–11.5	1425.8	9.9	1025.9	3.8	3.5
B3LYP-D3/6-31G(d,p)	3545.2	–42.9	1404.8	–11.1	1012.5	–9.6	2.6
B3LYP-D3/6-31+G(d,p)	3539.9	–48.2	1400.5	–15.4	1009.8	–12.3	2.0
B3LYP-D3/6-31++G(d,p)	3539.9	–48.2	1400.4	–15.5	1009.8	–12.3	2.0
B3LYP-D3/6-311G(d,p)	3557.6	–30.5	1407.2	–8.7	1014.7	–7.4	3.2
B3LYP-D3/6-311+G(d,p)	3554.9	–33.2	1405.0	–10.9	1013.4	–8.7	2.1
B3LYP-D3/6-311++G(d,p)	3554.8	–33.3	1405.0	–10.9	1013.3	–8.8	2.1
B3LYP-D3/6-311G(df,pd)	3568.8	–19.3	1410.7	–5.2	1017.4	–4.7	3.1
B3LYP-D3/6-311+G(df,pd)	3566.7	–21.4	1408.6	–7.3	1016.1	–6.0	2.0
B3LYP-D3/6-311++G(df,pd)	3566.6	–21.5	1408.5	–7.4	1016.1	–6.0	1.9
B3LYP-D3/6-311G(3df,3pd)	3591.7	3.6	1415.0	–0.9	1021.5	–0.6	2.4
B3LYP-D3/6-311+G(3df,3pd)	3587.7	–0.4	1414.4	–1.5	1020.9	–1.2	1.9
B3LYP-D3/6-311++G(3df,3pd)	3587.6	–0.5	1414.4	–1.5	1020.8	–1.3	1.9
B3LYP-D3/cc-pVDZ	3533.6	–54.5	1402.3	–13.6	1010.3	–11.8	1.3
B3LYP-D3/cc-pVTZ	3578.4	–9.7	1412.2	–3.7	1019.0	–3.1	2.0
B3LYP-D3/aug-cc-pVDZ	3531.8	–56.3	1398.9	–17.0	1008.3	–13.8	2.3

B3LYP-D3/aug-cc-pVTZ	3577.8	–10.3	1411.7	–4.2	1018.7	–3.4	1.9
B3LYP-D3/6-311G(2d,2p)	3575.1	–13.0	1411.5	–4.4	1018.4	–3.7	3.2
B3LYP-D3/6-311+G(2d,2p)	3572.1	–16.0	1410.3	–5.6	1017.5	–4.6	2.2
B3LYP-D3/6-311++G(2d,2p)	3572.0	–16.1	1410.3	–5.6	1017.5	–4.6	2.2
B3LYP-D3/6-311G(2df,2pd)	3584.6	–3.5	1414.1	–1.8	1020.5	–1.6	3.2
B3LYP-D3/6-311+G(2df,2pd)	3581.7	–6.4	1412.5	–3.4	1019.4	–2.7	2.1
B3LYP-D3/6-311++G(2df,2pd)	3581.7	–6.4	1412.5	–3.4	1019.4	–2.7	2.1
B3LYP-D3BJ/6-31G(d,p)	3549.6	–38.5	1409.7	–6.2	1015.4	–6.7	3.7
B3LYP-D3BJ/6-31+G(d,p)	3544.0	–44.1	1405.5	–10.4	1012.7	–9.4	3.0
B3LYP-D3BJ/6-31++G(d,p)	3544.0	–44.1	1405.5	–10.4	1012.7	–9.4	3.0
B3LYP-D3BJ/6-311G(d,p)	3561.9	–26.2	1411.9	–4.0	1017.5	–4.6	4.3
B3LYP-D3BJ/6-311+G(d,p)	3559.1	–29.0	1409.9	–6.0	1016.3	–5.8	3.1
B3LYP-D3BJ/6-311++G(d,p)	3559.0	–29.1	1409.9	–6.0	1016.2	–5.9	3.1
B3LYP-D3BJ/6-311G(df,pd)	3572.6	–15.5	1415.5	–0.4	1020.2	–1.9	4.2
B3LYP-D3BJ/6-311+G(df,pd)	3570.2	–17.9	1413.5	–2.4	1019.0	–3.1	3.0
B3LYP-D3BJ/6-311++G(df,pd)	3570.1	–18.0	1413.5	–2.4	1019.0	–3.1	2.9
B3LYP-D3BJ/6-311G(3df,3pd)	3595.1	7.0	1419.6	3.7	1024.2	2.1	3.5
B3LYP-D3BJ/6-311+G(3df,3pd)	3591.1	3.0	1419.1	3.2	1023.6	1.5	2.8
B3LYP-D3BJ/6-311++G(3df,3pd)	3591.0	2.9	1419.1	3.2	1023.6	1.5	2.8
B3LYP-D3BJ/cc-pVDZ	3538.2	–49.9	1407.2	–8.7	1013.2	–8.9	2.4
B3LYP-D3BJ/cc-pVTZ	3582.2	–5.9	1417.0	1.1	1021.7	–0.4	3.0
B3LYP-D3BJ/aug-cc-pVDZ	3536.2	–51.9	1403.9	–12.0	1011.3	–10.8	3.2
B3LYP-D3BJ/aug-cc-pVTZ	3581.5	–6.6	1416.6	0.7	1021.5	–0.6	2.9
B3LYP-D3BJ/6-311G(2d,2p)	3579.2	–8.9	1416.5	0.6	1021.3	–0.8	4.3
B3LYP-D3BJ/6-311+G(2d,2p)	3575.8	–12.3	1415.4	–0.5	1020.4	–1.7	3.2
B3LYP-D3BJ/6-311++G(2d,2p)	3575.7	–12.4	1415.4	–0.5	1020.4	–1.7	3.2
B3LYP-D3BJ/6-311G(2df,2pd)	3588.6	0.5	1419.0	3.1	1023.3	1.2	4.3
B3LYP-D3BJ/6-311+G(2df,2pd)	3585.4	–2.7	1417.5	1.6	1022.3	0.2	3.1
B3LYP-D3BJ/6-311++G(2df,2pd)	3585.4	–2.7	1417.4	1.5	1022.2	0.1	3.1
CAM-B3LYP-D3BJ/6-311G(d,p)	3602.8	14.8	1421.0	5.1	1025.6	3.5	4.3
CAM-B3LYP-D3BJ/ 6-311+G(d,p)	3600.1	12.0	1418.7	2.8	1024.2	2.1	3.2
CAM-B3LYP-D3BJ/ 6-311++G(d,p)	3600.0	11.9	1418.7	2.8	1024.1	2.0	3.1
CAM-B3LYP-D3BJ/cc-pVDZ	3576.7	–11.4	1412.5	–3.4	1019.1	–3.0	3.4
CAM-B3LYP-D3BJ/cc-pVTZ	3621.8	33.8	1425.4	9.5	1029.4	7.3	3.1
CAM-B3LYP-D3BJ/aug-cc-pVDZ	3579.2	–8.9	1415.9	0.0	1021.1	–1.0	2.5
CAM-B3LYP-D3BJ/aug-cc-pVTZ	3622.6	34.5	1426.0	10.1	1029.7	7.6	3.1
M06-2X/6-31G(d,p)	3583.2	–4.9	1418.1	2.2	1022.5	0.4	3.8
M06-2X/6-31+G(d,p)	3579.2	–8.9	1414.5	–1.4	1020.3	–1.8	3.3
M06-2X/6-31++G(d,p)	3579.2	–8.9	1414.4	–1.5	1020.3	–1.8	3.3
M06-2X/6-311G(d,p)	3591.7	3.6	1420.0	4.1	1024.1	2.0	4.3
M06-2X/6-311+G(d,p)	3590.1	2.0	1417.9	2.0	1022.9	0.8	3.3
M06-2X/6-311++G(d,p)	3589.9	1.8	1417.9	2.0	1022.9	0.8	3.2
M06-2X/6-311G(df,pd)	3600.6	12.5	1422.5	6.6	1026.2	4.1	4.1
M06-2X/6-311+G(df,pd)	3599.3	11.3	1420.5	4.6	1025.0	2.9	3.1
M06-2X/6-311++G(df,pd)	3599.3	11.3	1420.5	4.6	1025.0	2.9	3.0

M06-2X/6-311G(3df,3pd)	3620.9	32.8	1425.9	10.0	1029.5	7.4	3.5
M06-2X/6-311+G(3df,3pd)	3617.6	29.5	1425.7	9.8	1029.2	7.1	3.1
M06-2X/6-311++G(3df,3pd)	3617.5	29.4	1425.7	9.8	1029.2	7.1	3.1
M06-2X/cc-pVDZ	3574.5	–13.6	1416.3	0.4	1020.9	–1.2	2.7
M06-2X/cc-pVTZ	3609.6	21.5	1424.8	8.9	1028.1	6.0	3.2
M06-2X/aug-cc-pVDZ	3572.4	–15.7	1413.0	–2.9	1019.0	–3.1	3.4
M06-2X/aug-cc-pVTZ	3609.6	21.5	1424.5	8.6	1027.9	5.8	3.2
ωB97X-D/6-311G(d,p)	3592.6	4.5	1415.7	–0.2	1022.0	–0.1	3.8
ωB97X-D/6-311+G(d,p)	3592.5	4.4	1415.6	–0.3	1021.9	–0.2	3.7
ωB97X-D/6-311++G(d,p)	3594.3	6.3	1417.7	1.8	1023.2	1.1	4.7
ωB97X-D/cc-pVDZ	3570.3	–17.8	1409.3	–6.6	1016.9	–5.2	3.7
ωB97X-D/cc-pVTZ	3614.7	26.6	1422.0	6.1	1027.0	4.9	3.5
ωB97X-D/aug-cc-pVDZ	3572.8	–15.3	1412.1	–3.8	1018.6	–3.5	2.9
ωB97X-D/aug-cc-pVTZ	3615.1	27.0	1422.2	6.3	1027.2	5.1	3.5
CCSD/cc-pVDZ	3521.2	–66.9	1394.6	–21.3	1005.4	–16.7	3.7
CCSD(T)_ae/cc-pwCVTZ	3587.90	0.45[a]	1422.02	0.32[a]	1024.85	0.36[a]	
CCSD(T)_ae/cc-pwCVQZ, X_e^{BO}[b]	3599.31	0.13[a]	1424.81	0.12[a]	1027.22	0.13[a]	
Experimental (X_o)	3588.05		1415.91		1022.07		
Semiexperimental (X_e^{SE})[c]	3604.09		1426.57		1028.54		

[a] Deviation from semi-experimental equilibrium rotational constant X_e^{SE} in %.

[b] Rotational constants of the r_e^{BO} structure, i.e. of CCSD(T)_ae/cc-pwCVQZ quality.

[c] Derived with the B2PLYP-D3/6-311+G(3df,2pd) anharmonic (cubic) force field.

Table S-3b: Equilibrium rotational constants, X_e (X = A, B, C) of *anti*-2AT calculated at various levels of theory. The deviations ΔX between the calculated and the ground state experimental values X_0 are given in MHz. The relative deviations of the semi-experimental equilibrium structures with respect to X_e^{BO} are given in %. Θ is the tilt angle of the acetyl group out of the thiophene plane, *i.e.* deviation of the angle α from 180°. Imag stands for imaginary frequency.

Method/Basis Set	**A / MHz**	**ΔA / MHz**	**B / MHz**	**ΔB / MHz**	**C / MHz**	**ΔC / MHz**	**Θ / °**	***Imag***
MP2/6-31G(d,p)	3529.8	–25.6	1417.3	–1.5	1017.6	–3.1	0.01	No
MP2/6-31+G(d,p)	3525.7	–29.7	1413.7	–5.1	1016.7	–4.0	4.91	–[a]
MP2/6-31++G(d,p)	3524.7	–30.7	1412.9	–5.8	1017.6	–3.1	5.70	–[a]
MP2/6-311G(d,p)	3530.7	–24.7	1416.9	–1.8	1017.6	–3.2	0.04	No
MP2/6-311+G(d,p)	3529.4	–26.0	1415.4	–3.3	1018.5	–2.3	4.88	–[a]
MP2/6-311++G(d,p)	3528.4	–27.0	1414.7	–4.0	1019.3	–1.5	6.03	–[a]
MP2/6-311G(df,pd)	3557.8	2.4	1426.3	7.5	1024.6	3.8	0.02	No
MP2/6-311+G(df,pd)	3555.6	0.2	1423.0	4.2	1025.8	5.1	6.32	–[a]
MP2/6-311++G(df,pd)	3553.9	–1.5	1422.8	4.0	1026.6	5.9	6.85	–[a]
MP2/6-311G(2d,2p)	3539.3	–50.4	1422.1	6.4	1020.9	–1.0	0.03	No
MP2/6-311+G(2d,2p)	3538.7	–51.0	1422.7	7.0	1021.1	–0.7	0.01	No
MP2/6-311++G(2d,2p)	3538.8	–50.9	1422.7	7.0	1021.1	–0.7	0.02	No
MP2/6-311G(2df,2pd)	3563.5	–26.2	1431.2	15.5	1027.6	5.7	0.01	No
MP2/6-311+G(2df,2pd)	3563.0	–26.7	1431.1	15.4	1027.5	5.6	0.00	/[b]
MP2/6-311++G(2df,2pd)	3562.8	–26.9	1431.1	15.4	1027.5	5.6	0.00	/[b]
MP2/6-311G(3df,3pd)	3571.1	15.7	1431.7	13.0	1028.5	7.7	0.01	No
MP2/6-311+G(3df,3pd)	3568.6	13.2	1431.8	13.0	1028.3	7.5	0.04	No
MP2/6-311++G(3df,3pd)	3568.6	13.1	1431.8	13.0	1028.3	7.5	0.03	No
MP2/cc-pVDZ	3491.0	–64.5	1404.1	–14.7	1007.7	–13.0	0.04	No
MP2/cc-pVTZ	3554.8	–0.6	1427.8	9.0	1025.1	4.3	0.02	No
MP2/aug-cc-pVDZ	3484.7	–70.8	1404.0	–14.7	1007.2	–13.6	0.05	No
MP2/aug-cc-pVTZ	3553.9	–1.5	1428.4	9.6	1025.3	4.6	0.03	/[b]
B3LYP-D3/6-31G(d,p)	3510.9	–78.7	1404.8	–10.9	1009.6	–12.2	0.00	No
B3LYP-D3/6-31+G(d,p)	3509.3	–80.4	1402.9	–12.8	1008.5	–13.3	0.00	No
B3LYP-D3/6-31++G(d,p)	3509.3	–80.3	1402.9	–12.8	1008.5	–13.3	0.00	No
B3LYP-D3/6-311G(d,p)	3523.7	–66.0	1407.3	–8.4	1012.0	–9.9	0.01	No
B3LYP-D3/6-311+G(d,p)	3524.2	–65.4	1407.3	–8.4	1012.0	–9.9	0.01	No
B3LYP-D3/6-311++G(d,p)	3524.1	–65.5	1407.3	–8.4	1012.0	–9.9	0.01	No
B3LYP-D3/6-311G(df,pd)	3535.6	–54.1	1411.3	–4.4	1015.0	–6.9	0.03	No
B3LYP-D3/6-311+G(df,pd)	3536.0	–53.6	1411.4	–4.4	1015.1	–6.8	0.03	No
B3LYP-D3/6-311++G(df,pd)	3536.0	–53.7	1411.4	–4.3	1015.1	–6.8	0.03	No
B3LYP-D3/6-311G(3df,3pd)	3560.3	–29.3	1416.6	0.9	1019.8	–2.1	0.04	No
B3LYP-D3/6-311+G(3df,3pd)	3558.6	–31.1	1417.2	1.4	1019.9	–2.0	0.04	No
B3LYP-D3/6-311++G(3df,3pd)	3558.5	–31.2	1417.1	1.4	1019.9	–2.0	0.04	No
B3LYP-D3/cc-pVDZ	3499.7	–89.9	1401.8	–13.9	1007.2	–14.6	0.01	No
B3LYP-D3/cc-pVTZ	3547.7	–42.0	1414.2	–1.5	1017.5	–4.4	0.03	No

B3LYP-D3/aug-cc-pVDZ	3502.9	–86.7	1401.6	–14.1	1007.4	–14.5	0.01	No
B3LYP-D3/aug-cc-pVTZ	3548.0	–41.6	1414.5	–1.2	1017.7	–4.2	0.03	No
B3LYP-D3/6-311G(2d,2p)	3542.0	–47.7	1411.8	–3.9	1015.8	–6.1	0.01	No
B3LYP-D3/6-311+G(2d,2p)	3542.2	–47.5	1412.5	–3.2	1016.1	–5.7	0.02	No
B3LYP-D3/6-311++G(2d,2p)	3542.1	–47.6	1412.5	–3.2	1016.2	–5.7	0.02	No
B3LYP-D3/6-311G(2df,2pd)	3552.5	–37.2	1414.8	–0.9	1018.2	–3.7	0.01	No
B3LYP-D3/6-311+G(2df,2pd)	3552.8	–36.8	1415.2	–0.5	1018.4	–3.4	0.05	No
B3LYP-D3/6-311++G(2df,2pd)	3552.7	–36.9	1415.3	–0.4	1018.5	–3.4	0.04	No
B3LYP-D3BJ/6-31G(d,p)	3513.6	–41.8	1410.0	–8.8	1012.5	–8.2	0.01	No
B3LYP-D3BJ/6-31+G(d,p)	3512.2	–43.2	1408.1	–10.6	1011.5	–9.3	0.04	No
B3LYP-D3BJ/6-31++G(d,p)	3512.2	–43.2	1408.1	–10.7	1011.4	–9.3	0.02	No
B3LYP-D3BJ/6-311G(d,p)	3526.5	–28.9	1412.5	–6.3	1014.9	–5.9	0.01	No
B3LYP-D3BJ/6-311+G(d,p)	3526.9	–28.5	1412.6	–6.2	1015.0	–5.8	0.00	/[b]
B3LYP-D3BJ/6-311++G(d,p)	3526.8	–28.6	1412.6	–6.2	1015.0	–5.8	0.00	No
B3LYP-D3BJ/6-311G(df,pd)	3538.0	–17.5	1416.6	–2.1	1018.0	–2.8	0.03	No
B3LYP-D3BJ/6-311+G(df,pd)	3538.6	–16.8	1416.7	–2.1	1018.0	–2.7	0.03	No
B3LYP-D3BJ/6-311++G(df,pd)	3538.6	–16.9	1416.7	–2.0	1018.1	–2.7	0.02	No
B3LYP-D3BJ/6-311G(3df,3pd)	3562.3	6.8	1422.0	3.3	1022.7	2.0	0.03	No
B3LYP-D3BJ/6-311+G(3df,3pd)	3561.0	5.6	1422.5	3.8	1022.9	2.1	0.01	No
B3LYP-D3BJ/6-311++G(3df,3pd)	3560.9	5.5	1422.6	3.9	1022.9	2.2	0.06	No
B3LYP-D3BJ/cc-pVDZ	3502.5	–52.9	1407.1	–11.6	1010.2	–10.6	0.01	No
B3LYP-D3BJ/cc-pVTZ	3550.4	–5.0	1419.6	0.8	1020.5	–0.3	0.03	No
B3LYP-D3BJ/aug-cc-pVDZ	3505.9	–49.5	1407.1	–11.7	1010.4	–10.3	0.04	No
B3LYP-D3BJ/aug-cc-pVTZ	3550.9	–4.6	1419.9	1.1	1020.7	–0.1	0.02	No
B3LYP-D3BJ/6-311G(2d,2p)	3544.4	–45.3	1417.1	1.4	1018.7	–3.1	0.02	No
B3LYP-D3BJ/6-311+G(2d,2p)	3544.7	–45.0	1417.8	2.1	1019.1	–2.8	0.02	No
B3LYP-D3BJ/6-311++G(2d,2p)	3544.6	–45.1	1417.9	2.1	1019.1	–2.8	0.01	No
B3LYP-D3BJ/6-311G(2df,2pd)	3554.5	–35.1	1420.1	4.4	1021.1	–0.8	0.02	No
B3LYP-D3BJ/6-311+G(2df,2pd)	3555.0	–34.6	1420.5	4.8	1021.4	–0.5	0.01	No
B3LYP-D3BJ/6-311++G(2df,2pd)	3554.9	–34.7	1420.6	4.8	1021.4	–0.5	0.01	No
CAM-B3LYP-D3BJ/6-311G(d,p)	3564.2	–25.4	1421.5	5.8	1022.7	0.8	0.02	No
CAM-B3LYP-D3BJ/6-311+G(d,p)	3564.8	–24.9	1421.6	5.9	1022.7	0.9	0.01	No
CAM-B3LYP-D3BJ/ 6-311++G(d,p)	3564.8	–24.9	1421.6	5.9	1022.7	0.9	0.02	No
CAM-B3LYP-D3BJ/cc-pVDZ	3543.7	–45.9	1415.7	0.0	1018.0	–3.8	0.01	No
CAM-B3LYP-D3BJ/cc-pVTZ	3588.6	–1.1	1428.8	13.1	1028.4	6.5	0.00	No
CAM-B3LYP-D3BJ/aug-cc-pVDZ	3540.0	–49.7	1415.9	0.2	1017.8	–4.0	0.02	No
CAM-B3LYP-D3BJ/aug-cc-pVTZ	3588.1	–1.5	1428.6	12.9	1028.2	6.4	0.00	No
M06-2X/6-31G(d,p)	3547.2	–8.2	1420.5	1.7	1020.7	0.0	0.01	No
M06-2X/6-31+G(d,p)	3546.0	–9.5	1418.6	–0.1	1019.7	–1.1	0.02	No
M06-2X/6-31++G(d,p)	3546.0	–9.4	1418.7	–0.1	1019.7	–1.1	0.02	No
M06-2X/6-311G(d,p)	3557.4	2.0	1422.6	3.8	1022.7	1.9	0.01	No
M06-2X/6-311+G(d,p)	3558.2	2.8	1422.5	3.7	1022.7	1.9	0.00	No
M06-2X/6-311++G(d,p)	3558.2	2.7	1422.5	3.8	1022.7	1.9	0.01	No
M06-2X/6-311G(df,pd)	3567.4	11.9	1425.8	7.0	1025.1	4.4	0.03	No
M06-2X/6-311+G(df,pd)	3568.3	12.9	1425.6	6.8	1025.1	4.3	0.00	No
M06-2X/6-311++G(df,pd)	3568.3	12.9	1425.7	6.9	1025.1	4.4	0.01	No

M06-2X/6-311G(3df,3pd)	3590.0	34.6	1430.5	11.7	1029.4	8.6	0.03	No
M06-2X/6-311+G(3df,3pd)	3588.8	33.4	1431.0	12.3	1029.6	8.8	0.05	No
M06-2X/6-311++G(3df,3pd)	3588.8	33.3	1431.0	12.2	1029.6	8.8	0.05	No
M06-2X/cc-pVDZ	3538.9	−16.5	1418.1	−0.7	1018.9	−1.9	0.02	No
M06-2X/cc-pVTZ	3580.1	24.7	1429.4	10.6	1028.0	7.2	0.04	No
M06-2X/aug-cc-pVDZ	3542.6	−12.8	1417.6	−1.2	1018.9	−1.9	0.03	No
M06-2X/aug-cc-pVTZ	3581.0	25.6	1429.6	10.8	1028.2	7.4	0.01	No
ωB97X-D/6-311G(d,p)	3560.2	–29.5	1417.8	2.1	1020.4	–1.4	0.02	No
ωB97X-D/6-311+G(d,p)	3560.1	–29.6	1417.8	2.1	1020.4	–1.4	0.02	No
ωB97X-D/6-311++G(d,p)	3559.4	–30.3	1417.9	2.1	1020.4	–1.5	0.00	No
ωB97X-D/cc-pVDZ	3539.8	–49.8	1412.1	–3.7	1015.8	–6.0	0.01	No
ωB97X-D/cc-pVTZ	3584.6	–5.1	1424.8	9.1	1026.0	4.2	0.01	No
ωB97X-D/aug-cc-pVDZ	3536.0	–53.6	1411.6	–4.1	1015.3	–6.5	0.04	No
ωB97X-D/aug-cc-pVTZ	3584.0	–5.7	1424.4	8.7	1025.7	3.9	0.01	No
CCSD/cc-pVDZ	3484.8	−70.7	1395.1	−23.6	1002.6	−18.2	0.06	/[b]
CCSD(T)_ae/cc-pwCVTZ	3558.77		1424.67		1023.82			
CCSD(T)_ae/cc-pwCVQZ, X_e^BO [c]	3570.61		1428.09		1026.56			
Experimental (X_o)	3555.44		1418.76		1020.77			

[a] Non-planar structure.

[b] No frequency calculations.

[c] Rotational constants of the r_e^BO structure, i.e. of CCSD(T)_ae/cc-pwCVQZ quality.

Table S-4a: Coefficients of the one-dimensional Fourier expansion for the potential energy curves of *syn*-2AT given in Figure 3 calculated at the MP2 and B3LYP-D3BJ/6-311++G(d,p) levels of theory. The potential is expanded as $V(\varphi) = \sum_{i=0}^{2} a_i f_i$.

		MP2		**B3LYP-D3BJ**	
i	**f$_i$**	**a$_i$ / Hartree**	**a$_i$ / cm^{-1}**	**a$_i$ / Hartree**	**a$_i$ / cm^{-1}**
0	1	–704.3341292		–705.7929932	
1	cos 3α	0.0007304	160.3	0.0004994	109.6
2	cos 6α	0.0000291	6.4	0.0000117	2.6

Table S-4b: Coefficients of the one-dimensional Fourier expansion for the potential energy curves of *anti*-2AT given in Figure 3 calculated at the MP2 and B3LYP-D3BJ/6-311++G(d,p) levels of theory. The potential is expanded as $V(\varphi) = \sum_{i=0}^{i} a_i f_i$.

		MP2		**B3LYP-D3BJ**	
i	**f$_i$**	**a$_i$ / Hartree**	**a$_i$ / cm^{-1}**	**a$_i$ / Hartree**	**a$_i$ / cm^{-1}**
0	1	–704.3324313		–705.7919055	
1	cos 3α	0.0006596	144.8	0.0004413	96.9
2	cos 6α	0.0000929	20.4	0.0000353	7.7
3	cos 9α	–0.0000267	–5.9		
4	cos 12α	0.0000202	4.4		
5	cos 15α	–0.0000137	–3.0		

Table S-5: Observed frequencies ν_{obs} of 312 rotational transitions of *syn*-2AT with $\nu_{obs}-\nu_{calc}$ values obtained from a fit with the program *XIAM*.

No.	*J*	K_a	K_c	*J*	K_a	K_c	Species	ν_{obs}	$\nu_{obs}-\nu_{calc}$
	upper level			lower level				MHz	kHz
1	1	0	1	0	0	0	E	2437.9540	0.3
2	2	0	2	1	0	1	A	4827.2215	–1.0
3	2	0	2	1	0	1	E	4827.0671	–0.3
4	3	0	3	2	0	2	A	7123.4746	–2.5
5	3	0	3	2	0	2	E	7123.2863	1.1
6	4	0	4	3	0	3	A	9302.9890	–3.9
7	4	0	4	3	0	3	E	9302.7953	3.0
8	5	0	5	4	0	4	A	11380.1607	–4.1
9	5	0	5	4	0	4	E	11379.9751	4.1
10	6	0	6	5	0	5	A	13399.7133	–13.6
11	6	0	6	5	0	5	E	13399.5483	5.4
12	7	0	7	6	0	6	A	15404.1691	–7.0
13	7	0	7	6	0	6	E	15404.0070	7.3
14	8	0	8	7	0	7	A	17414.7711	–7.3
15	8	0	8	7	0	7	E	17414.6140	7.4
16	9	0	9	8	0	8	A	19436.1880	–9.3
17	9	0	9	8	0	8	E	19436.0369	9.1
18	10	0	10	9	0	9	A	21466.4740	–9.8
19	10	0	10	9	0	9	E	21466.3247	9.3
20	11	0	11	10	0	10	A	23502.6037	–10.1
21	11	0	11	10	0	10	E	23502.4568	10.7
22	3	0	3	2	1	2	A	5296.1503	–3.8
23	3	0	3	2	1	2	E	5296.3490	–0.7
24	4	0	4	3	1	3	A	7904.6992	–2.7
25	4	0	4	3	1	3	E	7904.7240	–0.6
26	5	0	5	4	1	4	A	10407.7568	–3.5
27	5	0	5	4	1	4	E	10407.6918	2.2
28	6	0	6	5	1	5	A	12779.7295	–4.7
29	6	0	6	5	1	5	E	12779.6164	3.5
30	7	0	7	6	1	6	A	15035.6542	–5.9
31	7	0	7	6	1	6	E	15035.5186	5.7
32	8	0	8	7	1	7	A	17206.9112	–6.5
33	8	0	8	7	1	7	E	17206.7643	6.2
34	9	0	9	8	1	8	A	19323.3404	–8.5
35	9	0	9	8	1	8	E	19323.1915	7.6
36	10	0	10	9	1	9	A	21406.9184	–9.4
37	10	0	10	9	1	9	E	21406.7700	9.2
38	11	0	11	10	1	10	A	23471.8440	–11.9
39	11	0	11	10	1	10	E	23471.6982	9.9
40	1	1	0	0	0	0	E	5004.3114	0.9
41	1	1	1	0	0	0	E	4609.5096	0.4
42	2	1	2	1	0	1	E	6654.0054	2.5

43	3	1	3	2	0	2	A	8521.7650	–3.1
44	3	1	3	2	0	2	E	8521.3570	4.0
45	4	1	4	3	0	3	A	10275.3962	–1.3
46	4	1	4	3	0	3	E	10275.0790	5.3
47	5	1	5	4	0	4	A	12000.1534	–4.1
48	5	1	5	4	0	4	E	11999.9072	6.2
49	6	1	6	5	0	5	A	13768.2355	–7.4
50	6	1	6	5	0	5	E	13768.0371	7.3
51	7	1	7	6	0	6	A	15612.0298	–7.1
52	7	1	7	6	0	6	E	15611.8559	7.7
53	8	1	8	7	0	7	A	17527.6193	–7.6
54	8	1	8	7	0	7	E	17527.4585	8.1
55	9	1	9	8	0	8	A	19495.7441	–9.1
56	9	1	9	8	0	8	E	19495.5914	9.0
57	10	1	10	9	0	9	A	21497.2314	–10.3
58	10	1	10	9	0	9	E	21497.0822	9.0
59	11	1	11	10	0	10	A	23518.2188	–11.2
60	11	1	11	10	0	10	E	23518.0728	10.3
61	1	1	0	1	0	1	E	2566.3579	1.1
62	3	1	2	3	0	3	A	3757.7619	5.4
63	3	1	2	3	0	3	E	3757.2974	2.9
64	5	1	4	5	0	5	E	6422.8475	–5.2
65	6	1	5	6	0	6	A	8336.8132	1.1
66	7	1	6	7	0	7	A	10516.5378	2.3
67	7	1	6	7	0	7	E	10514.6282	–10.2
68	8	1	7	8	0	8	A	12827.2192	6.7
69	8	1	7	8	0	8	E	12824.8940	–12.4
70	9	1	8	9	0	9	A	15152.1496	11.2
71	9	1	8	9	0	9	E	15149.4339	–12.3
72	4	1	3	3	1	2	A	10429.9204	–1.7
73	4	1	3	3	1	2	E	10429.4559	0.4
74	5	1	4	4	1	3	A	12919.4037	–2.3
75	5	1	4	4	1	3	E	12918.8666	0.6
76	6	1	5	5	1	4	A	15312.6086	–3.4
77	6	1	5	5	1	4	E	15312.0272	1.5
78	7	1	6	6	1	5	A	17583.8957	–3.8
79	7	1	6	6	1	5	E	17583.3068	4.1
80	8	1	7	7	1	6	A	19725.4501	–5.4
81	8	1	7	7	1	6	E	19724.8811	6.5
82	10	1	9	9	1	8	A	23738.9975	–8.5
83	10	1	9	9	1	8	E	23738.4825	10.2
84	2	1	2	1	1	1	A	4482.1968	–2.5
85	2	1	2	1	1	1	E	4482.4490	1.5
86	3	1	3	2	1	2	A	6694.4419	–3.2
87	3	1	3	2	1	2	E	6694.4195	2.1
88	4	1	4	3	1	3	A	8877.1025	–4.0
89	4	1	4	3	1	3	E	8877.0099	4.0

90	5	1	5	4	1	4	A	11027.7511	–1.8
91	5	1	5	4	1	4	E	11027.6239	4.3
92	6	1	6	5	1	5	A	13148.2441	–6.1
93	6	1	6	5	1	5	E	13148.1048	5.0
94	7	1	7	6	1	6	A	15243.5140	–6.9
95	7	1	7	6	1	6	E	15243.3677	6.4
96	8	1	8	7	1	7	A	17319.7588	–7.3
97	8	1	8	7	1	7	E	17319.6090	7.0
98	9	1	9	8	1	8	A	19382.8962	–8.6
99	9	1	9	8	1	8	E	19382.7469	8.4
100	10	1	10	9	1	9	A	21437.6760	–9.8
101	10	1	10	9	1	9	E	21437.5281	9.5
102	11	1	11	10	1	10	A	23487.4617	–10.4
103	11	1	11	10	1	10	E	23487.3157	11.0
104	5	1	4	4	2	3	A	7676.4351	–2.2
105	5	1	4	4	2	3	E	7677.7043	–1.4
106	6	1	5	5	2	4	A	10907.2980	–1.8
107	6	1	5	5	2	4	E	10907.7288	–2.2
108	7	1	6	6	2	5	A	14080.5150	–1.9
109	7	1	6	6	2	5	E	14080.5225	–0.9
110	8	1	7	7	2	6	A	17110.0454	–1.5
111	8	1	7	7	2	6	E	17109.8106	0.8
112	9	1	8	8	2	7	A	19935.9232	–2.3
113	9	1	8	8	2	7	E	19935.5532	3.3
114	3	2	1	2	0	2	A	17079.6166	–2.8
115	3	2	1	2	0	2	E	17081.0777	3.4
116	4	2	2	3	0	3	A	20119.0534	–4.0
117	4	2	2	3	0	3	E	20118.2935	5.2
118	2	2	1	2	0	2	A	9525.9979	–4.4
119	2	2	1	2	0	2	E	9512.1209	–3.4
120	3	2	2	3	0	3	A	9716.6417	–0.9
121	3	2	2	3	0	3	E	9712.1397	2.5
122	4	2	3	4	0	4	A	10127.6535	–1.0
123	4	2	3	4	0	4	E	10125.1195	1.5
124	5	2	4	5	0	5	A	10829.2383	–0.8
125	5	2	4	5	0	5	E	10827.1467	–0.7
126	2	2	1	2	1	2	A	7698.6793	0.0
127	2	2	1	2	1	2	E	7685.1898	1.0
128	3	2	2	3	1	3	A	8318.3561	4.6
129	3	2	2	3	1	3	E	8314.0688	–0.7
130	4	2	3	4	1	4	A	9155.2571	7.2
131	4	2	3	4	1	4	E	9152.8351	–1.5
132	5	2	4	5	1	5	A	10209.2552	8.7
133	5	2	4	5	1	5	E	10207.2155	–1.9
134	6	2	5	6	1	6	A	11471.6896	10.9
135	6	2	5	6	1	6	E	11469.6234	–4.5
136	7	2	6	7	1	7	A	12924.0871	3.8

137	7	2	6	7	1	7	E	12921.8492	–5.5
138	8	2	7	8	1	8	A	14539.5758	14.0
139	8	2	7	8	1	8	E	14537.0733	–6.9
140	2	2	0	1	1	0	E	11846.6738	–2.6
141	2	2	0	1	1	1	A	12229.7378	0.6
142	2	2	0	1	1	1	E	12241.4792	1.5
143	3	2	1	2	1	2	A	15252.2990	2.6
144	3	2	1	2	1	2	E	15254.1404	1.7
145	4	2	2	3	1	3	E	18720.2219	1.4
146	5	2	3	4	1	4	E	22731.9240	1.8
147	2	2	1	2	1	1	E	6503.4017	–3.8
148	2	2	0	2	1	1	A	6565.8886	–3.7
149	2	2	0	2	1	1	E	6577.2440	–3.0
150	3	2	1	3	1	2	A	6198.3856	–0.2
151	3	2	1	3	1	2	E	6200.4947	0.2
152	4	2	2	4	1	3	A	5931.3798	1.1
153	4	2	2	4	1	3	E	5931.5397	1.4
154	5	2	3	5	1	4	A	5901.7658	–0.3
155	5	2	3	5	1	4	E	5901.3856	5.7
156	6	2	4	6	1	5	A	6219.5530	2.1
157	6	2	4	6	1	5	E	6218.9050	5.1
158	2	2	0	2	1	2	E	7759.0332	3.0
159	4	2	2	4	1	4	E	9843.2133	–1.3
160	2	2	1	1	1	0	A	11786.9922	–4.2
161	2	2	1	1	1	0	E	11772.8346	–0.3
162	3	2	2	2	1	1	A	13831.1485	–2.6
163	3	2	2	2	1	1	E	13826.7036	0.0
164	4	2	3	3	1	2	A	15672.8880	–2.9
165	4	2	3	3	1	2	E	15670.6177	2.0
166	5	2	4	4	1	3	A	17324.7149	–3.3
167	5	2	4	4	1	3	E	17323.1648	4.1
168	6	2	5	5	1	4	A	18815.9889	–5.7
169	6	2	5	5	1	4	E	18814.8122	7.2
170	7	2	6	6	1	5	A	20199.3007	–7.4
171	7	2	6	6	1	5	E	20198.3777	10.2
172	8	2	7	7	1	6	A	21550.6421	–11.1
173	8	2	7	7	1	6	E	21549.9045	12.2
174	9	2	8	8	1	7	A	22954.8177	–9.8
175	9	2	8	8	1	7	E	22954.2012	13.6
176	3	2	2	2	1	2	E	15008.4882	1.3
177	4	2	3	3	1	3	E	18029.8435	1.0
178	2	2	1	1	1	1	E	12167.6338	–2.5
179	3	2	1	2	1	1	E	14072.3570	1.5
180	4	2	2	3	1	2	E	16360.9950	1.3
181	3	2	1	3	1	3	E	8559.7185	–2.8
182	4	2	3	3	2	2	A	9714.0026	–2.2
183	4	2	3	3	2	2	E	9715.7755	2.4

184	5	2	4	4	2	3	A	12081.7459	–3.5
185	5	2	4	4	2	3	E	12082.0039	3.5
186	6	2	5	5	2	4	A	14410.6809	–1.6
187	6	2	5	5	2	4	E	14410.5136	3.3
188	7	2	6	6	2	5	A	16695.9207	–4.8
189	7	2	6	6	2	5	E	16695.5927	4.5
190	8	2	7	7	2	6	A	18935.2393	–5.3
191	8	2	7	7	2	6	E	18934.8334	5.9
192	9	2	8	8	2	7	A	21129.6238	–6.0
193	9	2	8	8	2	7	E	21129.1760	6.1
194	3	2	1	2	2	0	A	7504.7592	0.7
195	3	2	1	2	2	0	E	7495.1102	1.7
196	4	2	2	3	2	1	A	10162.9130	–2.0
197	4	2	2	3	2	1	E	10160.5030	3.8
198	5	2	3	4	2	2	A	12889.7915	–1.9
199	5	2	3	4	2	2	E	12888.7107	3.1
200	6	2	4	5	2	3	A	15630.3943	–2.5
201	6	2	4	5	2	3	E	15629.5487	3.0
202	7	2	5	6	2	4	A	18329.3408	–1.7
203	7	2	5	6	2	4	E	18328.4813	2.8
204	8	2	6	7	2	5	A	20948.4078	–2.1
205	8	2	6	7	2	5	E	20947.4784	2.1
206	9	2	7	8	2	6	A	23461.1517	–4.1
207	9	2	7	8	2	6	E	23460.1649	2.3
208	3	2	2	2	2	0	E	7249.4583	1.7
209	4	2	3	3	2	1	E	9470.1223	1.1
210	3	2	1	2	2	1	E	7568.9561	6.1
211	4	2	2	3	2	2	E	10406.1548	3.7
212	8	2	6	7	3	5	A	12086.5886	2.1
213	8	2	6	7	3	5	E	12089.1567	2.6
214	5	3	2	5	0	5	E	23184.9532	–1.9
215	3	3	0	3	2	1	A	11639.5842	–0.8
216	3	3	0	3	2	1	E	11674.4427	–2.4
217	4	3	1	4	2	2	A	11338.8077	0.4
218	4	3	1	4	2	2	E	11366.2811	–3.3
219	5	3	2	5	2	3	A	10848.5264	–1.1
220	5	3	2	5	2	3	E	10860.7213	–1.2
221	6	3	3	6	2	4	A	10220.4406	0.8
222	6	3	3	6	2	4	E	10224.0592	–0.3
223	7	3	4	7	2	5	A	9580.7974	0.7
224	8	3	5	8	2	6	E	9094.5739	1.2
225	3	3	1	2	2	0	A	19140.5194	–0.9
226	4	3	2	3	2	1	A	21475.1931	–1.5
227	4	3	2	3	2	1	E	21439.8647	1.2
228	5	3	3	4	2	2	A	23634.0644	–2.5
229	5	3	3	4	2	2	E	23616.7249	1.2
230	3	3	0	2	2	0	E	19169.5546	1.0

231	4	3	1	3	2	1	E	21526.7890	5.4
232	5	3	2	4	2	2	E	23749.4308	0.7
233	3	3	1	3	2	1	E	11591.2548	1.8
234	4	3	2	4	2	2	E	11279.3625	–1.8
235	5	3	3	5	2	3	E	10728.0132	–2.9
236	4	3	1	4	2	3	E	12056.6612	–1.2
237	5	3	2	5	2	4	E	12357.8067	–0.9
238	3	3	0	2	2	1	A	19193.2021	–0.1
239	3	3	0	2	2	1	E	19243.3861	–9.0
240	4	3	1	3	2	2	A	21741.2212	–0.9
241	4	3	1	3	2	2	E	21772.4369	1.4
242	5	3	2	4	2	3	A	24426.7294	–1.5
243	5	3	2	4	2	3	E	24439.8108	2.7
244	3	3	0	3	2	2	E	11920.0952	–1.8
245	3	3	1	2	2	1	E	19160.2051	2.1
246	4	3	2	3	2	2	E	21685.5170	1.7
247	5	3	3	4	2	3	E	24307.1022	0.5
248	3	3	1	3	2	2	A	11875.2603	–1.3
249	3	3	1	3	2	2	E	11836.9052	0.3
250	4	3	2	4	2	3	A	12000.6911	1.6
251	4	3	2	4	2	3	E	11969.7403	–2.0
252	5	3	3	5	2	4	A	12240.7305	3.1
253	5	3	3	5	2	4	E	12225.0992	–2.1
254	6	3	4	6	2	5	A	12633.5980	1.4
255	6	3	4	6	2	5	E	12626.5831	–2.5
256	4	3	1	3	3	0	A	9862.1350	–2.3
257	4	3	1	3	3	0	E	9852.3415	3.0
258	5	3	2	4	3	1	A	12399.5108	–2.8
259	5	3	2	4	3	1	E	12383.1479	2.2
260	6	3	3	5	3	2	A	15002.3053	–3.8
261	6	3	3	5	3	2	E	14992.8863	3.6
262	8	3	5	7	3	4	A	20462.4957	–2.1
263	8	3	5	7	3	4	E	20460.5553	4.3
264	9	3	6	8	3	5	A	23288.7693	–1.3
265	9	3	6	8	3	5	E	23287.3590	5.3
266	4	3	2	3	3	1	A	9839.4319	–0.9
267	4	3	2	3	3	1	E	9848.6122	1.7
268	5	3	3	4	3	2	A	12321.7829	–4.5
269	5	3	3	4	3	2	E	12337.3628	3.4
270	6	3	4	5	3	3	A	14803.5470	–4.6
271	6	3	4	5	3	3	E	14811.9973	2.7
272	7	3	5	6	3	4	A	17273.7335	–4.0
273	8	3	6	7	3	5	A	19720.3064	–4.5
274	8	3	6	7	3	5	E	19720.8662	4.7
275	9	3	7	8	3	6	A	22132.0674	–5.2
276	9	3	7	8	3	6	E	22131.8834	5.8
277	5	3	2	4	3	2	E	12470.0674	1.6

278	5	3	3	4	3	1	E	12250.4415	2.2
279	4	4	1	4	3	2	A	16506.9480	–0.2
280	4	4	1	4	3	2	E	16479.4681	0.2
281	5	4	2	5	3	3	A	16483.7622	1.0
282	5	4	2	5	3	3	E	16441.4346	0.9
283	6	4	3	6	3	4	A	16471.8023	0.9
284	6	4	3	6	3	4	E	16424.8979	–2.2
285	7	4	4	7	3	5	A	16496.7850	0.1
286	7	4	4	7	3	5	E	16458.1726	–4.7
287	4	4	0	4	3	1	A	16480.6679	–0.3
288	4	4	0	4	3	1	E	16503.2533	–2.2
289	5	4	1	5	3	3	E	16551.8925	2.2
290	5	4	1	5	3	2	A	16381.7247	0.6
291	5	4	1	5	3	2	E	16419.1814	–2.5
292	6	4	2	6	3	3	A	16179.7629	–0.1
293	6	4	2	6	3	3	E	16221.8377	–1.9
294	7	4	3	7	3	4	A	15817.3904	–1.1
295	7	4	3	7	3	4	E	15851.2393	–0.2
296	5	4	2	5	3	2	E	16308.7244	–2.9
297	5	4	1	4	4	0	A	12300.5652	–4.3
298	5	4	1	4	4	0	E	12299.0768	2.8
299	6	4	2	5	4	1	A	14800.3429	–5.1
300	6	4	2	5	4	1	E	14795.5410	2.5
301	8	4	4	7	4	3	A	19893.4549	–5.5
302	8	4	4	7	4	3	E	19875.8324	3.8
303	5	4	2	4	4	1	A	12298.5969	–3.4
304	5	4	2	4	4	1	E	12299.3260	0.8
305	6	4	3	5	4	2	A	14791.5874	–4.5
306	6	4	3	5	4	2	E	14795.4621	1.1
307	8	4	5	7	4	4	A	19817.2491	–5.4
308	8	4	5	7	4	4	E	19833.5806	2.9
309	5	5	0	5	4	1	A	21220.7752	3.5
310	5	5	0	5	4	1	E	21232.5895	–2.5
311	5	5	1	5	4	2	A	21222.9759	1.7
312	5	5	1	5	4	2	E	21204.8729	5.0

Table S6: Observed frequencies ν_{obs} of 245 rotational transitions of *anti*-2AT with $\nu_{obs}-\nu_{calc}$ values obtained from a fit with the program *XIAM*.

No.	***J***	**K_a**	**K_c**	***J***	**K_a**	**K_c**	**Species**	**ν_{obs}**	**$\nu_{obs}-\nu_{calc}$**
	upper level			**lower level**				**MHz**	**kHz**
1	2	0	2	1	0	1	A	4830.2630	0.0
2	2	0	2	1	0	1	E	4829.9144	–2.1
3	3	0	3	2	0	2	A	7124.0106	–0.4
4	3	0	3	2	0	2	E	7123.6305	–1.6
5	4	0	4	3	0	3	A	9298.1055	0.5
6	4	0	4	3	0	3	E	9297.7760	–0.7
7	5	0	5	4	0	4	A	11369.2812	–0.5
8	5	0	5	4	0	4	E	11369.0267	0.5
9	6	0	6	5	0	5	A	13384.6171	0.1
10	6	0	6	5	0	5	E	13384.4106	0.3
11	7	0	7	6	0	6	A	15386.8784	0.3
12	7	0	7	6	0	6	E	15386.6903	–0.1
13	9	0	9	8	0	8	A	19416.8373	–0.9
14	9	0	9	8	0	8	E	19416.6521	0.0
15	10	0	10	9	0	9	A	21446.0507	–1.6
16	10	0	10	9	0	9	E	21445.8649	–0.5
17	2	1	2	1	1	1	A	4482.8079	–0.1
18	2	1	2	1	1	1	E	4483.0426	1.9
19	3	1	3	2	1	2	A	6694.3484	0.9
20	3	1	3	2	1	2	E	6694.2221	0.0
21	4	1	4	3	1	3	A	8875.3980	0.1
22	4	1	4	3	1	3	E	8875.1785	–0.2
23	5	1	5	4	1	4	A	11023.6480	0.0
24	5	1	5	4	1	4	E	11023.3967	–0.1
25	6	1	6	5	1	5	A	13141.2561	–0.3
26	6	1	6	5	1	5	E	13141.0005	0.3
27	7	1	7	6	1	6	A	15233.4817	0.1
28	7	1	7	6	1	6	E	15233.2327	–0.5
29	8	1	8	7	1	7	A	17306.7845	–0.6
30	8	1	8	7	1	7	E	17306.5497	0.1
31	9	1	9	8	1	8	A	19367.2215	2.2
32	9	1	9	8	1	8	E	19366.9922	–4.8
33	10	1	10	9	1	9	A	21419.5552	–1.4
34	10	1	10	9	1	9	E	21419.3452	–1.1
35	3	0	3	2	1	2	A	5335.9211	1.9
36	3	0	3	2	1	2	E	5335.6510	–3.6
37	4	0	4	3	1	3	A	7939.6766	–0.1
38	4	0	4	3	1	3	E	7939.2060	–3.1
39	5	0	5	4	1	4	A	10433.5601	–0.4
40	5	0	5	4	1	4	E	10433.0542	–2.4
41	6	0	6	5	1	5	A	12794.5289	–0.7
42	6	0	6	5	1	5	E	12794.0684	–1.8

43	7	0	7	6	1	6	A	15040.1516	0.2
44	7	0	7	6	1	6	E	15039.7597	–0.7
45	8	0	8	7	1	7	A	17203.0132	–0.5
46	8	0	8	7	1	7	E	17202.6861	–0.3
47	9	0	9	8	1	8	A	19313.0659	–0.9
48	9	0	9	8	1	8	E	19312.7888	0.0
49	10	0	10	9	1	9	A	21391.8988	–1.1
50	10	0	10	9	1	9	E	21391.6563	–0.9
51	1	1	1	0	0	0	E	4575.0944	–0.8
52	2	1	2	1	0	1	A	6618.3507	–4.1
53	2	1	2	1	0	1	E	6617.8939	–0.1
54	3	1	3	2	0	2	A	8482.4445	5.2
55	3	1	3	2	0	2	E	8482.2014	1.8
56	4	1	4	3	0	3	A	10233.8307	4.5
57	4	1	4	3	0	3	E	10233.7492	2.9
58	5	1	5	4	0	4	A	11959.3689	–0.3
59	6	1	6	5	0	5	A	13731.3431	–0.7
60	7	1	7	6	0	6	A	15580.2075	–0.8
61	7	1	7	6	0	6	E	15580.1649	1.6
62	8	1	8	7	0	7	A	17500.1145	–0.8
63	8	1	8	7	0	7	E	17500.0232	0.8
64	9	1	9	8	0	8	A	19470.9895	–1.2
65	9	1	9	8	0	8	E	19470.8606	0.4
66	10	1	10	9	0	9	A	21473.7071	–1.9
67	10	1	10	9	0	9	E	21473.5538	–0.7
68	2	1	1	1	1	0	A	5278.9916	0.4
69	3	1	2	2	1	1	A	7884.5543	–0.7
70	3	1	2	2	1	1	E	7883.7584	–0.1
71	4	1	3	3	1	2	A	10443.6288	–0.8
72	4	1	3	3	1	2	E	10442.6438	–2.0
73	5	1	4	4	1	3	A	12931.5750	–0.6
74	5	1	4	4	1	3	E	12930.4432	–3.3
75	6	1	5	5	1	4	A	15319.1476	0.2
76	6	1	5	5	1	4	E	15317.9923	–2.7
77	7	1	6	6	1	5	A	17580.4946	0.4
78	7	1	6	6	1	5	E	17579.4454	–0.6
79	8	1	7	7	1	6	A	19709.8626	1.3
80	8	1	7	7	1	6	E	19708.9856	1.7
81	9	1	8	8	1	7	A	21735.0646	2.0
82	10	1	9	9	1	8	A	23707.0041	3.3
83	10	1	9	9	1	8	E	23706.3611	3.9
84	2	2	1	2	1	2	A	7600.9096	–0.8
85	2	2	1	2	1	2	E	7585.6292	4.0
86	3	2	2	3	1	3	A	8227.9095	1.7
87	3	2	2	3	1	3	E	8223.1713	–1.4
88	4	2	3	4	1	4	A	9074.7495	–5.8
89	4	2	3	4	1	4	E	9072.0881	–0.6

90	5	2	4	5	1	5	A	10140.9574	–6.8
91	5	2	4	5	1	5	E	10138.5439	–1.2
92	6	2	5	6	1	6	A	11417.0445	–7.3
93	6	2	5	6	1	6	E	11414.3544	–1.0
94	7	2	6	7	1	7	A	12883.3730	–5.4
95	7	2	6	7	1	7	E	12880.1965	–0.5
96	8	2	7	8	1	8	A	14511.7789	–3.2
97	8	2	7	8	1	8	E	14508.0242	0.2
98	9	2	8	9	1	9	A	16269.3996	0.1
99	9	2	8	9	1	9	E	16265.0335	3.1
100	3	3	1	3	2	2	A	11702.8016	1.6
101	3	3	1	3	2	2	E	11661.0107	–2.2
102	4	3	2	4	2	3	A	11832.5516	2.4
103	4	3	2	4	2	3	E	11798.4272	0.4
104	5	3	3	5	2	4	A	12080.4586	2.0
105	5	3	3	5	2	4	E	12063.1522	1.7
106	6	3	4	6	2	5	A	12485.4247	2.7
107	6	3	4	6	2	5	E	12477.8655	–1.1
108	7	3	5	7	2	6	A	13079.7061	0.0
109	7	3	5	7	2	6	E	13075.3548	–0.4
110	8	3	6	8	2	7	A	13885.1520	–0.9
111	8	3	6	8	2	7	E	13881.6506	–0.7
112	3	2	2	2	2	1	A	7321.3452	0.3
113	3	2	2	2	2	1	E	7331.7730	3.4
114	4	2	3	3	2	2	A	9722.2452	–0.2
115	4	2	3	3	2	2	E	9724.0955	0.8
116	5	2	4	4	2	3	A	12089.8546	–2.3
117	6	2	5	5	2	4	A	14417.3434	–0.5
118	6	2	5	5	2	4	E	14416.8106	0.1
119	7	2	6	6	2	5	A	16699.8087	0.5
120	7	2	6	6	2	5	E	16699.0752	0.4
121	8	2	7	7	2	6	A	18935.1902	1.3
122	8	2	7	7	2	6	E	18934.3782	1.6
123	9	2	8	8	2	7	A	21124.8382	1.6
124	9	2	8	8	2	7	E	21124.0051	1.7
125	4	3	2	3	3	1	A	9851.9928	–1.9
126	4	3	2	3	3	1	E	9861.5092	0.6
127	5	3	3	4	3	2	A	12337.7636	–0.7
128	5	3	3	4	3	2	E	12354.5779	1.0
129	6	3	4	5	3	3	A	14822.3089	–0.3
130	6	3	4	5	3	3	E	14831.5264	–0.2
131	7	3	5	6	3	4	A	17294.0915	–0.7
132	7	3	5	6	3	4	E	17296.5640	0.6
133	8	3	6	7	3	5	A	19740.6365	0.8
134	8	3	6	7	3	5	E	19740.6735	0.8
135	9	3	7	8	3	6	A	22150.4908	0.8
136	9	3	7	8	3	6	E	22149.6328	2.7

137	2	2	1	2	0	2	A	9389.0045	2.3
138	2	2	1	2	0	2	E	9373.6019	–0.8
139	3	2	2	3	0	3	A	9586.3357	–0.4
140	3	2	2	3	0	3	E	9581.7410	0.8
141	4	2	3	4	0	4	A	10010.4761	–0.4
142	4	2	3	4	0	4	E	10008.0610	2.7
143	5	2	4	5	0	5	A	10731.0493	–2.4
144	5	2	4	5	0	5	E	10728.8862	1.0
145	6	2	5	6	0	6	A	11763.7734	–5.2
146	6	2	5	6	0	6	E	11761.2862	0.8
147	7	2	6	7	0	7	A	13076.7083	–0.3
148	7	2	6	7	0	7	E	13073.6700	0.1
149	3	2	1	2	2	0	A	7518.6799	–0.2
150	3	2	1	2	2	0	E	7507.2125	0.9
151	4	2	2	3	2	1	A	10185.6577	–1.0
152	4	2	2	3	2	1	E	10182.3581	2.1
153	5	2	3	4	2	2	A	12920.6521	–1.2
154	5	2	3	4	2	2	E	12918.7918	2.3
155	6	2	4	5	2	3	A	15665.8383	–1.4
156	6	2	4	5	2	3	E	15664.1181	1.2
157	7	2	5	6	2	4	A	18364.8570	–0.4
158	7	2	5	6	2	4	E	18363.0027	–0.7
159	8	2	6	7	2	5	A	20979.4631	0.6
160	8	2	6	7	2	5	E	20977.4620	–2.6
161	9	2	7	8	2	6	A	23482.8412	1.9
162	3	3	0	3	2	1	A	11458.8953	2.4
163	3	3	0	3	2	1	E	11498.5059	0.1
164	4	3	1	4	2	2	A	11149.3572	0.6
165	4	3	1	4	2	2	E	11181.3690	–6.6
166	5	3	2	5	2	3	A	10648.9668	0.1
167	5	3	2	5	2	3	E	10664.2365	–5.4
168	6	3	3	6	2	4	A	10015.9054	–0.4
169	6	3	3	6	2	4	E	10021.4307	–6.5
170	2	2	1	1	1	0	A	11685.6228	–3.7
171	2	2	1	1	1	0	E	11669.4869	2.4
172	3	2	2	2	1	1	A	13727.9771	–3.1
173	3	2	2	2	1	1	E	13723.0930	–4.6
174	4	2	3	3	1	2	A	15565.6670	–3.6
175	4	2	3	3	1	2	E	15563.4302	–3.7
176	5	2	4	4	1	3	A	17211.8939	–4.0
177	5	2	4	4	1	3	E	17210.6398	–1.4
178	6	2	5	5	1	4	A	18697.6624	–3.9
179	6	2	5	5	1	4	E	18697.0075	2.3
180	8	2	7	7	1	6	A	21433.0215	–0.1
181	2	2	0	1	1	1	A	12134.3571	1.7
182	2	2	0	1	1	1	E	12148.4728	5.4
183	3	2	1	2	1	2	A	15170.2303	2.9

184	3	2	1	2	1	2	E	15172.6379	–0.4
185	4	2	2	3	1	3	A	18661.5429	4.2
186	4	2	2	3	1	3	E	18660.7733	1.1
187	5	2	3	4	1	4	A	22706.8006	6.5
188	5	2	3	4	1	4	E	22704.3858	2.9
189	4	3	1	3	3	0	A	9876.1213	–1.2
190	4	3	1	3	3	0	E	9865.2238	–2.0
191	5	3	2	4	3	1	A	12420.2622	–1.2
192	5	3	2	4	3	1	E	12401.6576	1.8
193	6	3	3	5	3	2	A	15032.7775	–1.3
194	6	3	3	5	3	2	E	15021.3132	1.1
195	7	3	4	6	3	3	A	17732.7939	–1.3
196	7	3	4	6	3	3	E	17727.5857	2.6
197	8	3	5	7	3	4	A	20518.7472	–1.2
198	8	3	5	7	3	4	E	20515.4742	3.3
199	4	1	3	3	2	2	E	4603.3084	1.7
200	5	1	4	4	2	3	E	7809.6565	–2.0
201	6	1	5	5	2	4	A	11038.8234	–1.6
202	6	1	5	5	2	4	E	11037.7961	–4.2
203	7	1	6	6	2	5	A	14201.9737	–1.7
204	7	1	6	6	2	5	E	14200.4305	–5.2
205	9	1	8	8	2	7	A	20011.9038	1.6
206	9	1	8	8	2	7	E	20010.3028	–2.0
207	2	2	0	2	1	1	A	6457.2687	–3.5
208	2	2	0	2	1	1	E	6471.1314	1.9
209	3	2	1	3	1	2	A	6091.3941	–3.3
210	3	2	1	3	1	2	E	6094.5796	–3.0
211	4	2	2	4	1	3	A	5833.4261	–0.5
212	4	2	2	4	1	3	E	5834.2930	0.2
213	7	2	5	7	1	6	A	6953.5611	1.4
214	7	2	5	7	1	6	E	6952.3249	9.8
215	8	2	6	8	1	7	E	8220.8010	5.2
216	9	2	7	9	1	8	E	9967.2635	–1.3
217	10	2	8	10	1	9	E	12110.9938	–4.4
218	3	2	1	2	0	2	A	16958.3182	–1.1
219	3	2	1	2	0	2	E	16960.6174	1.6
220	4	2	2	3	0	3	A	20019.9689	1.9
221	4	2	2	3	0	3	E	20019.3440	4.3
222	3	3	0	2	2	1	A	19028.2122	2.3
223	4	3	1	3	2	2	A	21582.9893	1.8
224	4	3	1	3	2	2	E	21618.9801	5.0
225	5	3	2	4	2	3	A	24281.0066	1.1
226	5	3	2	4	2	3	E	24296.5345	–1.6
227	3	3	1	2	2	0	A	18973.5105	2.6
228	4	3	2	3	2	1	A	21306.8246	2.1
229	4	3	2	3	2	1	E	21267.2806	2.5
230	5	3	3	4	2	2	A	23458.9305	2.5

231	5	3	3	4	2	2	E	23439.4953	–3.7
232	2	2	0	2	1	2	E	7665.4300	3.3
233	3	2	1	3	1	3	E	8478.4169	0.7
234	2	2	1	2	1	1	E	6391.3275	–0.5
235	2	2	1	1	1	1	E	12068.6685	2.6
236	2	2	0	1	1	0	E	11749.2887	2.7
237	3	2	1	2	2	1	E	7587.0125	–0.6
238	3	2	2	2	1	2	E	14917.3920	–2.9
239	3	2	1	2	1	1	E	13978.3384	–2.7
240	3	3	1	2	2	1	E	18992.7838	1.2
241	3	3	0	2	2	0	E	19005.7156	–1.8
242	3	3	0	3	2	2	E	11753.7491	–0.2
243	4	3	1	3	2	1	E	21363.7337	2.1
244	4	3	1	4	2	3	E	11894.8786	–1.7
245	4	3	2	4	2	2	E	11084.9184	–3.7

Table S7a: Observed frequencies ν_{obs} of 101 rotational transitions of the ^{34}S(1) isotopologue (for atom numbering see Figure 1) of *syn*-2AT with $\nu_{obs}-\nu_{calc}$ values obtained from a fit with the program *XIAM*.

No.	***J***	K_a	K_c	***J***	K_a	K_c	**Species**	ν_{obs}	$\nu_{obs}-\nu_{calc}$
	upper level			**lower level**				**MHz**	**kHz**
1	4	0	4	3	0	3	E	9228.8710	1.3
2	4	0	4	3	0	3	A	9229.0614	–3.9
3	5	0	5	4	0	4	E	11284.2547	4.2
4	5	0	5	4	0	4	A	11284.4362	–3.8
5	6	0	6	5	0	5	E	13284.3109	4.1
6	6	0	6	5	0	5	A	13284.4834	–3.7
7	7	0	7	6	0	6	A	15271.6819	–5.4
8	7	0	7	6	0	6	E	15271.5219	7.7
9	4	0	4	3	1	3	A	7882.7979	–2.6
10	4	0	4	3	1	3	E	7882.8267	–0.7
11	5	0	5	4	1	4	A	10357.6989	–1.0
12	6	0	6	5	1	5	E	12700.3885	3.9
13	6	0	6	5	1	5	A	12700.4964	–3.1
14	7	0	7	6	1	6	A	14928.8076	–4.9
15	7	0	7	6	1	6	E	14928.6752	4.0
16	8	0	8	7	1	7	A	17075.0724	–3.5
17	8	0	8	7	1	7	E	17074.9291	7.4
18	2	1	2	1	0	1	A	6567.7968	–3.4
19	2	1	2	1	0	1	E	6567.2672	1.5
20	3	1	3	2	0	2	A	8417.7244	–1.2
21	3	1	3	2	0	2	E	8417.3197	3.7
22	4	1	4	3	0	3	A	10155.8035	–2.0

23	4	1	4	3	0	3	E	10155.4897	4.7
24	5	1	5	4	0	4	A	11868.4243	–3.3
25	5	1	5	4	0	4	E	11868.1803	7.6
26	6	1	6	5	0	5	A	13627.3545	–7.3
27	6	1	6	5	0	5	E	13627.1557	6.0
28	7	1	7	6	0	6	A	15462.7158	–4.7
29	7	1	7	6	0	6	E	15462.5399	7.0
30	8	1	8	7	0	7	A	17368.5627	–6.0
31	8	1	8	7	0	7	E	17368.4004	6.7
32	9	1	9	8	0	8	A	19324.9139	–7.3
33	9	1	9	8	0	8	E	19324.7601	7.7
34	10	1	10	9	0	9	A	21312.7858	–6.2
35	3	1	3	2	1	2	E	6644.7447	1.0
36	4	1	4	3	1	3	A	8809.5357	–4.9
37	4	1	4	3	1	3	E	8809.4442	1.5
38	5	1	5	4	1	4	A	10941.6855	–2.0
39	5	1	5	4	1	4	E	10941.5609	3.5
40	6	1	6	5	1	5	A	13043.3767	2.4
41	6	1	6	5	1	5	E	13043.2243	–3.2
42	7	1	7	6	1	6	A	15119.8391	–6.6
43	7	1	7	6	1	6	E	15119.6972	7.3
44	8	1	8	7	1	7	A	17177.5300	–5.4
45	8	1	8	7	1	7	E	17177.3828	7.8
46	9	1	9	8	1	8	A	19222.4557	–6.0
47	9	1	9	8	1	8	E	19222.3094	10.3
48	2	1	1	1	1	0	A	5240.8323	–0.9
49	2	1	1	1	1	0	E	5240.3113	1.0
50	3	1	2	2	1	1	A	7827.4660	–3.9
51	3	1	2	2	1	1	E	7827.0747	0.3
52	4	1	3	3	1	2	A	10367.8135	–3.3
53	4	1	3	3	1	2	E	10367.3583	–1.8
54	5	1	4	4	1	3	A	12837.3282	–2.7
55	5	1	4	4	1	3	E	12836.8033	0.2
56	6	1	5	5	1	4	A	15206.8897	–5.0
57	6	1	5	5	1	4	E	15206.3250	2.0
58	7	1	6	6	1	5	A	17450.8251	–3.3
59	7	1	6	6	1	5	E	17450.2526	5.5
60	8	1	7	7	1	6	A	19563.5627	–2.9
61	2	2	0	1	1	1	A	12041.2279	–0.5
62	2	2	0	1	1	1	E	12052.5912	1.6
63	3	2	1	2	1	2	A	15055.8407	–0.5
64	3	2	1	2	1	2	E	15057.5716	–1.0
65	4	2	2	3	1	3	A	18523.3457	1.0
66	4	2	2	3	1	3	E	18522.7812	–1.3
67	5	2	3	4	1	4	A	22541.5712	10.2
68	5	2	3	4	1	4	E	22540.0486	–0.5
69	3	2	2	3	1	3	A	8164.2594	–0.2

70	3	2	2	3	1	3	E	8160.1229	–2.6
71	4	2	3	4	1	4	A	9005.8395	–3.9
72	4	2	3	4	1	4	E	9003.4940	–2.3
73	2	2	1	1	1	0	A	11595.2391	–0.5
74	2	2	1	1	1	0	E	11581.4930	1.9
75	3	2	2	2	1	1	A	13622.2736	–0.8
76	3	2	2	2	1	1	E	13617.9753	–1.2
77	4	2	3	3	1	2	A	15445.9259	–3.0
78	4	2	3	3	1	2	E	15443.7179	2.2
79	5	2	4	4	1	3	A	17079.3562	–2.6
80	5	2	4	4	1	3	E	17077.8409	5.1
81	6	2	5	5	1	4	A	18553.4589	–5.0
82	6	2	5	5	1	4	E	18552.3028	6.5
83	7	2	6	6	1	5	A	19923.3919	–5.1
84	2	2	1	1	1	1	E	11977.9801	–1.0
85	4	2	2	3	2	1	E	10109.9537	0.1
86	3	2	2	2	2	1	A	7267.8631	–4.8
87	3	2	2	2	2	1	E	7276.7979	2.1
88	4	2	3	3	2	2	A	9651.1209	–3.5
89	4	2	3	3	2	2	E	9652.8142	0.7
90	3	3	0	3	2	1	E	11401.2237	–0.6
91	4	3	1	4	2	2	A	11058.6329	3.5
92	4	3	1	4	2	2	E	11085.3667	–3.0
93	5	3	2	5	2	3	A	10561.0786	3.1
94	5	3	2	5	2	3	E	10572.5054	–0.7
95	3	3	0	2	2	1	A	18881.2647	–1.0
96	4	3	1	3	2	2	A	21417.7141	–0.4
97	4	3	1	3	2	2	E	21448.0279	1.2
98	3	3	1	2	2	0	A	18826.8098	0.7
99	3	3	1	2	2	0	E	18773.4359	–3.9
100	4	3	2	3	2	1	A	21142.7914	–1.6
101	4	3	2	3	2	1	E	21108.4245	3.8

Table S7b: Observed frequencies ν_{obs} of 15 rotational transitions of the ^{13}C(2) isotopologue (for atom numbering see Figure 1) of *syn*-2AT with ν_{obs}–ν_{calc} values obtained from a fit with the program *XIAM*.

No.	J	K_a	K_c	J	K_a	K_c	Species	ν_{obs}	$\nu_{obs}-\nu_{calc}$
	upper level			lower level				MHz	kHz
1	4	1	4	3	0	3	A	10273.8004	–1.0
2	2	2	1	2	1	2	A	7695.9099	–2.3
3	2	2	1	1	1	0	A	11783.8983	–2.3
4	3	2	2	2	1	1	A	13827.8934	2.5
5	3	2	1	2	1	2	A	15249.4457	–1.9
6	4	2	2	3	1	3	A	18718.2489	1.8
7	3	3	0	3	2	1	A	11634.6232	–4.2
8	4	3	1	4	2	2	A	11333.6653	3.1
9	5	3	2	5	2	3	A	10843.1712	0.1
10	3	3	1	2	2	0	A	19135.4367	–0.4
11	4	3	2	3	2	1	A	21469.9412	–0.5
12	5	3	3	4	2	2	A	23628.5288	0.5
13	4	4	1	4	3	2	A	16500.1732	1.7
14	5	4	2	5	3	3	A	16476.9860	0.5
15	5	4	1	5	3	2	A	16374.8112	–0.2

Table S7c: Observed frequencies ν_{obs} of 52 rotational transitions of the ^{13}C(3) isotopologue (for atom numbering see Figure 1) of *syn*-2AT with ν_{obs}–ν_{calc} values obtained from a fit with the program *XIAM*.

No.	J	K_a	K_c	J	K_a	K_c	Species	ν_{obs}	$\nu_{obs}-\nu_{calc}$
	upper level			lower level				MHz	kHz
1	4	0	4	3	0	3	A	9265.1309	–1.0
2	4	0	4	3	0	3	E	9264.9402	–2.9
3	5	0	5	4	0	4	A	11328.1381	–2.0
4	5	0	5	4	0	4	E	11327.9575	–0.7
5	6	0	6	5	0	5	A	13335.7568	–2.3
6	6	0	6	5	0	5	E	13335.5886	2.0
7	9	0	9	8	0	8	A	19346.1255	–3.6
8	9	0	9	8	0	8	E	19345.9766	7.0
9	4	0	4	3	1	3	A	7916.9141	–2.4
10	5	0	5	4	1	4	A	10400.8150	1.2
11	5	0	5	4	1	4	E	10400.7392	–0.7
12	6	0	6	5	1	5	A	12751.9538	4.2
13	6	0	6	5	1	5	E	12751.8306	–0.2
14	7	0	7	6	1	6	A	14988.2157	–2.0
15	7	0	7	6	1	6	E	14988.0750	–1.4

16	8	0	8	7	1	7	A	17142.2776	–1.6
17	8	0	8	7	1	7	E	17142.1224	–5.1
18	4	1	3	3	1	2	A	10409.9206	2.0
19	3	1	3	2	0	2	A	8447.6690	1.2
20	3	1	3	2	0	2	E	8447.2789	–8.7
21	4	1	4	3	0	3	A	10192.4576	–0.6
22	4	1	4	3	0	3	E	10192.1611	–0.3
23	5	1	5	4	0	4	A	11911.9489	–0.7
24	5	1	5	4	0	4	E	11911.7167	2.7
25	6	1	6	5	0	5	A	13678.1911	–2.2
26	7	1	7	6	0	6	A	15521.2510	–1.7
27	7	1	7	6	0	6	E	15521.0864	9.1
28	8	1	8	7	0	7	A	17435.0070	–1.3
29	9	1	9	8	0	8	A	19399.3285	–4.0
30	4	1	4	3	1	3	A	8844.2458	3.0
31	4	1	4	3	1	3	E	8844.1466	1.8
32	5	1	5	4	1	4	A	10984.6212	–2.1
33	5	1	5	4	1	4	E	10984.4955	–0.2
34	6	1	6	5	1	5	A	13094.3812	–2.7
35	6	1	6	5	1	5	E	13094.2440	3.2
36	7	1	7	6	1	6	A	15178.8150	–3.4
37	7	1	7	6	1	6	E	15178.6720	4.7
38	8	1	8	7	1	7	A	17244.4095	1.9
39	8	1	8	7	1	7	E	17244.2566	4.2
40	2	2	1	1	1	0	A	11632.3654	–0.8
41	3	2	2	2	1	1	A	13667.2744	–0.9
42	4	2	3	3	1	2	A	15497.8261	7.6
43	5	2	4	4	1	3	A	17137.2631	–0.4
44	6	2	5	5	1	4	A	18616.7765	2.8
45	7	2	6	6	1	5	A	19991.9519	–4.0
46	2	2	0	1	1	1	A	12080.6069	–1.8
47	3	2	1	2	1	2	A	15108.2448	–1.4
48	4	2	2	3	1	3	A	18591.3580	0.5
49	3	3	0	2	2	1	A	18941.7165	–0.6
50	4	3	1	3	2	2	A	21488.7657	0.8
51	3	3	1	2	2	0	A	18886.8738	0.2
52	4	3	2	3	2	1	A	21211.8954	–0.7

Table S7d: Observed frequencies ν_{obs} of 52 rotational transitions of the ^{13}C(4) isotopologue (for atom numbering see Figure 1) of *syn*-2AT with ν_{obs}–ν_{calc} values obtained from a fit with the program *XIAM*.

No.	***J***	***K$_a$***	***K$_c$***	***J***	***K$_a$***	***K$_c$***	**Species**	**ν_{obs}**	**ν_{obs}–ν_{calc}**
	upper level			**lower level**				**MHz**	**kHz**
1	4	0	4	3	0	3	A	9205.8244	–1.9
2	4	0	4	3	0	3	E	9205.6329	0.8
3	5	0	5	4	0	4	A	11260.9987	–2.4
4	5	0	5	4	0	4	E	11260.8177	3.1
5	6	0	6	5	0	5	A	13259.2442	–2.5
6	6	0	6	5	0	5	E	13259.0757	5.3
7	3	0	3	2	1	2	A	5242.8148	–3.6
8	3	0	3	2	1	2	E	5242.9937	3.3
9	5	0	5	4	1	4	A	10300.5210	–2.4
10	5	0	5	4	1	4	E	10300.4490	4.4
11	6	0	6	5	1	5	A	12647.2114	–2.5
12	6	0	6	5	1	5	E	12647.0915	2.3
13	7	0	7	6	1	6	A	14879.0763	–2.4
14	4	1	3	3	1	2	A	10322.1764	0.2
15	4	1	3	3	1	2	E	10321.7131	–7.7
16	5	1	4	4	1	3	A	12785.6748	–1.1
17	6	1	5	5	1	4	A	15153.6716	–0.4
18	7	1	6	6	1	5	A	17400.7724	–0.6
19	7	1	6	6	1	5	E	17400.1954	1.0
20	8	1	7	7	1	6	A	19519.3488	1.4
21	3	1	3	2	0	2	A	8431.1589	0.8
22	3	1	3	2	0	2	E	8430.7677	–1.1
23	5	1	5	4	0	4	A	11873.0271	–6.8
24	5	1	5	4	0	4	E	11872.8035	7.8
25	7	1	7	6	0	6	A	15447.5886	5.0
26	7	1	7	6	0	6	E	15447.4066	–0.3
27	8	1	8	7	0	7	A	17343.3760	–4.2
28	3	1	3	2	1	2	A	6624.6517	–1.8
29	3	1	3	2	1	2	E	6624.6252	2.3
30	4	1	4	3	1	3	A	8784.4645	–4.4
31	4	1	4	3	1	3	E	8784.3731	3.6
32	5	1	5	4	1	4	A	10912.5635	7.3
33	5	1	5	4	1	4	E	10912.4295	3.7
34	6	1	6	5	1	5	A	13010.7723	–4.7
35	2	2	1	1	1	0	A	11659.9921	–0.7
36	3	2	2	2	1	1	A	13682.7119	0.9
37	4	2	3	3	1	2	A	15504.9674	–3.8
38	6	2	5	5	1	4	A	18614.4892	–3.6
39	6	2	5	5	1	4	E	18613.3772	–3.2
40	7	2	6	6	1	5	A	19983.0908	–0.1

41	7	2	6	6	1	5	E	19982.2205	4.5
42	2	2	0	1	1	1	A	12098.5074	–0.6
43	3	2	1	2	1	2	A	15090.3963	6.3
44	4	2	2	3	2	1	A	10058.3707	–2.5
45	5	2	3	4	2	2	A	12757.3388	–0.2
46	6	2	4	5	2	3	A	15469.7088	1.5
47	3	3	0	2	2	1	A	18986.4988	0.1
48	4	3	1	3	2	2	A	21508.3639	1.4
49	5	3	2	4	2	3	A	24166.6037	0.7
50	3	3	1	2	2	0	A	18934.2535	1.2
51	4	3	2	3	2	1	A	21244.5356	–1.1
52	5	3	3	4	2	2	A	23380.5364	–2.3

Table S7e: Observed frequencies ν_{obs} of 52 rotational transitions of the ^{13}C(5) isotopologue (for atom numbering see Figure 1) of *syn*-2AT with ν_{obs}–ν_{calc} values obtained from a fit with the program *XIAM*.

No.	***J***	***K*** $_a$	***K*** $_c$	***J***	***K*** $_a$	***K*** $_c$	**Species**	ν_{obs}	$\nu_{obs}-\nu_{calc}$
	upper level			**lower level**				**MHz**	**kHz**
1	4	0	4	3	0	3	A	9201.5158	–1.1
2	4	0	4	3	0	3	E	9201.3222	–0.5
3	5	0	5	4	0	4	A	11262.1456	–2.4
4	5	0	5	4	0	4	E	11261.9636	3.7
5	8	0	8	7	0	7	A	17237.0861	–2.0
6	3	0	3	2	1	2	A	5185.9231	0.7
7	3	0	3	2	1	2	E	5186.1304	–0.8
8	5	0	5	4	1	4	A	10255.0555	–1.3
9	5	0	5	4	1	4	E	10254.9986	4.1
10	6	0	6	5	1	5	A	12613.1286	–0.5
11	6	0	6	5	1	5	E	12613.0196	4.6
12	7	0	7	6	1	6	A	14855.8710	–3.3
13	7	0	7	6	1	6	E	14855.7400	6.5
14	2	1	2	1	0	1	A	6622.5767	–0.8
15	2	1	2	1	0	1	E	6622.0324	–2.4
16	3	1	3	2	0	2	A	8472.2200	–2.1
17	3	1	3	2	0	2	E	8471.8080	–2.2
18	5	1	5	4	0	4	A	11912.8653	–2.0
19	5	1	5	4	0	4	E	11912.6158	0.9
20	6	1	6	5	0	5	A	13656.0879	–2.9
21	6	1	6	5	0	5	E	13655.8870	4.5
22	7	1	7	6	0	6	A	15472.4960	0.4
23	7	1	7	6	0	6	E	15472.3199	7.6
24	8	1	8	7	0	7	A	17360.6081	–2.9
25	9	1	9	8	0	8	A	19302.5038	–4.8

26	4	1	4	3	1	3	A	8776.9964	–2.5
27	4	1	4	3	1	3	E	8776.9058	0.0
28	5	1	5	4	1	4	A	10905.7729	–3.1
29	5	1	5	4	1	4	E	10905.6523	2.8
30	6	1	6	5	1	5	A	13005.3693	–2.2
31	6	1	6	5	1	5	E	13005.2321	4.6
32	7	1	7	6	1	6	A	15080.2498	–3.4
33	7	1	7	6	1	6	E	15080.1061	6.3
34	4	1	3	3	1	2	A	10292.8874	–1.7
35	4	1	3	3	1	2	E	10292.4341	–5.3
36	5	1	4	4	1	3	A	12755.2910	–1.2
37	5	1	4	4	1	3	E	12754.7675	–4.9
38	6	1	5	5	1	4	A	15127.3592	2.1
39	6	1	5	5	1	4	E	15126.7893	–1.8
40	3	2	2	2	1	1	A	13799.1296	–2.3
41	4	2	3	3	1	2	A	15624.6643	–0.2
42	6	2	5	5	1	4	A	18745.5455	1.7
43	4	2	2	3	1	3	A	18579.3377	6.8
44	4	2	2	3	2	1	A	10018.5013	–1.0
45	4	2	2	3	2	1	E	10015.9106	0.5
46	5	2	3	4	2	2	A	12703.9302	1.0
47	3	3	0	2	2	1	A	19175.7193	–2.5
48	4	3	1	3	2	2	A	21686.3554	–3.4
49	3	3	1	2	2	0	A	19126.0273	0.7
50	4	3	2	3	2	1	A	21435.3493	–0.9
51	5	3	3	4	2	2	A	23577.3983	0.6
52	3	3	1	3	2	2	A	11951.1091	4.2

Table S7f: Observed frequencies ν_{obs} of 57 rotational transitions of the ^{13}C(6) isotopologue (for atom numbering see Figure 1) of *syn*-2AT with ν_{obs}–ν_{calc} values obtained from a fit with the program *XIAM*.

No.	***J***	***K_a***	***K_c***	***J***	***K_a***	***K_c***	**Species**	**ν_{obs}**	**ν_{obs}–ν_{calc}**
	upper level			**lower level**				**MHz**	**kHz**
1	3	0	3	2	0	2	E	7082.3227	2.4
2	4	0	4	3	0	3	A	9252.8636	–2.6
3	4	0	4	3	0	3	E	9252.6725	4.9
4	5	0	5	4	0	4	E	11321.6964	5.4
5	6	0	6	5	0	5	E	13332.4374	12.8
6	5	0	5	4	1	4	A	10332.3192	–2.2
7	5	0	5	4	1	4	E	10332.2543	–0.9
8	6	0	6	5	1	5	A	12697.4709	–4.7
9	6	0	6	5	1	5	E	12697.3615	3.7
10	7	0	7	6	1	6	A	14946.8973	–8.2

11	7	0	7	6	1	6	E	14946.7620	0.9
12	1	1	1	0	0	0	A	4605.1618	–0.2
13	2	1	2	1	0	1	A	6638.7860	–8.4
14	2	1	2	1	0	1	E	6638.2545	3.2
15	3	1	3	2	0	2	A	8497.3292	–4.6
16	4	1	4	3	0	3	A	10242.4220	–6.2
17	5	1	5	4	0	4	A	11957.0091	–5.9
18	5	1	5	4	0	4	E	11956.7635	5.7
19	6	1	6	5	0	5	A	13712.7561	–8.3
20	6	1	6	5	0	5	E	13712.5595	8.2
21	7	1	7	6	0	6	E	15542.8130	6.1
22	8	1	8	7	0	7	E	17444.8320	0.2
23	4	1	3	3	1	2	A	10362.0824	–0.6
24	5	1	4	4	1	3	A	12838.2129	–1.9
25	5	1	4	4	1	3	E	12837.6830	0.0
26	6	1	5	5	1	4	A	15221.0495	–1.2
27	6	1	5	5	1	4	E	15220.4750	3.0
28	4	1	4	3	1	3	A	8827.6014	–2.5
29	4	1	4	3	1	3	E	8827.5122	6.5
30	5	1	5	4	1	4	E	10967.3260	4.0
31	6	1	6	5	1	5	A	13077.6293	–3.5
32	6	1	6	5	1	5	E	13077.4880	3.5
33	7	1	7	6	1	6	A	15162.8256	–12.1
34	7	1	7	6	1	6	E	15162.6830	2.8
35	2	2	1	1	1	0	A	11781.8452	0.7
36	2	2	1	1	1	0	E	11767.5071	1.0
37	3	2	2	2	1	1	A	13815.4714	–2.2
38	4	2	3	3	1	2	A	15649.2106	–7.5
39	5	2	4	4	1	3	A	17295.0990	–3.1
40	5	2	4	4	1	3	E	17293.5410	7.0
41	6	2	5	5	1	4	A	18781.3527	–6.8
42	6	2	5	5	1	4	E	18780.1692	6.8
43	2	2	0	1	1	1	A	12218.4270	1.4
44	3	2	1	2	1	2	A	15215.7355	2.3
45	3	2	1	2	1	2	E	15217.6521	–1.1
46	4	2	2	3	1	3	A	18650.6426	–2.4
47	4	2	2	3	1	3	E	18650.1396	2.9
48	3	2	2	3	1	3	A	8326.2547	5.8
49	3	2	2	3	1	3	E	8321.9001	–2.8
50	3	2	2	2	2	1	A	7268.0645	–6.0
51	3	3	1	2	2	0	A	19133.5990	2.9
52	3	3	1	2	2	0	E	19079.2916	–3.6
53	4	3	2	3	2	1	A	21455.7555	0.4
54	5	3	3	4	2	2	A	23606.3727	0.9
55	5	3	3	4	2	2	E	23588.5896	1.7
56	3	3	0	3	2	1	A	11683.6259	1.3
57	3	3	0	3	2	1	E	11718.3825	–3.9

Table S7g: Observed frequencies ν_{obs} of 54 rotational transitions of the ^{13}C(8) isotopologue (for atom numbering see Figure 1) of *syn*-2AT with $\nu_{obs}-\nu_{calc}$ values obtained from a fit with the program *XIAM*.

No.	J	K_a	K_c	J	K_a	K_c	Species	ν_{obs}	$\nu_{obs}-\nu_{calc}$
	upper level			lower level				MHz	kHz
1	2	0	2	1	0	1	A	4747.6477	–1.1
2	2	0	2	1	0	1	E	4747.5023	–2.6
3	3	0	3	2	0	2	A	7008.9898	–0.9
4	3	0	3	2	0	2	E	7008.8088	–2.2
5	4	0	4	3	0	3	A	9157.6858	4.0
6	4	0	4	3	0	3	E	9157.4934	2.0
7	5	0	5	4	0	4	A	11206.1878	–2.6
8	5	0	5	4	0	4	E	11206.0082	4.1
9	6	0	6	5	0	5	A	13196.7304	–12.3
10	3	0	3	2	1	2	A	5180.5269	–1.1
11	3	0	3	2	1	2	E	5180.7530	7.2
12	4	0	4	3	1	3	A	7750.8299	0.3
13	4	0	4	3	1	3	E	7750.8796	3.0
14	6	0	6	5	1	5	A	12563.1125	–2.7
15	6	0	6	5	1	5	E	12563.0071	–6.2
16	3	1	2	2	1	1	A	7736.9698	–1.0
17	3	1	2	2	1	1	E	7736.5850	–6.2
18	4	1	3	3	1	2	A	10252.5662	–1.0
19	5	1	4	4	1	3	A	12703.2558	0.6
20	6	1	5	5	1	4	A	15062.2374	0.2
21	3	1	3	2	0	2	A	8415.8404	–2.6
22	3	1	3	2	0	2	E	8415.4245	–1.3
23	4	1	4	3	0	3	A	10143.1645	0.5
24	4	1	4	3	0	3	E	10142.8375	2.4
25	5	1	5	4	0	4	E	11839.5619	6.2
26	6	1	6	5	0	5	A	13576.6959	–7.6
27	6	1	6	5	0	5	E	13576.4912	4.7
28	5	1	5	4	1	4	A	10854.3388	3.1
29	5	1	5	4	1	4	E	10854.2173	5.4
30	6	1	6	5	1	5	A	12943.0729	–3.1
31	6	1	6	5	1	5	E	12942.9397	4.7
32	7	1	7	6	1	6	A	15007.1191	–7.6
33	7	1	7	6	1	6	E	15006.9826	6.5
34	8	1	8	7	1	7	E	17052.2408	5.1
35	2	2	1	1	1	0	A	11677.0879	1.3
36	3	2	2	2	1	1	A	13689.8922	–0.9
37	4	2	3	3	1	2	A	15505.2311	6.0
38	5	2	4	4	1	3	A	17134.8765	–1.8
39	6	2	5	5	1	4	A	18606.5469	–1.8
40	2	2	0	1	1	1	A	12108.2367	–3.1

41	3	2	1	2	1	2	A	15072.4498	–0.7
42	4	2	2	3	1	3	A	18468.2707	2.9
43	3	2	1	2	2	0	A	7374.2255	0.2
44	4	2	2	3	2	1	A	9983.1967	–0.9
45	5	2	3	4	2	2	A	12660.2135	0.4
46	6	2	4	5	2	3	A	15353.3020	1.1
47	3	3	0	2	2	1	A	19014.2715	–1.4
48	4	3	1	3	2	2	A	21516.4860	–1.1
49	5	3	2	4	2	3	A	24149.7539	–0.3
50	3	3	1	2	2	0	A	18963.9264	–0.4
51	4	3	2	3	2	1	A	21262.2144	0.6
52	3	3	1	3	2	2	A	11819.0809	2.5
53	4	3	2	4	2	3	A	11939.2866	–1.3
54	5	3	3	5	2	4	A	12169.6230	1.3

Table S-8a: Observed frequencies ν_{obs} of 63 rotational transitions of the ^{34}S(1) isotopologue (for atom numbering see Figure 1) of *anti*-2AT with ν_{obs}–ν_{calc} values obtained from a fit with the program *XIAM*.

No.	***J***	***K$_a$***	***K$_c$***	***J***	***K$_a$***	***K$_c$***	**Species**	**ν_{obs}**	**ν_{obs}–ν_{calc}**
	upper level			**lower level**				**MHz**	**kHz**
1	2	0	2	1	0	1	A	4799.7839	–0.8
2	2	0	2	1	0	1	E	4799.4338	–2.9
3	3	0	3	2	0	2	A	7074.1520	–1.3
4	3	0	3	2	0	2	E	7073.7786	0.1
5	4	0	4	3	0	3	A	9226.1908	1.3
6	4	0	4	3	0	3	E	9225.8724	1.0
7	5	0	5	4	0	4	A	11275.4921	2.4
8	5	0	5	4	0	4	E	11275.2480	1.3
9	6	0	6	5	0	5	A	13271.5844	0.6
10	6	0	6	5	0	5	E	13271.3877	–0.5
11	7	0	7	6	0	6	A	15257.1026	–1.3
12	7	0	7	6	0	6	E	15256.9240	–1.2
13	8	0	8	7	0	7	A	17250.9398	–1.1
14	8	0	8	7	0	7	E	17250.7635	–0.6
15	9	0	9	8	0	8	A	19255.9165	–0.3
16	9	0	9	8	0	8	E	19255.7384	0.2
17	4	0	4	3	1	3	A	7923.4659	0.1
18	4	0	4	3	1	3	E	7922.9792	–1.1
19	5	0	5	4	1	4	A	10388.5892	–2.7
20	5	0	5	4	1	4	E	10388.0881	3.6
21	6	0	6	5	1	5	A	12719.7455	–0.1
22	7	0	7	6	1	6	A	14937.3648	1.4
23	7	0	7	6	1	6	E	14936.9818	–0.8
24	3	1	3	2	0	2	A	8376.8705	–6.5
25	3	1	3	2	0	2	E	8376.6705	0.8

26	4	1	4	3	0	3	A	10113.0854	–1.9
27	4	1	4	3	0	3	E	10113.0340	0.3
28	5	1	5	4	0	4	A	11827.3248	–3.1
29	5	1	5	4	0	4	E	11827.3452	2.2
30	6	1	6	5	0	5	A	13591.3284	4.1
31	7	1	7	6	0	6	A	15432.9083	–0.7
32	7	1	7	6	0	6	E	15432.8681	–1.0
33	8	1	8	7	0	7	A	17344.0105	0.5
34	9	1	9	8	0	8	A	19303.8247	–0.1
35	9	1	9	8	0	8	E	19303.6969	–1.6
36	4	1	4	3	1	3	A	8810.3638	0.3
37	5	1	5	4	1	4	A	10940.4309	0.8
38	5	1	5	4	1	4	E	10940.1819	1.1
39	6	1	6	5	1	5	A	13039.4856	–0.5
40	6	1	6	5	1	5	E	13039.2355	1.1
41	7	1	7	6	1	6	A	15113.1714	2.9
42	7	1	7	6	1	6	E	15112.9271	0.5
43	9	1	9	8	1	8	A	19210.7578	2.0
44	9	1	9	8	1	8	E	19210.5410	–0.8
45	5	1	4	4	1	3	A	12854.8587	–0.4
46	6	1	5	5	1	4	A	15218.3979	0.4
47	7	1	6	6	1	5	A	17451.3925	–0.6
48	8	1	7	7	1	6	A	19550.9600	–0.5
49	2	2	1	1	1	0	A	11487.0696	–4.4
50	3	2	2	2	1	1	A	13512.7123	–5.1
51	4	2	3	3	1	2	A	15332.3707	7.9
52	2	2	0	1	1	1	A	11940.0670	3.0
53	3	2	1	2	1	2	A	14970.9564	–0.9
54	4	2	2	3	1	3	A	18465.7994	5.4
55	3	2	2	3	1	3	A	8067.4215	–2.6
56	3	3	0	3	2	1	A	11170.2119	1.3
57	4	3	1	4	2	2	A	10852.1345	5.0
58	3	3	1	2	2	0	A	18648.5461	–1.0
59	4	3	2	3	2	1	A	20963.6163	–1.0
60	5	3	3	4	2	2	A	23092.1148	–1.9
61	3	3	0	2	2	1	A	18705.3866	–3.0
62	4	3	1	3	3	0	A	9823.5251	–2.1
63	4	3	1	3	3	0	E	9812.1617	–0.2

Table S-8b: Observed frequencies ν_{obs} of 10 rotational transitions of the ^{13}C(4) isotopologue (for atom numbering see Figure 1) of *anti*-2AT with $\nu_{obs}-\nu_{calc}$ values obtained from a fit with the program *XIAM*.

No.	***J***	***K$_a$***	***K$_c$***	***J***	***K$_a$***	***K$_c$***	**Species**	**ν_{obs}**	**$\nu_{obs}-\nu_{calc}$**
	upper level			**lower level**				**MHz**	**kHz**
1	4	0	4	3	0	3	A	9199.6654	0.5
2	6	0	6	5	0	5	A	13244.2061	1.8
3	5	0	5	4	1	4	A	10317.7121	0.9
4	6	0	6	5	1	5	A	12655.3432	–0.8
5	3	1	3	2	0	2	A	8398.6726	0.9
6	4	1	4	3	0	3	A	10131.6664	–2.0
7	5	1	5	4	0	4	A	11838.5763	1.2
8	7	1	7	6	0	6	A	15419.1082	–0.5
9	3	1	3	2	1	2	A	6622.8479	–1.1
10	4	1	4	3	1	3	A	8780.8686	–1.6

Table S-8c: Observed frequencies ν_{obs} of 11 rotational transitions of the ^{13}C(5) isotopologue (for atom numbering see Figure 1) of *anti*-2AT with $\nu_{obs}-\nu_{calc}$ values obtained from a fit with the program *XIAM*.

No.	***J***	***K$_a$***	***K$_c$***	***J***	***K$_a$***	***K$_c$***	**Species**	**ν_{obs}**	**$\nu_{obs}-\nu_{calc}$**
	upper level			**lower level**				**MHz**	**kHz**
1	4	0	4	3	0	3	A	9196.6294	0.7
2	5	0	5	4	0	4	A	11251.1826	–1.5
3	6	0	6	5	1	5	A	12628.9231	–0.6
4	5	1	5	4	0	4	A	11870.6874	–1.4
5	4	1	4	3	1	3	A	8775.0477	0.4
6	2	2	1	1	1	0	A	11672.5008	–3.7
7	3	2	2	2	1	1	A	13693.5005	3.0
8	4	2	3	3	1	2	A	15514.9364	–2.6
9	5	2	4	4	1	3	A	17149.0402	4.3
10	2	2	0	1	1	1	A	12108.7493	–2.7
11	3	2	1	2	1	2	A	15093.3946	2.2

Table S-9a: Observed frequencies ν_{obs} of 5 rotational transitions of the ^{13}C(6) isotopologue (for atom numbering see Figure 1) of *anti*-2AT with $\nu_{obs}-\nu_{calc}$ values obtained from a fit with the program *XIAM*.

No.	***J***	***K_a***	***K_c***	***J***	***K_a***	***K_c***	**Species**	**ν_{obs}**	**$\nu_{obs}-\nu_{calc}$**
	upper level			**lower level**				**MHz**	**kHz**
1	5	0	5	4	0	4	A	11309.3166	4.6
2	6	0	6	5	0	5	A	13315.4302	−8.7
3	7	0	7	6	0	6	A	15307.2960	5.0
4	6	0	6	5	1	5	A	12710.1858	0.0
5	5	1	5	4	1	4	A	10961.4417	−1.0

Table S-9b: Observed frequencies ν_{obs} of 9 rotational transitions of the ^{13}C(3) isotopologue (for atom numbering see Figure 1) of *anti*-2AT with $\nu_{obs}-\nu_{calc}$ values obtained from a fit with the program *XIAM*.

No.	***J***	***K_a***	***K_c***	***J***	***K_a***	***K_c***	**Species**	**ν_{obs}**	**$\nu_{obs}-\nu_{calc}$**
	upper level			**lower level**				**MHz**	**kHz**
1	4	0	4	3	0	3	A	9258.7938	−16.5
2	5	0	5	4	0	4	A	11315.9877	−4.2
3	6	0	6	5	0	5	A	13319.4859	−61.5
4	4	1	4	3	1	3	A	8841.1585	−12.5
5	5	1	5	4	1	4	A	10978.9239	−27.9
6	6	1	6	5	1	5	A	13085.7459	67.5
7	7	1	7	6	1	6	A	15166.9951	32.5
8	8	1	8	7	1	7	A	17229.5229	0.6
9	2	2	0	1	1	1	A	11991.8085	4.2

Table S-9c: Observed frequencies ν_{obs} of 7 rotational transitions of the ^{13}C(2) and ^{13}C(8) isotopologues (for atom numbering see Figure 1) of *anti*-2AT. A fit was not possible.

No.	**^{13}C**	**J**	**K_a**	**K_c**	**J**	**K_a**	**K_c**	**Species**	**ν_{obs}**
		upper level			**lower level**				**[MHz]**
1	**C(2)**	4	1	3	3	1	2	A	10442.6442
2	**C(2)**	2	2	1	1	1	0	A	11680.9726
3	**C(2)**	2	2	0	1	1	1	A	12130.4247
4	**C(8)**	4	0	4	3	0	3	A	9176.9291
5	**C(8)**	4	1	3	3	1	2	A	10299.0271
6	**C(8)**	2	2	1	1	1	0	A	11568.2513
7	**C(8)**	2	2	0	1	1	1	A	12008.2391

Table S-10: Molecular parameters of ^{13}C(3)- and ^{13}C(6)-isotopologues of *anti*-2AT obtained with the program *XIAM*.

Par.[a]	**Unit**	**^{13}C(3)**	**^{13}C(6)**
A_0	MHz	3507.206(45)	3554.856(54)
B_0	MHz	1417.755(32)	1408.849(13)
C_0	MHz	1016.4673(47)	1015.7426(29)
Δ_c[c]	u$Å^2$	–3.370	–3.337
N_A[d]	-	9	5
σ[e]	kHz	46.1	11.1

[a] All parameters refer to the principal axis system. Watson's S reduction and I^r representation were used. [b] Values of all centrifugal distortion constants were fixed to those of the main isotopologue listed in Table 2. [c] Pseudo inertial defect. [d] Number of A species transitions. [e] Standard deviation of the fit.

Table S-11a: Observed frequencies ν_{obs} of 53 rotational transitions of thiophene with $\nu_{obs}-\nu_{calc}$ values obtained from a fit with the program *XIAM*.

No.	J	K_a	K_c	J	K_a	K_c	ν_{obs}	$\nu_{obs}-\nu_{calc}$
	upper level			**lower level**			**MHz**	**kHz**
1	1	0	1	0	0	0	8654.0412	0.5
2	2	0	2	1	0	1	16401.6345	0.7
3	2	1	2	1	1	1	15125.5902	0.6
4	2	1	1	1	1	0	19490.5337	0.4
5	2	1	1	2	1	2	6547.4230	–0.1
6	3	0	3	2	0	2	23044.1927	2.2
7	3	1	3	2	1	2	22202.3216	2.7
8	3	2	2	2	2	1	25962.0490	5.0
9	3	1	2	3	1	3	12833.9824	1.2
10	3	2	1	3	2	2	3824.2748	–0.2
11	4	1	3	4	1	4	20212.5488	2.2
12	4	2	3	4	0	4	23245.2961	1.2
13	4	2	2	4	2	3	9061.3091	–0.9
14	5	2	3	5	2	4	16217.6486	0.8
15	5	3	2	5	3	3	5111.4661	0.2
16	6	2	4	6	2	5	24377.7926	0.8
17	6	3	3	6	3	4	11099.7337	–0.1
18	7	3	4	7	3	5	19089.5166	1.2
19	7	4	3	7	4	4	6139.0405	0.3
20	8	4	4	8	4	5	12774.9279	1.4
21	9	4	5	9	4	6	21548.1703	1.2
22	9	5	4	9	5	5	6958.8187	–0.1
23	10	5	5	10	5	6	14150.9665	–1.1
24	10	6	4	10	6	5	2998.5411	0.4
25	11	6	5	11	6	6	7605.2573	–0.1
26	12	6	6	12	6	7	15270.7729	–1.5
27	12	7	5	12	7	6	3281.0970	1.5
28	13	7	6	13	7	7	8104.0418	1.3
29	14	7	7	14	7	8	16166.2706	–1.0
30	14	8	6	14	8	7	3495.3390	0.3
31	15	8	7	15	8	8	8475.6931	–0.2
32	16	8	8	16	8	9	16862.9940	–2.1
33	16	9	7	16	9	8	3651.0061	0.2
34	17	9	8	17	9	9	8737.3523	–0.2
35	18	9	9	18	9	10	17382.4533	3.4
36	18	10	8	18	10	9	3756.4651	1.0
37	19	10	9	19	10	10	8903.7305	–1.3
38	20	10	10	20	10	11	17743.4050	–0.7
39	3	1	2	2	1	1	28488.8735	–3.5
40	3	2	1	2	2	0	28879.8913	–1.0
41	4	0	4	3	0	3	29317.3760	–0.2

42	4	1	4	3	1	3	28967.7303	–0.8
43	4	1	3	3	1	2	36346.2952	–1.3
44	4	2	3	3	2	2	33880.1269	0.2
45	4	2	2	3	2	1	39117.1576	–4.0
46	4	3	2	3	3	1	35899.3113	–1.2
47	4	3	1	3	3	0	37250.5108	–2.3
48	5	0	5	4	0	4	35664.8532	2.1
49	5	1	5	4	1	4	35552.1018	1.5
50	5	2	4	5	0	5	28866.9078	–4.4
51	5	1	4	5	1	5	27612.1348	–2.8
52	6	2	5	6	0	6	35031.4805	1.6
53	6	1	5	6	1	6	34596.3624	2.5

Table S-11b: Observed frequencies ν_{obs} of 26 rotational transitions of the ^{34}S(1) isotopologue (for atom numbering see Figure 6) of thiophene with ν_{obs}–ν_{calc} values obtained from a fit with the program *XIAM*.

No.	***J***	***K$_a$***	***K$_c$***	***J***	***K$_a$***	***K$_c$***	**ν_{obs}**	**$\nu_{obs}-\nu_{calc}$**
	upper level			**lower level**			**MHz**	**kHz**
1	1	0	1	0	0	0	8458.0270	1.5
2	2	0	2	1	0	1	16100.1520	0.6
3	2	1	2	1	1	1	14825.7000	0.5
4	2	1	1	1	1	0	19006.3630	–0.6
5	2	1	1	2	1	2	6271.0030	–0.6
6	3	0	3	2	0	2	22693.7400	2.4
7	3	1	3	2	1	2	21798.2050	1.6
8	3	2	2	2	2	1	25374.0050	5.2
9	3	1	2	3	1	3	12323.9367	0.0
10	4	1	3	4	1	4	19532.5175	4.2
11	4	2	2	4	2	3	8404.5020	–2.9
12	5	2	3	5	2	4	15232.9810	–3.2
13	6	3	3	6	3	4	9951.7062	5.3
14	7	3	4	7	3	5	17500.2147	–0.1
15	9	5	4	9	5	5	5531.1179	–0.9
16	3	1	2	2	1	1	27851.1322	–4.3
17	3	2	1	2	2	0	28054.2561	–2.2
18	4	0	4	3	0	3	28875.7365	–1.3
19	4	1	4	3	1	3	28475.0220	–0.6
20	4	1	3	3	1	2	35683.5962	–3.0
21	4	2	3	3	2	2	33172.9006	2.0
22	4	2	2	3	2	1	38081.2639	–1.6
23	4	3	2	3	3	1	35008.1875	0.0
24	4	3	1	3	3	0	36160.8187	–0.7
25	5	0	5	4	0	4	35108.1135	0.8
26	5	1	5	4	1	4	34969.3261	1.2

Table S-11c: Observed frequencies ν_{obs} of 25 rotational transitions of the ^{13}C(2) isotopologue (for atom numbering see Figure 6) of thiophene with $\nu_{obs}-\nu_{calc}$ values obtained from a fit with the program *XIAM*.

No.	J	K_a	K_c	J	K_a	K_c	ν_{obs}	$\nu_{obs}-\nu_{calc}$
	upper level			**lower level**			**MHz**	**kHz**
1	1	0	1	0	0	0	8623.2089	–0.2
2	2	0	2	1	0	1	16275.1988	0.0
3	2	1	2	1	1	1	15032.8106	0.9
4	2	1	1	1	1	0	19459.9874	0.5
5	2	1	1	2	1	2	6640.7693	–4.1
6	3	0	3	2	0	2	22802.8919	2.6
7	3	1	3	2	1	2	22031.4103	2.1
8	3	2	2	2	2	1	25869.5563	6.7
9	3	1	2	3	1	3	12982.8012	–2.4
10	4	1	3	4	1	4	20321.4057	4.3
11	4	2	3	4	0	4	22890.8029	–0.2
12	4	2	2	4	2	3	9443.1864	2.4
13	5	2	3	5	2	4	16706.3696	–0.4
14	6	3	3	6	3	4	11892.284	–0.2
15	3	1	2	2	1	1	28373.4359	–2.5
16	3	2	1	2	2	0	28936.2012	–3.3
17	4	0	4	3	0	3	29011.9713	–2.4
18	4	1	4	3	1	3	28713.2119	–2.2
19	4	1	3	3	1	2	36051.8094	–2.4
20	4	2	3	3	2	2	33700.2646	–1.0
21	4	2	2	3	2	1	39105.5958	–0.3
22	4	3	2	3	3	1	35844.9441	–1.7
23	4	3	1	3	3	0	37360.5802	0.9
24	5	0	5	4	0	4	35311.1689	1.7
25	5	1	5	4	1	4	35221.0393	1.6

Table S-11c: Observed frequencies ν_{obs} of 25 rotational transitions of the ^{13}C(3) isotopologue (for atom numbering see Figure 6) of thiophene with ν_{obs}–ν_{calc} values obtained from a fit with the program *XIAM*.

No.	***J***	***K$_a$***	***K$_c$***	***J***	***K$_a$***	***K$_c$***	**ν_{obs}**	**ν_{obs}–ν_{calc}**
	upper level			**lower level**			**MHz**	**kHz**
1	1	0	1	0	0	0	8509.9242	1.8
2	2	0	2	1	0	1	16157.6790	0.4
3	2	1	2	1	1	1	14891.1492	1.7
4	2	1	1	1	1	0	19148.5038	0.8
5	2	1	1	2	1	2	6386.0383	–2.4
6	3	0	3	2	0	2	22730.9485	1.8
7	3	1	3	2	1	2	21873.1888	2.0
8	3	1	2	3	1	3	12531.3151	0.8
9	3	2	2	2	2	1	25529.6906	0.8
10	4	1	3	4	1	4	19788.0675	2.6
11	4	2	3	4	0	4	22987.4129	–0.6
12	4	2	2	4	2	3	8725.4490	–1.3
13	5	2	3	5	2	4	15697.3295	1.5
14	6	3	3	6	3	4	10546.0745	–0.1
15	3	1	2	2	1	1	28018.4579	–2.5
16	3	2	1	2	2	0	28328.4283	–1.7
17	4	0	4	3	0	3	28919.7995	–0.6
18	4	1	4	3	1	3	28552.4378	–2.3
19	4	1	3	3	1	2	35809.1884	–2.3
20	4	2	3	3	2	2	33341.0812	1.7
21	4	2	2	3	2	1	38405.6410	–2.4
22	4	3	2	3	3	1	35269.2515	0.8
23	4	3	1	3	3	0	36527.0927	0.0
24	5	0	5	4	0	4	35173.1968	0.7
25	5	1	5	4	1	4	35051.2017	1.5

Table S-12: Ab initio structures of 2AT (bond lengths in Å, angles in degree).

Method	**CCSD(T)_ae**	**MP2(ae)**	**MP2(ae)**	**r_e(BO)** [a]
Basis set	**cc-pwCVTZ**	**cc-pwCVQZ**	**cc-pwCVTZ**	
***anti*-2AT**				
S-C5	1.7095	1.6901	1.6937	1.7059
S-C2	1.7260	1.7044	1.7080	1.7225
C-S-C	91.896	92.6137	92.5191	91.990
C4=C5	1.3722	1.3776	1.3786	1.3712
S-C5=C4	111.995	111.5599	111.6030	111.952
C2=C3	1.3750	1.3817	1.3825	1.3742
S-C2=C3	111.019	110.7981	110.8112	111.006
C5-H	1.0775	1.0756	1.0762	1.0769
S-C5-H	120.145	120.2746	120.3060	120.114
C2-C6	1.4804	1.4708	1.4721	1.4790
S-C2-C6	123.481	123.1423	123.3239	123.299
C4-H	1.0793	1.0772	1.0780	1.0786
C5=C4-H	124.375	124.6499	124.6463	124.378
C3-H	1.0793	1.0774	1.0780	1.0787
C2=C3-H	125.476	125.9372	125.9385	125.475
C6-O	1.2164	1.2172	1.2187	1.2150
C2-C6=O	120.190	120.1798	120.2019	120.167
C6-C8	1.5098	1.5013	1.5034	1.5076
C2-C6-C8	117.708	117.7275	117.6606	117.774
C8-Hs	1.0859	1.0825	1.0833	1.0851
C6-C8-Hs	109.185	109.1644	109.1439	109.206
C8-Ha	1.0911	1.0872	1.0880	1.0903
C6-C8-Ha	110.232	110.3083	110.3144	110.226
C2-C6-C8-Ha	59.278	59.3239	59.3356	59.267
***syn*-2AT**				
S-C5	1.7095	1.6907	1.6940	1.7063
S-C2	1.7229	1.7022	1.7060	1.7191
C-S-C	91.491	92.147	92.064	91.574
C4=C5	1.3719	1.3766	1.3776	1.3708
S-C5=C4	112.537	112.163	112.196	112.503
C2=C3	1.3763	1.3830	1.3838	1.3754
S-C2=C3	111.460	111.239	111.249	111.450
C5-H	1.0777	1.0758	1.0764	1.0771
S-C5-H	120.111	120.194	120.250	120.055
C2-C6	1.4740	1.4646	1.4658	1.4728
S-C2-C6	119.295	119.247	119.139	119.403
C4-H	1.0793	1.0772	1.0779	1.0785
C5=C4-H	123.723	124.687	124.663	123.748
C3-H	1.0800	1.0777	1.0784	1.0793
C2=C3-H	123.258	124.491	124.462	123.287

C6-O	1.2177	1.2189	1.2204	1.2162
C2-C6=O	120.883	120.9621	121.0125	120.832
C6-C8	1.5106	1.5016	1.5038	1.5083
C2-C6-C8	117.032	116.9066	116.8089	117.130
C8-Hs	1.0860	1.0824	1.0833	1.0851
C6-C8-Hs	108.896	108.9780	108.9562	108.918
C8-Ha	1.0905	1.0866	1.0874	1.0897
C6-C8-Ha	110.302	110.2829	110.2991	110.286
C2-C6-C8-Ha	59.454	59.409	59.421	59.443

[a] See Eq. (1).

Table S13: Semi-experimental equilibrium rotational constants for *syn*-2AT and residuals of the fit (all values in MHz).

	A_e	**Exp.–Calc.**	B_e	**Exp.–Calc.**	C_e	**Exp.–Calc.**
Parent	3604.051	0.033	1426.549	0.005	1028.525	0.005
^{34}S	3542.552	–0.002	1419.546	–0.003	1019.845	–0.001
^{13}C(2)	3603.014	0.100	1426.432	–0.012	1028.381	0.003
^{13}C(3)	3553.989	0.000	1425.514	0.001	1023.872	0.000
^{13}C(4)	3564.950	0.003	1411.935	–0.001	1017.744	0.000
^{13}C(5)	3603.904	–0.018	1406.024	0.000	1017.801	–0.000
^{13}C(6)	3603.954	0.018	1416.266	–0.001	1023.16	0.001
^{13}C(8)	3572.365	–0.002	1401.074	–0.001	1012.685	–0.001

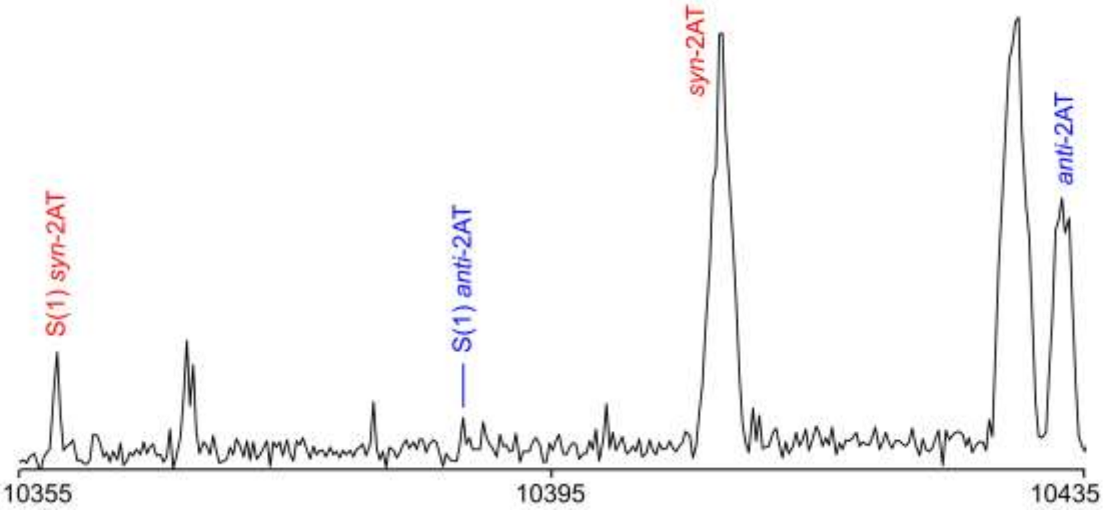

Figure S-1: A portion of the scan of 2AT in the frequency range from 10355 to 10435 MHz recorded by overlapping spectra with 50 co-added decays per each spectrum. Lines belonging to the $5_{05} \leftarrow 4_{14}$ transition of the parent species and of the ^{34}S-isotopologue are labelled with the corresponding conformer. The intensities are given in a logarithmic scale in an arbitrary unit. The temperature of the molecular jet was approximately 1-2 K.