Supplementary information for: Structural and Spectroscopic Characterization of *E*- and *Z*- Isomers of Azobenzene

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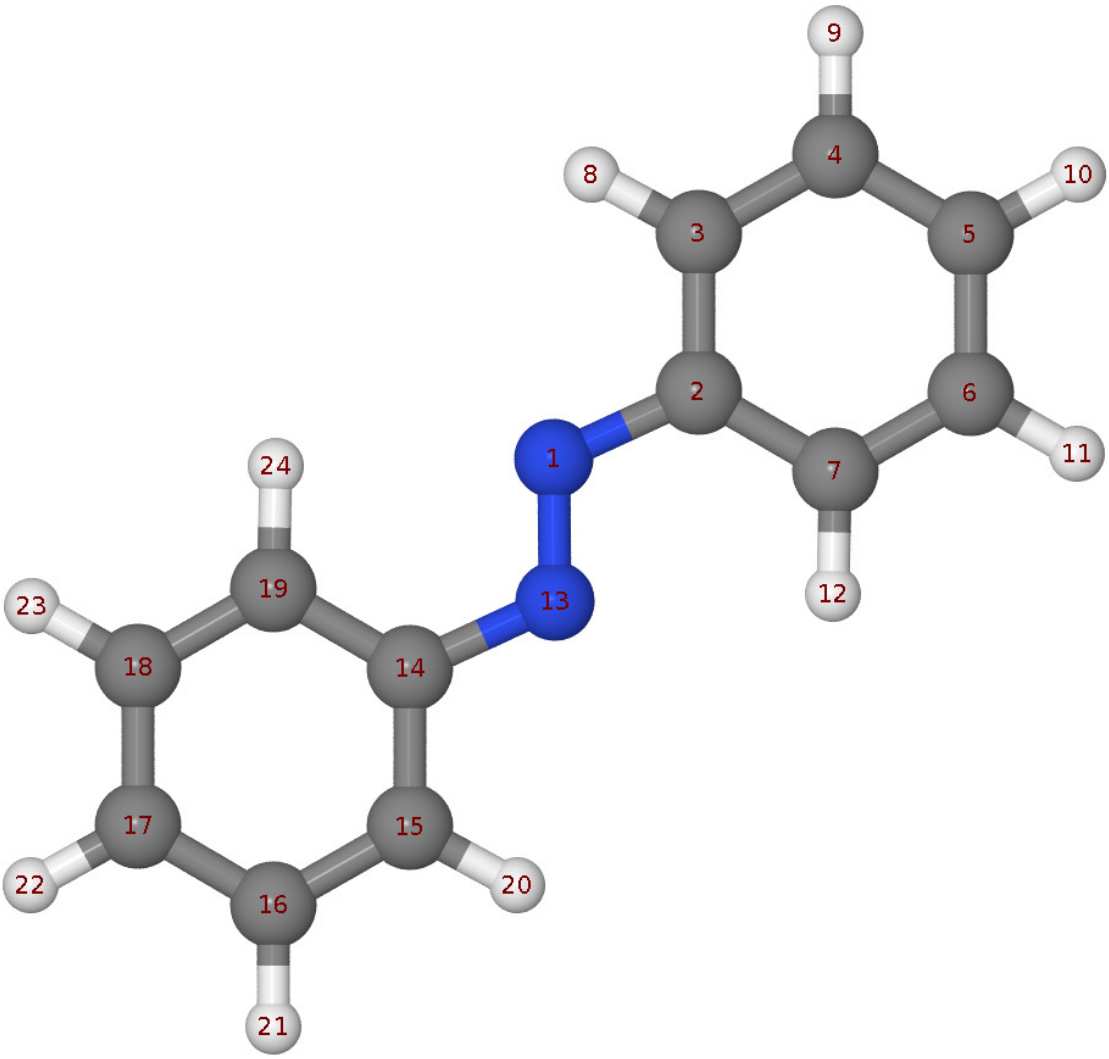

Figure S1: Atom numbering scheme of azobenzene used in the definition of the internal symmetry coordinates of the normal mode analysis.

Table S1: Mean unsigned errors (MUE) of each theoretical approach relatively to a set of experimental frequencies of azobenzene.

Method	**Basis Set**	**MUE[a] / cm^{-1}**	**References**
BP86	6-311++G(3df,3pd)	15	Present work
	cc-pVTZ	10	Present work
	TZVP	15	Ref. 1
PW91	6-311++G(3df,3pd)	12	Present work
	cc-pVTZ	7	Present work
B3LYP	6-311++G(3df,3pd)	25	Present work
	cc-pVTZ	28	Present work
B97-1	6-311++G(3df,3pd)	18	Present work
	cc-pVTZ	22	Ref. 2
	aug-cc-pVTZ	19	Ref. 2
OLYP	6-311++G(3df,3pd)	11	Present work
	cc-pVTZ	7	Ref. 2
MP2	cc-pVTZ	23	Ref. 1

[a] Vibrational frequencies of both the *E* and *Z* forms of azobenzene were used in the calculation of the MUE except with the aug-cc-pVTZ basis set where they were only available for the *E* form.

References

(1) Fliegl, H.; Köhn, A.; Hättig, C.; Ahlrichs, R. *J. Am. Chem. Soc.* **2003**, *125*, 9821–9827.

(2) Klug, R. L.; Burcl, R. *J. Phys. Chem. A* **2010**, *114*, 6401–6407.

Table S2: Theoretical Frequencies (ν/ cm^{-1}) and IR Intensities (I/ km mol^{-1}) of *E*-AB and *Z*-AB forms. The calculated frequencies are not scaled. Raman scattering activities (S/ Å^4 a.m.u.$^{-1}$) calculated at the PW91/cc-pVTZ level are also given.

***E*-AB**							
BP86 / 6-311++G(3df,3pd)		BP86 / cc-pVTZ		B3LYP / 6-311++G(3df,3pd)		B3LYP / cc-pVTZ	
ν	I	ν	I	ν	I	ν	I
3133.9	0.0	3128.6	0.0	3215.7	8.2	3212.4	8.8
3133.9	12.8	3128.6	13.6	3215.6	0.0	3212.3	0.0
3123.0	0.0	3118.2	0.0	3200.1	0.0	3196.9	0.0
3122.8	38.5	3118.0	43.4	3200.0	27.5	3196.7	31.9
3113.2	0.0	3108.6	0.0	3190.2	0.0	3187.1	0.0
3113.1	30.9	3108.5	33.6	3190.1	33.8	3187.0	40.2
3102.5	17.0	3098.4	0.0	3179.3	18.2	3176.3	0.0
3102.5	0.0	3098.4	18.0	3179.2	0.0	3176.3	20.9
3091.4	0.0	3088.3	0.0	3168.0	0.0	3165.9	0.0
3091.3	4.4	3088.2	5.0	3167.9	2.5	3165.8	2.8
1584.8	0.0	1589.2	0.0	1640.1	0.0	1644.7	0.0
1581.4	6.1	1586.2	5.9	1633.9	3.0	1639.1	3.1
1567.7	0.0	1573.3	0.0	1622.6	0.0	1628.6	0.0
1563.7	2.9	1569.4	3.9	1617.0	3.5	1623.1	4.7
1471.5	0.0	1475.3	0.0	1547.9	0.0	1550.9	0.0
1462.3	7.3	1467.4	9.5	1517.1	9.6	1521.9	12.5
1446.5	0.0	1452.4	0.0	1503.6	0.0	1509.0	0.0
1434.4	10.5	1440.6	12.5	1484.0	10.2	1489.8	12.6
1407.9	0.0	1409.5	0.0	1477.1	0.0	1481.7	0.0
1343.5	0.0	1346.0	0.0	1348.9	4.9	1352.3	5.6
1340.3	7.1	1343.0	6.8	1348.3	0.0	1351.1	0.0
1291.6	0.0	1295.1	0.0	1342.6	0.0	1345.6	0.0
1287.3	1.2	1291.4	1.8	1333.7	5.4	1336.9	4.9
1213.1	18.7	1217.1	18.2	1246.9	17.7	1251.5	17.6
1168.4	0.0	1172.0	0.0	1204.5	0.0	1208.0	0.0
1145.9	0.0	1147.9	0.4	1182.5	0.0	1183.7	0.0
1145.9	0.4	1147.9	0.0	1182.4	0.4	1183.7	0.3
1134.5	34.6	1136.5	33.0	1175.7	33.2	1177.5	31.4
1115.8	0.0	1119.5	0.0	1156.4	0.0	1160.5	0.0
1066.8	13.7	1069.0	15.1	1101.1	11.7	1103.2	12.6
1063.0	0.0	1064.8	0.0	1097.5	0.0	1099.2	0.0
1009.8	12.8	1012.6	0.0	1040.1	11.9	1043.5	0.0
1009.7	0.0	1012.0	13.7	1039.6	0.0	1043.2	13.1
965.6	0.0	990.1	3.2	1011.1	0.0	1021.6	2.1
965.5	0.0	989.9	0.0	1010.8	0.1	1021.4	0.0
965.3	0.1	977.9	0.4	1000.9	0.0	1019.7	0.5
964.2	2.8	977.4	0.0	999.5	0.01	1019.2	0.0
955.5	0.0	962.3	0.0	998.3	0.0	1003.8	0.0
953.8	0.03	961.6	0.02	997.2	2.4	1003.0	0.004
913.9	7.8	924.8	7.9	955.5	8.2	964.9	8.0
907.9	0.0	919.0	0.0	949.5	0.0	959.1	0.0
903.9	0.0	909.6	0.0	932.7	0.0	937.6	0.0
826.2	0.0	831.5	0.0	861.7	0.0	866.0	0.0
824.6	0.1	830.1	0.1	860.4	0.1	864.7	0.1
808.3	0.4	815.0	0.5	831.9	0.3	838.1	0.5
764.0	75.5	777.4	52.6	794.2	79.2	806.0	55.5
743.8	0.0	757.0	0.0	773.9	0.0	785.4	0.0
666.1	64.9	683.9	79.6	693.0	67.2	710.2	80.0
660.0	0.0	679.9	0.0	683.5	0.0	705.5	0.0
657.2	0.0	663.1	0.0	683.5	0.0	686.5	0.0
609.0	0.8	611.9	0.6	631.9	0.6	634.7	0.5
602.5	0.0	605.6	0.0	626.1	0.0	629.0	0.0
533.9	12.5	540.4	13.9	557.3	13.4	563.2	14.4
529.1	5.6	530.6	6.5	548.2	5.3	549.7	6.0
512.8	24.4	512.7	23.7	529.0	25.7	528.9	25.3
463.6	0.0	470.7	0.0	486.0	0.0	492.3	0.0
400.9	0.0	405.3	0.0	420.0	0.0	423.6	0.0
397.4	0.0003	401.7	0.0	416.9	0.004	420.4	0.003
298.5	0.0	298.3	0.0	307.5	0.0	309.1	0.6
289.9	0.9	294.3	0.6	305.2	0.8	307.4	0.0
233.6	0.0	238.3	0.0	249.2	0.0	253.2	0.0
216.1	0.0	216.1	0.0	223.5	0.0	223.8	0.0
86.8	0.0	95.3	0.0	92.4	0.0	99.2	0.0
83.0	2.0	82.6	1.9	86.3	2.0	86.3	1.9
60.6	1.5	60.1	1.4	63.5	1.4	63.2	1.3
19.3	0.1	20.4	0.1	21.5	0.04	22.0	0.04

Table S2 (Cont.)

***E*-AB**								
B97-1 / 6-311++G(3df,3pd)		OLYP / cc-pVTZ		PW91 / 6-311++G(3df,3pd)		PW91 / cc-pVTZ		
ν	I	ν	I	ν	I	ν	I	S
3208.5	9.6	3176.5	9.6	3149.0	0.0	3142.5	0.0	164.6
3208.4	0.0	3176.4	0.0	3149.0	13.1	3142.5	13.9	0.0
3195.9	0.0	3159.6	0.0	3139.6	0.0	3133.5	0.0	597.7
3195.7	28.7	3159.4	35.0	3139.4	36.1	3133.3	40.5	0.0
3186.1	0.0	3149.0	0.0	3129.8	0.0	3124.0	0.0	354.0
3186.0	27.7	3148.9	39.7	3129.8	27.5	3123.9	30.6	0.0
3175.5	15.1	3136.3	21.3	3119.4	0.0	3113.9	0.0	324.5
3175.5	0.0	3136.3	0.0	3119.4	15.8	3113.9	17.0	0.0
3164.2	0.0	3124.1	0.0	3108.3	0.0	3103.9	0.0	88.2
3164.1	2.5	3124.0	5.5	3108.2	4.4	3103.8	5.0	0.0
1632.4	0.0	1599.3	0.0	1593.5	0.0	1598.2	0.0	830.8
1627.0	3.0	1595.1	6.3	1589.8	6.4	1594.8	6.2	0.0
1616.0	0.0	1579.8	0.0	1575.5	0.0	1581.6	0.0	26.0
1610.0	3.6	1575.7	2.4	1571.4	2.7	1577.6	3.8	0.0
1539.2	0.0	1487.6	0.0	1479.4	0.0	1483.1	0.0	727.0
1506.8	8.6	1473.7	6.3	1467.6	7.0	1472.8	9.4	0.0
1492.7	0.0	1457.2	0.0	1451.5	0.0	1457.7	0.0	518.4
1474.6	10.5	1443.3	10.3	1439.5	10.7	1446.0	13.1	0.0
1468.4	0.0	1425.3	0.0	1417.6	0.0	1419.6	0.0	3851.0
1342.9	0.0	1355.0	0.0	1353.4	0.0	1355.7	0.0	108.0
1341.3	7.1	1351.5	7.4	1350.1	6.9	1352.6	6.5	0.0
1331.6	0.0	1302.3	0.0	1295.1	0.0	1298.8	0.0	319.3
1324.6	3.0	1297.3	1.3	1290.8	1.0	1295.2	1.7	0.0
1245.2	20.8	1215.9	17.2	1221.0	20.8	1225.1	20.4	0.0
1199.2	0.0	1176.9	0.0	1173.0	0.0	1176.9	0.0	868.6
1175.3	0.4	1156.8	0.0	1148.1	0.0	1149.9	0.4	0.0
1175.0	0.0	1156.8	0.3	1148.1	0.5	1149.9	0.0	33.8
1165.7	32.9	1148.8	36.6	1137.9	33.5	1139.6	32.1	0.0
1151.0	0.0	1122.5	0.0	1121.9	0.0	1125.5	0.0	2514.4
1091.9	11.8	1079.2	11.9	1070.6	13.8	1072.9	15.2	0.0
1087.5	0.0	1075.3	0.0	1066.9	0.0	1068.5	0.0	23.9
1032.3	12.7	1020.4	10.0	1014.9	13.1	1017.8	0.0	28.3
1032.1	0.0	1019.8	0.0	1014.9	0.0	1017.1	13.5	0.0
1003.4	0.0	970.5	0.0	968.2	0.0	993.5	0.0	362.9
1003.2	0.05	970.3	0.04	968.0	0.04	993.4	3.4	0.0
993.6	0.0	961.7	0.0	967.3	0.0	979.8	0.4	0.0
992.1	0.01	961.1	0.0	965.6	2.8	979.3	0.0	1.2
990.5	0.0	960.4	0.02	958.2	0.0	962.7	0.0	0.5
989.2	2.4	958.4	2.6	956.7	0.02	961.9	0.001	0.0
948.8	8.0	919.6	7.3	916.7	7.6	927.6	7.2	0.0
942.9	0.0	913.8	0.0	910.7	0.0	921.7	0.0	0.1
927.3	0.0	903.5	0.0	906.7	0.0	913.5	0.0	6.9
857.5	0.0	830.5	0.0	827.5	0.0	832.8	0.0	2.9
856.1	0.1	829.3	0.1	826.0	0.1	831.3	0.04	0.0
826.6	0.3	806.2	0.3	812.0	0.4	819.7	0.6	0.0
789.6	83.6	766.8	76.1	764.8	75.8	780.0	48.3	0.0
769.6	0.0	745.5	0.0	744.3	0.0	759.1	0.0	0.2
688.3	65.8	664.3	61.4	664.8	63.1	685.2	76.8	0.0
677.9	0.0	660.5	0.0	661.5	0.0	681.7	0.0	0.8
676.8	0.0	654.4	0.0	655.6	0.0	664.7	0.0	7.0
625.1	0.7	609.0	0.8	610.3	0.8	613.3	0.6	0.0
618.8	0.0	602.5	0.0	603.6	0.0	606.8	0.0	23.0
553.9	13.5	537.2	11.8	534.2	12.6	541.3	13.7	0.0
541.7	3.7	528.9	5.0	530.5	5.4	532.1	6.3	0.0
523.8	27.1	514.4	25.3	514.6	24.3	514.5	23.5	0.0
481.5	0.0	465.4	0.0	463.8	0.0	471.3	0.0	0.3
415.8	0.0	401.1	0.0	401.5	0.0	406.2	0.0	0.01
412.7	0.01	398.0	0.01	398.0	0.004	402.7	0.001	0.0
304.6	0.0	299.0	0.0	299.8	0.0	299.6	0.0	1.8
303.0	0.8	290.7	0.9	290.5	0.9	295.2	0.6	0.0
247.6	0.0	227.2	0.0	234.2	0.0	239.0	0.0	3.8
218.2	0.0	214.3	0.0	217.1	0.0	217.1	0.0	1.0
91.2	0.0	80.7	2.0	86.3	0.0	94.8	0.0	3.3
80.7	2.0	78.0	0.0	82.4	2.0	82.3	1.9	0.0
63.7	1.5	60.6	1.4	61.5	1.5	60.9	1.4	0.0
22.3	0.0	13.0	0.1	15.6	0.03	14.8	0.03	0.0

Table S2 (Cont.)

Z-AB								
BP86 / 6-311++G(3df,3pd)		BP86 / cc-pVTZ		B3LYP / 6-311++G(3df,3pd)		B3LYP / cc-pVTZ	
ν	I	ν	I	ν	I	ν	I
3126.6	3.1	3121.5	4.4	3204.6	2.9	3200.6	4.0
3126.6	4.7	3121.4	7.4	3204.5	1.6	3200.5	2.4
3121.4	1.2	3116.7	0.9	3197.3	1.9	3194.0	1.8
3121.1	35.2	3116.5	38.9	3197.0	30.0	3193.8	36.2
3113.3	5.6	3108.7	5.9	3189.3	6.0	3186.0	6.8
3113.3	14.6	3108.7	16.1	3189.2	14.2	3185.9	16.8
3102.1	1.1	3098.2	1.0	3178.2	0.9	3175.2	0.9
3102.0	9.2	3098.1	9.2	3178.2	9.7	3175.2	10.7
3093.6	0.5	3090.5	0.6	3169.5	0.2	3167.1	0.3
3093.5	1.8	3090.4	1.9	3169.4	1.3	3167.0	1.4
1581.9	5.2	1586.3	3.5	1641.1	13.6	1644.9	10.6
1576.2	1.8	1581.4	2.2	1629.0	4.9	1634.6	5.3
1563.8	0.4	1569.1	0.5	1618.3	0.8	1623.9	1.2
1556.9	4.1	1562.1	4.7	1610.9	4.8	1616.3	5.8
1505.5	45.8	1506.6	48.6	1597.1	21.0	1600.3	24.8
1458.3	3.8	1464.2	4.9	1513.5	6.8	1518.7	8.5
1452.0	1.2	1456.9	0.8	1510.7	6.7	1515.6	6.9
1433.1	3.0	1438.9	3.3	1482.9	2.5	1488.2	2.7
1426.6	6.1	1432.3	7.2	1476.5	5.4	1481.7	6.6
1334.1	0.1	1337.1	0.03	1353.3	0.0007	1356.7	0.004
1327.7	2.0	1330.9	1.8	1351.2	0.1	1354.7	0.2
1294.6	0.05	1298.4	0.1	1327.6	0.1	1330.4	0.1
1289.4	1.7	1292.8	2.0	1317.6	2.2	1320.5	2.2
1164.3	0.5	1167.0	0.7	1201.5	0.5	1203.7	0.6
1164.0	0.3	1166.9	0.3	1201.0	0.5	1203.4	0.6
1146.7	0.1	1148.8	0.2	1183.0	0.1	1184.3	0.1
1146.4	0.02	1148.6	0.04	1182.6	0.1	1183.9	0.1
1123.4	2.5	1127.7	1.9	1164.9	0.8	1169.5	0.5
1099.5	0.1	1104.5	0.1	1142.8	0.3	1148.2	0.2
1069.9	1.0	1072.3	1.2	1102.5	0.7	1104.8	0.8
1067.8	12.6	1070.3	12.9	1100.9	11.5	1103.1	11.7
1015.1	2.8	1019.0	2.0	1044.1	4.5	1048.8	1.9
1015.0	4.3	1018.6	4.8	1044.1	2.9	1048.6	5.0
971.7	1.1	989.5	1.1	1011.1	0.5	1020.5	0.9
970.9	0.1	988.8	0.4	1011.0	0.0001	1020.1	0.4
962.4	0.03	965.8	0.05	1002.7	0.1	1008.4	0.1
962.2	0.3	965.8	0.5	1002.6	0.9	1008.2	0.7
947.0	0.2	947.6	0.2	992.5	0.3	990.0	0.2
946.8	0.5	947.2	0.6	992.4	0.2	989.6	0.4
898.9	20.2	903.3	21.1	942.0	21.9	945.8	22.7
894.8	0.2	898.8	0.4	937.4	0.5	940.4	0.7
827.4	4.2	827.9	2.8	865.1	5.8	865.5	4.4
819.2	1.7	821.8	1.5	855.7	1.0	857.5	0.9
816.9	6.1	819.3	6.8	854.3	3.0	856.2	3.3
758.0	14.6	764.6	12.9	790.1	16.0	795.8	14.1
752.2	37.4	755.8	34.2	778.0	46.2	781.2	41.7
738.6	0.2	741.0	0.04	762.2	0.04	764.4	0.01
688.7	95.7	690.7	76.4	716.2	88.6	717.6	82.7
675.5	18.6	686.2	20.4	703.6	19.9	713.1	21.2
668.7	7.1	684.1	23.6	693.5	5.0	708.0	7.9
609.9	0.2	613.2	0.3	634.1	0.3	637.2	0.5
606.7	0.04	609.7	0.1	630.1	0.05	632.8	0.1
585.8	4.8	589.4	5.4	611.7	4.2	615.1	4.6
527.1	0.3	528.9	0.3	548.5	0.4	550.2	0.4
490.5	5.1	492.2	5.0	509.3	4.5	510.9	4.4
434.9	4.8	437.3	4.9	452.5	2.2	454.6	2.3
412.8	3.4	414.3	3.1	434.7	3.6	436.0	3.2
396.7	0.03	399.3	0.02	414.3	0.04	416.6	0.04
392.3	4.6	395.6	4.6	411.5	3.6	414.3	3.6
273.0	5.8	273.6	5.8	290.5	5.4	291.0	5.4
262.8	0.3	263.5	0.3	271.5	0.3	272.1	0.3
168.8	0.2	168.0	0.2	172.9	0.2	172.3	0.2
150.3	3.9	151.0	3.9	156.0	2.7	156.7	2.6
67.9	0.5	67.1	0.5	68.2	0.5	67.8	0.5
49.2	0.02	49.5	0.01	46.8	0.005	46.7	0.001
40.3	1.4	41.1	1.5	42.2	1.2	42.8	1.3

Table S2 (Cont.)

Z-AB

B97-1 / 6-311++G(3df,3pd)		OLYP / cc-pVTZ		PW91 / 6-311++G(3df,3pd)		PW91 / cc-pVTZ		
ν	I	ν	I	ν	I	ν	I	S
3197.7	4.0	3169.6	1.0	3142.2	4.2	3136.0	5.2	469.7
3197.6	3.3	3169.6	4.1	3142.1	6.8	3135.9	9.8	77.0
3192.7	1.1	3158.3	2.1	3137.7	0.5	3131.5	0.2	182.0
3192.4	27.7	3158.1	36.3	3137.4	30.6	3131.3	33.9	22.8
3184.7	4.6	3150.0	16.8	3130.0	4.6	3124.0	4.9	104.9
3184.5	11.7	3149.9	7.8	3129.9	12.6	3123.9	14.2	72.8
3173.5	0.7	3136.7	12.4	3119.0	1.0	3113.6	1.0	168.9
3173.4	7.7	3136.7	1.3	3118.9	8.1	3113.5	8.4	97.9
3165.0	0.3	3127.0	0.5	3110.6	0.5	3106.0	0.6	39.7
3164.9	1.5	3126.9	2.2	3110.4	1.8	3105.9	1.9	19.8
1633.2	11.2	1599.2	8.5	1591.0	6.3	1595.6	4.2	102.4
1622.8	4.7	1591.1	2.7	1584.6	1.8	1590.2	2.2	94.3
1612.5	0.6	1577.1	0.4	1571.7	0.3	1577.3	0.5	3.3
1605.1	4.7	1570.0	4.0	1564.6	4.0	1570.1	4.7	25.2
1588.7	22.3	1535.5	40.3	1518.6	44.2	1520.1	47.2	519.0
1504.2	6.6	1469.7	3.6	1463.2	3.6	1469.2	4.9	0.5
1501.5	6.6	1464.5	2.2	1457.6	2.0	1462.8	1.7	156.8
1474.4	2.7	1443.3	2.3	1438.2	2.8	1444.4	3.1	6.2
1467.9	5.4	1436.3	5.6	1431.6	6.3	1437.6	7.6	3.7
1343.3	0.002	1345.1	0.04	1343.8	0.1	1346.6	0.05	14.3
1341.2	0.3	1340.1	1.9	1336.9	2.3	1339.9	2.1	0.1
1324.2	0.1	1304.4	0.01	1298.1	0.03	1301.9	0.1	1.4
1314.2	1.9	1298.6	1.9	1293.2	1.6	1296.7	1.9	1.3
1194.8	0.4	1175.4	0.6	1168.0	0.2	1171.0	0.2	13.7
1194.8	0.5	1174.8	0.4	1167.6	0.5	1170.2	0.7	12.6
1175.9	0.1	1157.6	0.1	1148.8	0.1	1150.6	0.2	11.1
1175.3	0.04	1157.4	0.03	1148.6	0.003	1150.4	0.02	2.9
1161.6	1.5	1131.1	1.6	1131.1	2.7	1135.0	2.0	43.4
1140.8	0.1	1106.1	0.2	1107.2	0.2	1111.9	0.2	360.7
1095.7	0.7	1080.9	0.8	1074.1	1.0	1076.4	1.2	1.7
1094.5	11.8	1078.8	11.3	1072.0	12.8	1074.4	13.1	4.7
1038.6	2.8	1024.4	3.7	1020.3	3.0	1024.1	2.1	40.4
1038.5	4.1	1024.2	2.9	1020.2	4.2	1023.7	4.6	7.3
1003.4	0.4	971.1	0.6	974.4	1.1	993.2	1.2	9.2
1003.3	0.0004	970.7	0.001	973.5	0.04	992.5	0.4	105.3
995.6	0.9	964.6	0.9	966.2	0.03	968.0	0.04	0.4
995.5	0.04	963.6	0.01	966.1	0.3	967.8	0.6	0.9
984.6	0.4	953.1	0.5	951.1	0.2	949.2	0.3	4.8
984.5	0.2	953.0	0.2	951.1	0.4	948.8	0.5	0.0
936.0	22.7	902.9	18.3	902.4	20.0	906.9	20.8	1.9
929.9	0.4	899.4	0.4	898.4	0.2	902.2	0.3	2.4
863.1	6.7	828.2	1.8	830.9	4.2	831.1	2.6	27.9
850.8	1.1	824.1	1.6	821.5	1.6	824.0	1.4	12.2
849.5	2.5	819.7	10.3	819.6	5.7	822.0	6.4	16.4
785.5	15.2	760.5	17.7	760.9	14.8	768.3	12.5	23.8
773.2	48.2	753.1	31.2	756.0	37.2	760.1	32.8	1.6
758.6	0.2	736.0	0.3	742.6	0.3	745.4	0.02	9.7
712.4	91.3	690.2	94.2	690.6	97.8	692.6	71.8	11.6
699.0	19.5	676.3	19.1	676.1	17.8	688.3	19.2	0.2
687.3	4.4	666.4	2.9	668.8	6.3	686.6	26.4	0.8
628.2	0.5	612.3	0.3	611.4	0.2	614.9	0.3	15.1
622.9	0.1	607.8	0.04	607.9	0.04	611.0	0.1	3.2
606.5	4.0	590.1	4.2	587.7	4.6	591.7	5.1	84.8
544.7	0.4	531.4	0.5	528.4	0.2	530.4	0.2	1.1
504.4	4.8	492.0	4.9	492.7	5.0	494.5	4.7	0.1
447.2	1.9	435.5	4.5	435.8	4.8	438.7	5.0	2.9
432.3	3.3	415.4	3.8	415.4	3.5	416.8	3.1	21.7
409.7	0.1	395.3	0.01	397.7	0.1	400.6	0.04	23.2
406.3	3.5	393.5	5.2	393.0	4.5	396.7	4.4	1.2
286.9	5.3	281.2	5.9	274.9	5.8	275.3	5.8	2.2
271.1	0.3	259.6	0.3	263.9	0.2	264.8	0.2	14.4
171.2	0.2	163.0	0.2	170.1	0.2	168.9	0.2	30.5
153.8	2.5	150.3	3.7	150.4	4.0	151.3	4.0	5.4
68.4	0.4	64.7	0.6	68.8	0.5	68.0	0.5	11.9
48.1	0.01	47.6	0.001	49.2	0.03	49.9	0.02	24.6
40.2	1.1	45.8	1.6	40.2	1.4	41.1	1.4	3.0

Table S3: Cartesian coordinates of the optimized geometries of E-AB and Z-AB forms.

Atom	E-AB											
	BP86 / 6-311++G(3df,3pd)			BP86 / cc-pVTZ			B3LYP / 6-311++(3df,3pd)			B3LYP / cc-pVTZ		
	x	**y**	**z**	**x**	**y**	**z**	**x**	**y**	**z**	**x**	**y**	**z**
N	-0.000884	0.633676	0.000000	-0.002308	0.633516	0.000000	0.000929	0.624347	0.000000	-0.000271	0.624194	0.000000
C	1.284523	1.232570	0.000000	1.284192	1.233287	0.000000	1.279243	1.233610	0.000000	1.278960	1.234135	0.000000
C	1.293411	2.637660	0.000000	1.292884	2.638031	0.000000	1.279243	2.628933	0.000000	1.278960	2.629271	0.000000
C	2.503058	3.333243	0.000000	2.502322	3.333468	0.000000	2.478619	3.328569	0.000000	2.478187	3.328772	0.000000
C	3.710825	2.629036	0.000000	3.709861	2.629245	0.000000	3.683525	2.636217	0.000000	3.682907	2.636325	0.000000
C	3.704878	1.225478	0.000000	3.704050	1.225889	0.000000	3.685524	1.241001	0.000000	3.685009	1.241255	0.000000
C	2.503058	0.524728	0.000000	2.502322	0.525459	0.000000	2.493689	0.537041	0.000000	2.493194	0.537567	0.000000
H	0.335461	3.159251	0.000000	0.334539	3.158787	0.000000	0.328277	3.143435	0.000000	0.327522	3.143012	0.000000
H	2.504555	4.423959	0.000000	2.504077	4.424193	0.000000	2.472889	4.410022	0.000000	2.472703	4.410373	0.000000
H	4.658617	3.169341	0.000000	4.657630	3.169597	0.000000	4.620039	3.177542	0.000000	4.619534	3.177756	0.000000
H	4.650038	0.679885	0.000000	4.649334	0.680474	0.000000	4.625169	0.704677	0.000000	4.624869	0.704994	0.000000
H	2.478719	-0.564254	0.000000	2.476091	-0.563476	0.000000	2.481189	-0.542337	0.000000	2.478968	-0.541861	0.000000
N	0.000884	-0.633676	0.000000	0.002308	-0.633516	0.000000	-0.000929	-0.624347	0.000000	0.000271	-0.624194	0.000000
C	-1.284523	-1.232570	0.000000	-1.284192	-1.233287	0.000000	-1.279243	-1.233610	0.000000	-1.278960	-1.234135	0.000000
C	-1.293411	-2.637660	0.000000	-1.292884	-2.638031	0.000000	-1.279243	-2.628933	0.000000	-1.278960	-2.629271	0.000000
C	-2.503058	-3.333243	0.000000	-2.502322	-3.333468	0.000000	-2.478619	-3.328569	0.000000	-2.478187	-3.328772	0.000000
C	-3.710825	-2.629036	0.000000	-3.709861	-2.629245	0.000000	-3.683525	-2.636217	0.000000	-3.682907	-2.636325	0.000000
C	-3.704878	-1.225478	0.000000	-3.704050	-1.225889	0.000000	-3.685524	-1.241001	0.000000	-3.685009	-1.241255	0.000000
C	-2.503058	-0.524728	0.000000	-2.502322	-0.525459	0.000000	-2.493689	-0.537041	0.000000	-2.493194	-0.537567	0.000000
H	-0.335461	-3.159251	0.000000	-0.334539	-3.158787	0.000000	-0.328277	-3.143435	0.000000	-0.327522	-3.143012	0.000000
H	-2.504555	-4.423959	0.000000	-2.504077	-4.424193	0.000000	-2.472889	-4.410022	0.000000	-2.472703	-4.410373	0.000000
H	-4.658617	-3.169341	0.000000	-4.657630	-3.169597	0.000000	-4.620039	-3.177542	0.000000	-4.619534	-3.177756	0.000000
H	-4.650038	-0.679885	0.000000	-4.649334	-0.680474	0.000000	-4.625169	-0.704677	0.000000	-4.624869	-0.704994	0.000000
H	-2.478719	0.564254	0.000000	-2.476091	0.563476	0.000000	-2.481189	0.542337	0.000000	-2.478968	0.541861	0.000000

Table S3 (Cont.)

Atom	*E*-AB											
	B97-1 / 6-311++(3df,3pd)			OLYP / 6-311++(3df,3pd)			PW91 / 6-311++(3df,3pd)			PW91 / cc-pVTZ		
	x	**y**	**z**	**x**	**y**	**z**	**x**	**y**	**z**	**x**	**y**	**z**
N	0.000771	0.626393	0.000000	0.001006	0.631288	0.000000	-0.000526	0.632020	0.000000	-0.002264	0.631954	0.000000
C	1.284991	1.227353	0.000000	1.284120	1.234003	0.000000	1.280567	1.230998	0.000000	1.280084	1.231851	0.000000
C	1.291863	2.625692	0.000000	1.284120	2.638571	0.000000	1.289495	2.633214	0.000000	1.288755	2.633777	0.000000
C	2.497762	3.320215	0.000000	2.484914	3.345198	0.000000	2.496549	3.327371	0.000000	2.495669	3.327776	0.000000
C	3.701298	2.619376	0.000000	3.698256	2.655189	0.000000	3.701769	2.624530	0.000000	3.700707	2.624862	0.000000
C	3.695797	1.220991	0.000000	3.704427	1.254292	0.000000	3.695899	1.223895	0.000000	3.694972	1.224373	0.000000
C	2.497762	0.521639	0.000000	2.511033	0.542539	0.000000	2.496549	0.524709	0.000000	2.495669	0.525474	0.000000
H	0.341373	3.145843	0.000000	0.327873	3.154504	0.000000	0.333074	3.153345	0.000000	0.331792	3.152977	0.000000
H	2.498138	4.403763	0.000000	2.474328	4.432228	0.000000	2.498122	4.415987	0.000000	2.497536	4.416531	0.000000
H	4.642657	3.156491	0.000000	4.637606	3.202804	0.000000	4.647753	3.163784	0.000000	4.646790	3.164218	0.000000
H	4.634419	0.678671	0.000000	4.650988	0.718415	0.000000	4.639293	0.679432	0.000000	4.638610	0.680033	0.000000
H	2.478426	-0.560037	0.000000	2.507711	-0.541933	0.000000	2.471548	-0.562316	0.000000	2.468477	-0.561581	0.000000
N	-0.000771	-0.626393	0.000000	-0.001006	-0.631288	0.000000	0.000526	-0.632020	0.000000	0.002264	-0.631954	0.000000
C	-1.284991	-1.227353	0.000000	-1.284120	-1.234003	0.000000	-1.280567	-1.230998	0.000000	-1.280084	-1.231851	0.000000
C	-1.291863	-2.625692	0.000000	-1.284120	-2.638571	0.000000	-1.289495	-2.633214	0.000000	-1.288755	-2.633777	0.000000
C	-2.497762	-3.320215	0.000000	-2.484914	-3.345198	0.000000	-2.496549	-3.327371	0.000000	-2.495669	-3.327776	0.000000
C	-3.701298	-2.619376	0.000000	-3.698256	-2.655189	0.000000	-3.701769	-2.624530	0.000000	-3.700707	-2.624862	0.000000
C	-3.695797	-1.220991	0.000000	-3.704427	-1.254292	0.000000	-3.695899	-1.223895	0.000000	-3.694972	-1.224373	0.000000
C	-2.497762	-0.521639	0.000000	-2.511033	-0.542539	0.000000	-2.496549	-0.524709	0.000000	-2.495669	-0.525474	0.000000
H	-0.341373	-3.145843	0.000000	-0.327873	-3.154504	0.000000	-0.333074	-3.153345	0.000000	-0.331792	-3.152977	0.000000
H	-2.498138	-4.403763	0.000000	-2.474328	-4.432228	0.000000	-2.498122	-4.415987	0.000000	-2.497536	-4.416531	0.000000
H	-4.642657	-3.156491	0.000000	-4.637606	-3.202804	0.000000	-4.647753	-3.163784	0.000000	-4.646790	-3.164218	0.000000
H	-4.634419	-0.678671	0.000000	-4.650988	-0.718415	0.000000	-4.639293	-0.679432	0.000000	-4.638610	-0.680033	0.000000
H	-2.478426	0.560037	0.000000	-2.507711	0.541933	0.000000	-2.471548	0.562316	0.000000	-2.468477	0.561581	0.000000

Table S3 (Cont.)

Atom	*Z*-AB											
	BP86 / 6-311++G(3df,3pd)			BP86 / cc-pVTZ			B3LYP / 6-311++(3df,3pd)			B3LYP / cc-pVTZ		
	x	**y**	**z**	**x**	**y**	**z**	**x**	**y**	**z**	**x**	**y**	**z**
N	-0.007786	0.627126	1.933590	-0.008320	0.626774	1.929146	-0.027187	0.619120	1.936520	-0.027550	0.618845	1.932564
C	-0.136152	1.429766	0.752868	-0.136414	1.432195	0.748892	-0.158303	1.419761	0.756544	-0.158471	1.421759	0.753107
C	0.638792	2.600167	0.702810	0.640602	2.601283	0.702221	0.633671	2.565759	0.686383	0.635503	2.566590	0.685612
C	0.485678	3.493179	-0.357061	0.486432	3.500192	-0.352061	0.487932	3.444936	-0.376931	0.488774	3.451189	-0.372759
C	-0.485678	3.260390	-1.337695	-0.486432	3.273241	-1.332278	-0.487932	3.218213	-1.342682	-0.488774	3.229851	-1.337853
C	-1.297248	2.122835	-1.255565	-1.299252	2.136665	-1.254504	-1.313052	2.102589	-1.241292	-1.315202	2.115142	-1.240123
C	-1.121181	1.200382	-0.224306	-1.122852	1.208965	-0.228065	-1.148279	1.197241	-0.202303	-1.149980	1.204894	-0.205458
H	1.359058	2.786963	1.500400	1.361258	2.783261	1.500529	1.358347	2.749754	1.467751	1.360784	2.746036	1.467578
H	1.109094	4.387036	-0.405759	1.110819	4.393555	-0.397401	1.121071	4.319591	-0.440163	1.122972	4.325447	-0.433211
H	-0.623358	3.972106	-2.152429	-0.625107	3.989499	-2.142857	-0.616262	3.915075	-2.159502	-0.618117	3.930948	-2.151081
H	-2.073377	1.951136	-2.002969	-2.076555	1.969665	-2.001761	-2.088619	1.934187	-1.976351	-2.092120	1.951083	-1.974950
H	-1.752847	0.314811	-0.160678	-1.756560	0.324598	-0.167766	-1.790002	0.331803	-0.125693	-1.793634	0.340479	-0.131440
N	0.007786	-0.627126	1.933590	0.008320	-0.626774	1.929146	0.027187	-0.619120	1.936520	0.027550	-0.618845	1.932564
C	0.136152	-1.429766	0.752868	0.136414	-1.432195	0.748892	0.158303	-1.419761	0.756544	0.158471	-1.421759	0.753107
C	-0.638792	-2.600167	0.702810	-0.640602	-2.601283	0.702221	-0.633671	-2.565759	0.686383	-0.635503	-2.566590	0.685612
C	-0.485678	-3.493179	-0.357061	-0.486432	-3.500192	-0.352061	-0.487932	-3.444936	-0.376931	-0.488774	-3.451189	-0.372759
C	0.485678	-3.260390	-1.337695	0.486432	-3.273241	-1.332278	0.487932	-3.218213	-1.342682	0.488774	-3.229851	-1.337853
C	1.297248	-2.122835	-1.255565	1.299252	-2.136665	-1.254504	1.313052	-2.102589	-1.241292	1.315202	-2.115142	-1.240123
C	1.121181	-1.200382	-0.224306	1.122852	-1.208965	-0.228065	1.148279	-1.197241	-0.202303	1.149980	-1.204894	-0.205458
H	-1.359058	-2.786963	1.500400	-1.361258	-2.783261	1.500529	-1.358347	-2.749754	1.467751	-1.360784	-2.746036	1.467578
H	-1.109094	-4.387036	-0.405759	-1.110819	-4.393555	-0.397401	-1.121071	-4.319591	-0.440163	-1.122972	-4.325447	-0.433211
H	0.623358	-3.972106	-2.152429	0.625107	-3.989499	-2.142857	0.616262	-3.915075	-2.159502	0.618117	-3.930948	-2.151081
H	2.073377	-1.951136	-2.002969	2.076555	-1.969665	-2.001761	2.088619	-1.934187	-1.976351	2.092120	-1.951083	-1.974950
H	1.752847	-0.314811	-0.160678	1.756560	-0.324598	-0.167766	1.790002	-0.331803	-0.125693	1.793634	-0.340479	-0.131440

Table S3 (Cont.)

Atom	*Z*-AB											
	B97-1 / 6-311++(3df,3pd)			OLYP / 6-311++(3df,3pd)			PW91 / 6-311++(3df,3pd)			PW91 / cc-pVTZ		
	x	**y**	**z**	**x**	**y**	**z**	**x**	**y**	**z**	**x**	**y**	**z**
N	-0.029506	0.621005	1.952643	-0.016539	0.624003	1.906325	-0.009675	0.625655	1.934938	-0.009323	0.625356	1.928016
C	-0.160962	1.413208	0.764727	-0.147878	1.442892	0.737749	-0.139046	1.423261	0.756489	-0.137898	1.426844	0.750758
C	0.628858	2.563875	0.690023	0.658246	2.590718	0.679622	0.634401	2.590787	0.701174	0.637330	2.593547	0.701064
C	0.485789	3.434881	-0.384574	0.502032	3.502096	-0.360793	0.483703	3.475697	-0.362018	0.484675	3.487043	-0.354226
C	-0.485789	3.195225	-1.355794	-0.502032	3.315415	-1.315247	-0.483703	3.237604	-1.341117	-0.484675	3.256817	-1.333080
C	-1.309740	2.075131	-1.249028	-1.342700	2.203784	-1.224389	-1.293719	2.102754	-1.254197	-1.295287	2.122247	-1.253071
C	-1.147430	1.177272	-0.199259	-1.165620	1.261869	-0.212760	-1.119984	1.188240	-0.219482	-1.120373	1.199892	-0.225503
H	1.350475	2.756474	1.475221	1.407335	2.746996	1.451265	1.352010	2.781254	1.497519	1.355537	2.777408	1.498486
H	1.117487	4.312818	-0.452409	1.149816	4.373697	-0.414026	1.105942	4.367589	-0.414693	1.107586	4.378934	-0.401612
H	-0.612077	3.885367	-2.181366	-0.640340	4.040794	-2.112671	-0.619535	3.943169	-2.158695	-0.622384	3.969127	-2.144663
H	-2.081993	1.897223	-1.988421	-2.142795	2.065726	-1.947846	-2.066714	1.926935	-2.000851	-2.069704	1.952598	-1.999877
H	-1.786187	0.306943	-0.118093	-1.824943	0.402895	-0.146094	-1.749028	0.303286	-0.152941	-1.751293	0.315821	-0.164092
N	0.029506	-0.621005	1.952643	0.016539	-0.624003	1.906325	0.009675	-0.625655	1.934938	0.009323	-0.625356	1.928016
C	0.160962	-1.413208	0.764727	0.147878	-1.442892	0.737749	0.139046	-1.423261	0.756489	0.137898	-1.426844	0.750758
C	-0.628858	-2.563875	0.690023	-0.658246	-2.590718	0.679622	-0.634401	-2.590787	0.701174	-0.637330	-2.593547	0.701064
C	-0.485789	-3.434881	-0.384574	-0.502032	-3.502096	-0.360793	-0.483703	-3.475697	-0.362018	-0.484675	-3.487043	-0.354226
C	0.485789	-3.195225	-1.355794	0.502032	-3.315415	-1.315247	0.483703	-3.237604	-1.341117	0.484675	-3.256817	-1.333080
C	1.309740	-2.075131	-1.249028	1.342700	-2.203784	-1.224389	1.293719	-2.102754	-1.254197	1.295287	-2.122247	-1.253071
C	1.147430	-1.177272	-0.199259	1.165620	-1.261869	-0.212760	1.119984	-1.188240	-0.219482	1.120373	-1.199892	-0.225503
H	-1.350475	-2.756474	1.475221	-1.407335	-2.746996	1.451265	-1.352010	-2.781254	1.497519	-1.355537	-2.777408	1.498486
H	-1.117487	-4.312818	-0.452409	-1.149816	-4.373697	-0.414026	-1.105942	-4.367589	-0.414693	-1.107586	-4.378934	-0.401612
H	0.612077	-3.885367	-2.181366	0.640340	-4.040794	-2.112671	0.619535	-3.943169	-2.158695	0.622384	-3.969127	-2.144663
H	2.081993	-1.897223	-1.988421	2.142795	-2.065726	-1.947846	2.066714	-1.926935	-2.000851	2.069704	-1.952598	-1.999877
H	1.786187	-0.306943	-0.118093	1.824943	-0.402895	-0.146094	1.749028	-0.303286	-0.152941	1.751293	-0.315821	-0.164092

Table S4: Internal symmetry coordinates used in the normal mode analysis of *E*-azobenzene.[a]

Coord.	Definition	Sym.	Appr. Description
S_1	$r_{1,13}$	A_g	ν(N=N)
S_2	$r_{1,2} + r_{13,14}$	A_g	ν(NC)
S_3	$r_{1,2} - r_{13,14}$	B_u	ν(NC)
S_4	$r_{2,3} - r_{3,4} + r_{4,5} - r_{5,6} + r_{6,7} - r_{7,2} + r_{14,15} - r_{15,16} + r_{16,17} - r_{17,18} + r_{18,19} - r_{19,14}$	A_g	$\nu(CC)_1$
S_5	$r_{2,3} - r_{3,4} + r_{4,5} - r_{5,6} + r_{6,7} - r_{7,2} - r_{14,15} + r_{15,16} - r_{16,17} + r_{17,18} - r_{18,19} + r_{19,14}$	B_u	$\nu(CC)_2$
S_6	$-r_{2,3} + 2r_{3,4} - r_{4,5} - r_{5,6} + 2r_{6,7} - r_{7,2} - r_{14,15} + 2r_{15,16} - r_{16,17} - r_{17,18} + 2r_{18,19} - r_{19,14}$	A_g	$\nu(CC)_3$
S_7	$-r_{2,3} + 2r_{3,4} - r_{4,5} - r_{5,6} + 2r_{6,7} - r_{7,2} + r_{14,15} - 2r_{15,16} + r_{16,17} + r_{17,18} - 2r_{18,19} + r_{19,14}$	B_u	$\nu(CC)_4$
S_8	$r_{2,3} - r_{4,5} + r_{5,6} - r_{7,2} + r_{14,15} - r_{16,17} + r_{17,18} - r_{19,14}$	A_g	$\nu(CC)_5$
S_9	$r_{2,3} - r_{4,5} + r_{5,6} - r_{7,2} - r_{14,15} + r_{16,17} - r_{17,18} + r_{19,14}$	B_u	$\nu(CC)_6$
S_{10}	$r_{2,3} + 2r_{3,4} + r_{4,5} - r_{5,6} - 2r_{6,7} - r_{7,2} + r_{14,15} + 2r_{15,16} + r_{16,17} - r_{17,18} - 2r_{18,19} + r_{19,14}$	A_g	$\nu(CC)_7$
S_{11}	$r_{2,3} + 2r_{3,4} + r_{4,5} - r_{5,6} - 2r_{6,7} - r_{7,2} - r_{14,15} - 2r_{15,16} - r_{16,17} + r_{17,18} + 2r_{18,19} + r_{19,14}$	B_u	$\nu(CC)_8$
S_{12}	$r_{2,3} - r_{4,5} - r_{5,6} + r_{7,2} + r_{14,15} - r_{16,17} - r_{17,18} + r_{19,14}$	A_g	$\nu(CC)_9$
S_{13}	$r_{2,3} - r_{4,5} - r_{5,6} + r_{7,2} - r_{14,15} + r_{16,17} + r_{17,18} - r_{19,14}$	B_u	$\nu(CC)_{10}$
S_{14}	$r_{2,3} + r_{3,4} + r_{4,5} + r_{5,6} + r_{6,7} + r_{7,2} + r_{14,15} + r_{15,16} + r_{16,17} + r_{17,18} + r_{18,19} + r_{19,14}$	A_g	$\nu(CC)_{11}$
S_{15}	$r_{2,3} + r_{3,4} + r_{4,5} + r_{5,6} + r_{6,7} + r_{7,2} - r_{14,15} - r_{15,16} - r_{16,17} - r_{17,18} - r_{18,19} - r_{19,14}$	B_u	$\nu(CC)_{12}$
S_{16}	$r_{7,12} + r_{19,24}$	A_g	ν_s(CH)
S_{17}	$r_{7,12} - r_{19,24}$	B_u	ν_{as}(CH)
S_{18}	$r_{6,11} + r_{5,10} + r_{4,9} + r_{3,8} + r_{18,23} + r_{17,22} + r_{16,21} + r_{15,20}$	A_g	$\nu(CH)_1$
S_{19}	$r_{6,11} + r_{5,10} + r_{4,9} + r_{3,8} - r_{18,23} - r_{17,22} - r_{16,21} - r_{15,20}$	B_u	$\nu(CH)_2$
S_{20}	$r_{6,11} + r_{5,10} - r_{4,9} - r_{3,8} + r_{18,23} + r_{17,22} - r_{16,21} - r_{15,20}$	A_g	$\nu(CH)_3$
S_{21}	$r_{6,11} + r_{5,10} - r_{4,9} - r_{3,8} - r_{18,23} - r_{17,22} + r_{16,21} + r_{15,20}$	B_u	$\nu(CH)_4$
S_{22}	$r_{6,11} - r_{5,10} + r_{4,9} - r_{3,8} + r_{18,23} - r_{17,22} + r_{16,21} - r_{15,20}$	A_g	$\nu(CH)_5$
S_{23}	$r_{6,11} - r_{5,10} + r_{4,9} - r_{3,8} - r_{18,23} + r_{17,22} - r_{16,21} + r_{15,20}$	B_u	$\nu(CH)_6$

S_{24}	$r_{6,11}$ - $r_{5,10}$ - $r_{4,9}$ + $r_{3,8}$ + $r_{18,23}$ - $r_{17,22}$ - $r_{16,21}$ + $r_{15,20}$	A_g	$\nu(CH)_7$
S_{25}	$r_{6,11}$ - $r_{5,10}$ - $r_{4,9}$ + $r_{3,8}$ - $r_{18,23}$ + $r_{17,22}$ + $r_{16,21}$ - $r_{15,20}$	B_u	$\nu(CH)_8$
S_{26}	$\beta_{13,1,2}$ + $\beta_{1,13,14}$	A_g	δ(NNC)
S_{27}	$\beta_{13,1,2}$ - $\beta_{1,13,14}$	B_u	δ(NNC)
S_{28}	$\beta_{1,2,3}$ - $\beta_{1,2,7}$+ $\beta_{13,14,15}$ - $\beta_{13,14,19}$	A_g	δ(NCC)
S_{29}	$\beta_{1,2,3}$ - $\beta_{1,2,7}$- $\beta_{13,14,15}$ + $\beta_{13,14,19}$	B_u	δ(NCC)
S_{30}	$\beta_{7,2,3}$ - $\beta_{2,3,4}$ + $\beta_{3,4,5}$ - $\beta_{4,5,6}$ + $\beta_{5,6,7}$ - $\beta_{6,7,2}$ + $\beta_{19,14,15}$ - $\beta_{14,15,16}$ + $\beta_{15,16,17}$ - $\beta_{16,17,18}$ + $\beta_{17,18,19}$ - $\beta_{18,19,14}$	A_g	δ(ring1)
S_{31}	$\beta_{7,2,3}$ - $\beta_{2,3,4}$ + $\beta_{3,4,5}$ - $\beta_{4,5,6}$ + $\beta_{5,6,7}$ - $\beta_{6,7,2}$ - $\beta_{19,14,15}$ + $\beta_{14,15,16}$ - $\beta_{15,16,17}$ + $\beta_{16,17,18}$ - $\beta_{17,18,19}$ + $\beta_{18,19,14}$	B_u	δ(ring2)
S_{32}	$2\beta_{7,2,3}$ - $\beta_{2,3,4}$ - $\beta_{3,4,5}$ + $2\beta_{4,5,6}$ - $\beta_{5,6,7}$ - $\beta_{6,7,2}$ + $2\beta_{19,14,15}$ - $\beta_{14,15,16}$ - $\beta_{15,16,17}$ + $2\beta_{16,17,18}$ - $\beta_{17,18,19}$ - $\beta_{18,19,14}$	A_g	δ(ring3)
S_{33}	$2\beta_{7,2,3}$ - $\beta_{2,3,4}$ - $\beta_{3,4,5}$ + $2\beta_{4,5,6}$ - $\beta_{5,6,7}$ - $\beta_{6,7,2}$ - $2\beta_{19,14,15}$ + $\beta_{14,15,16}$ + $\beta_{15,16,17}$ - $2\beta_{16,17,18}$ + $\beta_{17,18,19}$ + $\beta_{18,19,14}$	B_u	δ(ring4)
S_{34}	$\beta_{2,3,4}$ - $\beta_{3,4,5}$ + $\beta_{5,6,7}$ - $\beta_{6,7,2}$ + $\beta_{14,15,16}$ - $\beta_{15,16,17}$ + $\beta_{17,18,19}$ - $\beta_{18,19,14}$	A_g	δ(ring5)
S_{35}	$\beta_{2,3,4}$ - $\beta_{3,4,5}$ + $\beta_{5,6,7}$ - $\beta_{6,7,2}$ - $\beta_{14,15,16}$ + $\beta_{15,16,17}$ - $\beta_{17,18,19}$ + $\beta_{18,19,14}$	B_u	δ(ring6)
S_{36}	$\beta_{8,3,2}$ - $\beta_{8,3,4}$ - $\beta_{9,4,3}$ + $\beta_{9,4,5}$ - $2\beta_{10,5,4}$ + $2\beta_{10,5,6}$ - $\beta_{11,6,5}$ + $\beta_{11,6,7}$ + $\beta_{12,7,6}$ - $\beta_{12,7,2}$ + $\beta_{20,15,14}$ - $\beta_{20,15,16}$ - $\beta_{21,16,15}$ + $\beta_{21,16,17}$ - $2\beta_{22,17,16}$ + $2\beta_{22,17,18}$ - $\beta_{23,18,27}$ + $\beta_{23,18,19}$ + $\beta_{24,19,18}$ - $\beta_{24,19,14}$	A_g	$\delta(CH)_1$
S_{37}	$\beta_{8,3,2}$ - $\beta_{8,3,4}$ - $\beta_{9,4,3}$ + $\beta_{9,4,5}$ - $2\beta_{10,5,4}$ + $2\beta_{10,5,6}$ - $\beta_{11,6,5}$ + $\beta_{11,6,7}$+ $\beta_{12,7,6}$ - $\beta_{12,7,2}$ - $\beta_{20,15,14}$ + $\beta_{20,15,16}$ + $\beta_{21,16,15}$ - $\beta_{21,16,17}$ + $2\beta_{22,17,16}$ - $2\beta_{22,17,18}$ + $\beta_{23,18,27}$ - $\beta_{23,18,19}$ - $\beta_{24,19,18}$ + $\beta_{24,19,14}$	B_u	$\delta(CH)_2$
S_{38}	$\beta_{8,3,2}$ - $\beta_{8,3,4}$ - $\beta_{9,4,3}$ + $\beta_{9,4,5}$ + $2\beta_{10,5,4}$ - $2\beta_{10,5,6}$ - $\beta_{11,6,5}$ + $\beta_{11,6,7}$+ $\beta_{12,7,6}$ - $\beta_{12,7,2}$ + $\beta_{20,15,14}$ - $\beta_{20,15,16}$ - $\beta_{21,16,15}$ + $\beta_{21,16,17}$ + $2\beta_{22,17,16}$- $2\beta_{22,17,18}$ - $\beta_{23,18,27}$ + $\beta_{23,18,19}$ + $\beta_{24,19,18}$ - $\beta_{24,19,14}$	A_g	$\delta(CH)_3$
S_{39}	$\beta_{8,3,2}$ - $\beta_{8,3,4}$ - $\beta_{9,4,3}$ + $\beta_{9,4,5}$ + $2\beta_{10,5,4}$ - $2\beta_{10,5,6}$ - $\beta_{11,6,5}$ + $\beta_{11,6,7}$ + $\beta_{12,7,6}$ - $\beta_{12,7,2}$ - $\beta_{20,15,14}$ + $\beta_{20,15,16}$ + $\beta_{21,16,15}$ - $\beta_{21,16,17}$ - $2\beta_{22,17,16}$ + $2\beta_{22,17,18}$ + $\beta_{23,18,27}$ - $\beta_{23,18,19}$ - $\beta_{24,19,18}$ + $\beta_{24,19,14}$	B_u	$\delta(CH)_4$

S_{40}	$\beta_{8,3,2}$ - $\beta_{8,3,4}$ + $\beta_{9,4,3}$ - $\beta_{9,4,5}$ + $\beta_{11,6,5}$ - $\beta_{11,6,7}$ + $\beta_{12,7,6}$ - $\beta_{12,7,2}$ + $\beta_{20,15,14}$- $\beta_{20,15,16}$ + $\beta_{21,16,15}$ - $\beta_{21,16,17}$ + $\beta_{23,18,27}$ - $\beta_{23,18,19}$ + $\beta_{24,19,18}$ - $\beta_{24,19,14}$	A_g	$\delta(CH)_5$
S_{41}	$\beta_{8,3,2}$ - $\beta_{8,3,4}$ + $\beta_{9,4,3}$ - $\beta_{9,4,5}$ + $\beta_{11,6,5}$ - $\beta_{11,6,7}$ + $\beta_{12,7,6}$ - $\beta_{12,7,2}$ - $\beta_{20,15,14}$ + $\beta_{20,15,16}$ - $\beta_{21,16,15}$ + $\beta_{21,16,17}$ - $\beta_{23,18,27}$ + $\beta_{23,18,19}$ - $\beta_{24,19,18}$ + $\beta_{24,19,14}$	B_u	$\delta(CH)_6$
S_{42}	$\beta_{8,3,2}$ - $\beta_{8,3,4}$ + $\beta_{9,4,3}$ - $\beta_{9,4,5}$ - $\beta_{11,6,5}$ + $\beta_{11,6,7}$ - $\beta_{12,7,6}$ + $\beta_{12,7,2}$ + $\beta_{20,15,14}$- $\beta_{20,15,16}$ + $\beta_{21,16,15}$ - $\beta_{21,16,17}$ - $\beta_{23,18,27}$ + $\beta_{23,18,19}$ - $\beta_{24,19,18}$ + $\beta_{24,19,14}$	A_g	$\delta(CH)_7$
S_{43}	$\beta_{8,3,2}$ - $\beta_{8,3,4}$ + $\beta_{9,4,3}$ - $\beta_{9,4,5}$ - $\beta_{11,6,5}$ + $\beta_{11,6,7}$ - $\beta_{12,7,6}$ + $\beta_{12,7,2}$ - $\beta_{20,15,14}$ + $\beta_{20,15,16}$ - $\beta_{21,16,15}$ + $\beta_{21,16,17}$ + $\beta_{23,18,27}$ - $\beta_{23,18,19}$ + $\beta_{24,19,18}$ - $\beta_{24,19,14}$	B_u	$\delta(CH)_8$
S_{44}	$\beta_{8,3,2}$ - $\beta_{8,3,4}$ - $\beta_{9,4,3}$ + $\beta_{9,4,5}$ + $\beta_{11,6,5}$ - $\beta_{11,6,7}$ - $\beta_{12,7,6}$ + $\beta_{12,7,2}$ - $\beta_{20,15,14}$ + $\beta_{20,15,16}$ + $\beta_{21,16,15}$ - $\beta_{21,16,17}$ - $\beta_{23,18,27}$ + $\beta_{23,18,19}$ + $\beta_{24,19,18}$ - $\beta_{24,19,14}$	B_u	$\delta(CH)_9$
S_{45}	$\beta_{8,3,2}$ - $\beta_{8,3,4}$ - $\beta_{9,4,3}$ + $\beta_{9,4,5}$ + $\beta_{11,6,5}$ - $\beta_{11,6,7}$ - $\beta_{12,7,6}$ + $\beta_{12,7,2}$ + $\beta_{20,15,14}$ - $\beta_{20,15,16}$ - $\beta_{21,16,15}$ + $\beta_{21,16,17}$ + $\beta_{23,18,27}$ - $\beta_{23,18,19}$ - $\beta_{24,19,18}$ + $\beta_{24,19,14}$	A_g	$\delta(CH)_{10}$
S_{46}	$\tau_{2,1,13,14}$	A_u	τ(CNNC)
S_{47}	$\tau_{13,1,2,3}$ + $\tau_{13,1,2,7}$ + $\tau_{1,13,14,15}$ + $\tau_{1,13,14,19}$	A_u	τ(NNCC)
S_{48}	$\tau_{13,1,2,3}$ + $\tau_{13,1,2,7}$ - $\tau_{1,13,14,15}$ - $\tau_{1,13,14,19}$	B_g	τ(NNCC)
S_{49}	$\tau_{7,2,3,4}$ - $\tau_{2,3,4,5}$ + $\tau_{3,4,5,6}$ - $\tau_{4,5,6,7}$ + $\tau_{5,6,7,2}$ - $\tau_{6,7,2,3}$ + $\tau_{19,14,15,16}$ - $\tau_{14,15,16,17}$ + $\tau_{15,16,17,18}$ - $\tau_{16,17,18,19}$ + $\tau_{17,18,19,14}$ - $\tau_{18,19,14,15}$	A_u	τ(ring1)
S_{50}	$\tau_{7,2,3,4}$ - $\tau_{2,3,4,5}$ + $\tau_{3,4,5,6}$ - $\tau_{4,5,6,7}$ + $\tau_{5,6,7,2}$ - $\tau_{6,7,2,3}$ - $\tau_{19,14,15,16}$ + $\tau_{14,15,16,17}$ - $\tau_{15,16,17,18}$ + $\tau_{16,17,18,19}$ - $\tau_{17,18,19,14}$ + $\tau_{18,19,14,15}$	B_g	τ(ring2)
S_{51}	$\tau_{7,2,3,4}$ - $\tau_{3,4,5,6}$ + $\tau_{4,5,6,7}$ - $\tau_{6,7,2,3}$ + $\tau_{19,14,15,16}$ - $\tau_{15,16,17,18}$ + $\tau_{16,17,18,19}$ - $\tau_{18,19,14,15}$	A_u	τ(ring3)
S_{52}	$\tau_{7,2,3,4}$ - $\tau_{3,4,5,6}$ + $\tau_{4,5,6,7}$ - $\tau_{6,7,2,3}$ - $\tau_{19,14,15,16}$ + $\tau_{15,16,17,18}$ - $\tau_{16,17,18,19}$ + $\tau_{18,19,14,15}$	B_g	τ(ring4)
S_{53}	- $\tau_{7,2,3,4}$ + $2\tau_{2,3,4,5}$ - $\tau_{3,4,5,6}$ - $\tau_{4,5,6,7}$ + $2\tau_{5,6,7,2}$ - $\tau_{6,7,2,3}$ - $\tau_{19,14,15,16}$ + $2\tau_{14,15,16,17}$ - $\tau_{15,16,17,18}$ - $\tau_{16,17,18,19}$ + $2\tau_{17,18,19,14}$ - $\tau_{18,19,14,15}$	A_u	τ(ring5)

S_{54}	$-\tau_{7,2,3,4} + 2\tau_{2,3,4,5} - \tau_{3,4,5,6} - \tau_{4,5,6,7} + 2\tau_{5,6,7,2} - \tau_{6,7,2,3}$ $+ \tau_{19,14,15,16} - 2\tau_{14,15,16,17} + \tau_{15,16,17,18} + \tau_{16,17,18,19}$ $- 2\tau_{17,18,19,14} + \tau_{18,19,14,15}$	B_g	τ(ring6)
S_{55}	$\tau_{1,3,2,7} + \tau_{13,15,14,19}$	A_u	γ(NC)
S_{56}	$\tau_{1,3,2,7} - \tau_{13,15,14,19}$	B_g	γ(NC)
S_{57}	$2\tau_{12,2,7,6} - 3\tau_{11,7,6,5} + 2\tau_{10,6,5,4} - 3\tau_{9,5,4,3} + 2\tau_{8,4,3,2}$ $+ 2\tau_{24,14,19,18} - 3\tau_{23,19,18,17} + 2\tau_{22,18,17,16}$ $- 3\tau_{21,17,16,15} + 2\tau_{20,16,15,14}$	A_u	$\gamma(CH)_1$
S_{58}	$2\tau_{12,2,7,6} - 3\tau_{11,7,6,5} + 2\tau_{10,6,5,4} - 3\tau_{9,5,4,3} + 2\tau_{8,4,3,2}$ $- 2\tau_{24,14,19,18} + 3\tau_{23,19,18,17} - 2\tau_{22,18,17,16}$ $+ 3\tau_{21,17,16,15} - 2\tau_{20,16,15,14}$	B_g	$\gamma(CH)_2$
S_{59}	$\tau_{12,2,7,6} + \tau_{11,7,6,5} + \tau_{10,6,5,4} + \tau_{9,5,4,3} + \tau_{8,4,3,2} + \tau_{24,14,19,18}$ $+ \tau_{23,19,18,17} + \tau_{22,18,17,16} + \tau_{21,17,16,15} + \tau_{20,16,15,14}$	A_u	$\gamma(CH)_3$
S_{60}	$\tau_{12,2,7,6} + \tau_{11,7,6,5} + \tau_{10,6,5,4} + \tau_{9,5,4,3} + \tau_{8,4,3,2} - \tau_{24,14,19,18}$ $- \tau_{23,19,18,17} - \tau_{22,18,17,16} - \tau_{21,17,16,15} - \tau_{20,16,15,14}$	B_g	$\gamma(CH)_4$
S_{61}	$\tau_{12,2,7,6} + \tau_{11,7,6,5} - \tau_{9,5,4,3} - \tau_{8,4,3,2} + \tau_{24,14,19,18} + \tau_{23,19,18,17}$ $- \tau_{21,17,16,15} - \tau_{20,16,15,14}$	A_u	$\gamma(CH)_5$
S_{62}	$\tau_{12,2,7,6} + \tau_{11,7,6,5} - \tau_{9,5,4,3} - \tau_{8,4,3,2} - \tau_{24,14,19,18} - \tau_{23,19,18,17}$ $+ \tau_{21,17,16,15} + \tau_{20,16,15,14}$	B_g	$\gamma(CH)_6$
S_{63}	$\tau_{12,2,7,6} - \tau_{11,7,6,5} + \tau_{9,5,4,3} - \tau_{8,4,3,2} + \tau_{24,14,19,18} - \tau_{23,19,18,17}$ $+ \tau_{21,17,16,15} - \tau_{20,16,15,14}$	A_u	$\gamma(CH)_7$
S_{64}	$\tau_{12,2,7,6} - \tau_{11,7,6,5} + \tau_{9,5,4,3} - \tau_{8,4,3,2} - \tau_{24,14,19,18} + \tau_{23,19,18,17}$ $- \tau_{21,17,16,15} + \tau_{20,16,15,14}$	B_g	$\gamma(CH)_8$
S_{65}	$\tau_{12,2,7,6} - 2\tau_{10,6,5,4} + \tau_{8,4,3,2} + \tau_{24,14,19,18} - 2\tau_{22,18,17,16}$ $+ \tau_{20,16,15,14}$	A_u	$\gamma(CH)_9$
S_{66}	$\tau_{12,2,7,6} - 2\tau_{10,6,5,4} + \tau_{8,4,3,2} - \tau_{24,14,19,18} + 2\tau_{22,18,17,16}$ $- \tau_{20,16,15,14}$	B_g	$\gamma(CH)_{10}$

[a] Atom numbering is shown in Figure S1; $r_{i,j}$ is the distance between atoms A_i and A_j; $\beta_{i,j,k}$ is the angle between vectors A_kA_i and A_kA_j; $\tau_{i,j,k,l}$ is the dihedral angle between the plane defined by A_i, A_j, A_k and the plane defined by A_j, A_k, A_l atoms; ν - stretching, δ - in-plane bending, γ - out-of-plane bending, τ - torsion; normalization constants not given.

Table S5: Theoretical wavenumbers (ν/ cm^{-1}), Raman scattering activities (S/ Å^4 a.m.u.$^{-1}$) and potential energy distributions (PED, %) for the Raman-active A_g and B_g normal modes of *E*-AB calculated at the PW91/cc-pVTZ level.

Calculated			
ν[a]	S / Å^4 a.m.u.$^{-1}$	Sym.	PED[b] (%)
3142.5	164.6	A_g	ν_s (CH) (93)
3133.5	597.7	A_g	$\nu(CH)_1$ (83), $\nu(CH)_3$ (12)
3124.0	354.0	A_g	$\nu(CH)_3$ (57), $\nu(CH)_7$ (30)
3113.9	324.5	A_g	$\nu(CH)_7$ (55), $\nu(CH)_3$ (28), $\nu(CH)_5$ (11)
3103.9	88.2	A_g	$\nu(CH)_5$ (82), $\nu(CH)_7$ (14)
1598.2	830.8	A_g	$\nu(CC)_3$ (62), $\delta(CH)_{10}$ (16)
1581.6	26.0	A_g	$\nu(CC)_5$ (66)
1483.1	727.0	A_g	ν(N=N) (31), $\delta(CH)_7$ (30), $\nu(CC)_9$ (20)
1457.7	518.4	A_g	$\delta(CH)_1$ (31), $\nu(CC)_7$ (24), $\delta(CH)_7$ (23), $\nu(CC)_9$ (11)
1419.6	3851.0	A_g	ν(N=N) (51), $\delta(CH)_1$ (14), $\delta(CH)_7$ (11)
1355.7	108.0	A_g	$\nu(CC)_1$ (89)
1298.8	319.3	A_g	$\delta(CH)_5$ (75)
1176.9	868.6	A_g	$\delta(CH)_{10}$ (41), ν(NC) (20), $\nu(CC)_3$ (14)
1149.9	33.8	A_g	$\delta(CH)_3$ (77)
1125.5	2514.4	A_g	$\delta(CH)_{10}$ (35), ν(NC) (27), δ(ring1) (11)
1068.5	23.9	A_g	$\delta(CH)_1$ (42), $\nu(CC)_7$ (10)
1017.8	28.3	A_g	$\nu(CC)_9$ (49), $\delta(CH)_7$ (25), $\nu(CC)_{11}$ (23)
993.5	362.9	A_g	δ(ring1) (61), $\nu(CC)_{11}$ (35)
979.3	1.2	B_g	$\gamma(CH)_2$ (108), $\gamma(CH)_8$ (14)
962.7	0.5	B_g	$\gamma(CH)_8$ (98), $\gamma(CH)_2$ (14)
921.7	0.1	B_g	$\gamma(CH)_{10}$ (94)
913.5	6.9	A_g	δ(NNC) (42), $\nu(CC)_{11}$ (17), δ(ring1) (12)
832.8	2.9	B_g	$\gamma(CH)_6$ (100)
759.1	0.2	B_g	$\gamma(CH)_4$ (52), τ(ring2) (27), γ(NC) (18)
681.7	0.8	B_g	τ(ring2) (85), $\gamma(CH)_4$ (32)
664.7	7.0	A_g	δ(ring3) (60), δ(NNC) (18)
606.8	23.0	A_g	δ(ring5) (87)
471.3	0.3	B_g	γ(NC) (45), τ(ring4) (49)
406.2	0.01	B_g	τ(ring6) (111)
299.6	1.8	A_g	δ(NCC) (43), ν(NC) (17), δ(ring3) (16)
239.0	3.8	B_g	τ(ring4) (47), γ(NC) (34), τ(NNCC) (16)
217.1	1.0	A_g	δ(NCC) (39), δ(NNC) (22), ν(NC) (17), δ(ring3) (12)
94.8	3.3	B_g	τ(NNCC) (82), τ(ring4) (16)

[a] Theoretical frequencies (ν/ cm^{-1}) were not scaled.

[b] PED's lower than 10% not included. Definition of symmetry coordinates is given in Table S4.

Table S6: Internal symmetry coordinates used in the normal mode analysis of *Z*-azobenzene.[a]

Coord.	Definition	Sym.	Appr. Description
S_1	$r_{1,13}$	A	ν(N=N)
S_2	$r_{1,2} + r_{13,14}$	A	ν(NC)
S_3	$r_{1,2} - r_{13,14}$	B	ν(NC)
S_4	$r_{2,3} - r_{3,4} + r_{4,5} - r_{5,6} + r_{6,7} - r_{7,2} + r_{14,15} - r_{15,16} + r_{16,17} - r_{17,18} + r_{18,19} - r_{19,14}$	A	$\nu(CC)_1$
S_5	$r_{2,3} - r_{3,4} + r_{4,5} - r_{5,6} + r_{6,7} - r_{7,2} - r_{14,15} + r_{15,16} - r_{16,17} + r_{17,18} - r_{18,19} + r_{19,14}$	B	$\nu(CC)_2$
S_6	$- r_{2,3} + 2r_{3,4} - r_{4,5} - r_{5,6} + 2r_{6,7} - r_{7,2} - r_{14,15} + 2r_{15,16} - r_{16,17} - r_{17,18} + 2r_{18,19} - r_{19,14}$	A	$\nu(CC)_3$
S_7	$- r_{2,3} + 2r_{3,4} - r_{4,5} - r_{5,6} + 2r_{6,7} - r_{7,2} + r_{14,15} - 2r_{15,16} + r_{16,17} + r_{17,18} - 2r_{18,19} + r_{19,14}$	B	$\nu(CC)_4$
S_8	$r_{2,3} - r_{4,5} + r_{5,6} - r_{7,2} + r_{14,15} - r_{16,17} + r_{17,18} - r_{19,14}$	A	$\nu(CC)_5$
S_9	$r_{2,3} - r_{4,5} + r_{5,6} - r_{7,2} - r_{14,15} + r_{16,17} - r_{17,18} + r_{19,14}$	B	$\nu(CC)_6$
S_{10}	$r_{2,3} + 2r_{3,4} + r_{4,5} - r_{5,6} - 2r_{6,7} - r_{7,2} + r_{14,15} + 2r_{15,16} + r_{16,17} - r_{17,18} - 2r_{18,19} + r_{19,14}$	A	$\nu(CC)_7$
S_{11}	$r_{2,3} + 2r_{3,4} + r_{4,5} - r_{5,6} - 2r_{6,7} - r_{7,2} - r_{14,15} - 2r_{15,16} - r_{16,17} + r_{17,18} + 2r_{18,19} + r_{19,14}$	B	$\nu(CC)_8$
S_{12}	$r_{2,3} - r_{4,5} - r_{5,6} + r_{7,2} + r_{14,15} - r_{16,17} - r_{17,18} + r_{19,14}$	A	$\nu(CC)_9$
S_{13}	$r_{2,3} - r_{4,5} - r_{5,6} + r_{7,2} - r_{14,15} + r_{16,17} + r_{17,18} - r_{19,14}$	B	$\nu(CC)_{10}$
S_{14}	$r_{2,3} + r_{3,4} + r_{4,5} + r_{5,6} + r_{6,7} + r_{7,2} + r_{14,15} + r_{15,16} + r_{16,17} + r_{17,18} + r_{18,19} + r_{19,14}$	A	$\nu(CC)_{11}$
S_{15}	$r_{2,3} + r_{3,4} + r_{4,5} + r_{5,6} + r_{6,7} + r_{7,2} - r_{14,15} - r_{15,16} - r_{16,17} - r_{17,18} - r_{18,19} - r_{19,14}$	B	$\nu(CC)_{12}$
S_{16}	$r_{7,12} + r_{6,11} + r_{5,10} + r_{4,9} + r_{3,8} + r_{19,24} + r_{18,23} + r_{17,22} + r_{16,21} + r_{15,20}$	A	$\nu(CH)_1$
S_{17}	$r_{7,12} + r_{6,11} + r_{5,10} + r_{4,9} + r_{3,8} - r_{19,24} - r_{18,23} - r_{17,22} - r_{16,21} - r_{15,20}$	B	$\nu(CH)_2$
S_{18}	$2r_{7,12} - 3r_{6,11} + 2r_{5,10} - 3r_{4,9} + 2r_{3,8} + 2r_{19,24} - 3r_{18,23} + 2r_{17,22} - 3r_{16,21} + 2r_{15,20}$	A	$\nu(CH)_3$
S_{19}	$2r_{7,12} - 3r_{6,11} + 2r_{5,10} - 3r_{4,9} + 2r_{3,8} - 2r_{19,24} + 3r_{18,23} - 2r_{17,22} + 3r_{16,21} - 2r_{15,20}$	B	$\nu(CH)_4$
S_{20}	$r_{7,12} - r_{6,11} + r_{4,9} - r_{3,8} + r_{19,24} - r_{18,23} + r_{16,21} - r_{15,20}$	A	$\nu(CH)_5$

S_{21}	$r_{7,12}$ - $r_{6,11}$ + $r_{4,9}$ - $r_{3,8}$ - $r_{19,24}$ + $r_{18,23}$ - $r_{16,21}$ + $r_{15,20}$	B	$\nu(CH)_6$
S_{22}	$r_{7,12}$ + $r_{6,11}$ - $r_{4,9}$ - $r_{3,8}$ + $r_{19,24}$ + $r_{18,23}$ - $r_{16,21}$ - $r_{15,20}$	A	$\nu(CH)_7$
S_{23}	$r_{7,12}$ + $r_{6,11}$ - $r_{4,9}$ - $r_{3,8}$ - $r_{19,24}$ - $r_{18,23}$ + $r_{16,21}$ + $r_{15,20}$	B	$\nu(CH)_8$
S_{24}	$r_{7,12}$ - $2r_{5,10}$ + $r_{3,8}$ + $r_{19,24}$ - $2r_{17,22}$ + $r_{15,20}$	A	$\nu(CH)_9$
S_{25}	$r_{7,12}$ - $2r_{5,10}$ + $r_{3,8}$ - $r_{19,24}$ + $2r_{17,22}$ - $r_{15,20}$	B	$\nu(CH)_{10}$
S_{26}	$\beta_{13,1,2}$ + $\beta_{1,13,14}$	A	δ(NNC)
S_{27}	$\beta_{13,1,2}$ - $\beta_{1,13,14}$	B	δ(NNC)
S_{28}	$\beta_{1,2,3}$ - $\beta_{1,2,7}$+ $\beta_{13,14,15}$ - $\beta_{13,14,19}$	A	δ(NCC)
S_{29}	$\beta_{1,2,3}$ - $\beta_{1,2,7}$- $\beta_{13,14,15}$ + $\beta_{13,14,19}$	B	δ(NCC)
S_{30}	$\beta_{7,2,3}$ - $\beta_{2,3,4}$ + $\beta_{3,4,5}$ - $\beta_{4,5,6}$ + $\beta_{5,6,7}$ - $\beta_{6,7,2}$ + $\beta_{19,14,15}$ - $\beta_{14,15,16}$ + $\beta_{15,16,17}$ - $\beta_{16,17,18}$ + $\beta_{17,18,19}$ - $\beta_{18,19,14}$	A	δ(ring1)
S_{31}	$\beta_{7,2,3}$ - $\beta_{2,3,4}$ + $\beta_{3,4,5}$ - $\beta_{4,5,6}$ + $\beta_{5,6,7}$ - $\beta_{6,7,2}$ - $\beta_{19,14,15}$ + $\beta_{14,15,16}$ - $\beta_{15,16,17}$ + $\beta_{16,17,18}$ - $\beta_{17,18,19}$ + $\beta_{18,19,14}$	B	δ(ring2)
S_{32}	$2\beta_{7,2,3}$ - $\beta_{2,3,4}$ - $\beta_{3,4,5}$ + $2\beta_{4,5,6}$ - $\beta_{5,6,7}$ - $\beta_{6,7,2}$ + $2\beta_{19,14,15}$ - $\beta_{14,15,16}$ - $\beta_{15,16,17}$ + $2\beta_{16,17,18}$ - $\beta_{17,18,19}$ - $\beta_{18,19,14}$	A	δ(ring3)
S_{33}	$2\beta_{7,2,3}$ - $\beta_{2,3,4}$ - $\beta_{3,4,5}$ + $2\beta_{4,5,6}$ - $\beta_{5,6,7}$ - $\beta_{6,7,2}$ - $2\beta_{19,14,15}$ + $\beta_{14,15,16}$ + $\beta_{15,16,17}$ - $2\beta_{16,17,18}$ + $\beta_{17,18,19}$ + $\beta_{18,19,14}$	B	δ(ring4)
S_{34}	$\beta_{2,3,4}$ - $\beta_{3,4,5}$ + $\beta_{5,6,7}$ - $\beta_{6,7,2}$ + $\beta_{14,15,16}$ - $\beta_{15,16,17}$ + $\beta_{17,18,19}$ - $\beta_{18,19,14}$	A	δ(ring5)
S_{35}	$\beta_{2,3,4}$ - $\beta_{3,4,5}$ + $\beta_{5,6,7}$ - $\beta_{6,7,2}$ - $\beta_{14,15,16}$ + $\beta_{15,16,17}$ - $\beta_{17,18,19}$ + $\beta_{18,19,14}$	B	δ(ring6)
S_{36}	$\beta_{8,3,2}$ - $\beta_{8,3,4}$ - $\beta_{9,4,3}$ + $\beta_{9,4,5}$ - $2\beta_{10,5,4}$ + $2\beta_{10,5,6}$ - $\beta_{11,6,5}$ + $\beta_{11,6,7}$ + $\beta_{12,7,6}$ - $\beta_{12,7,2}$ + $\beta_{20,15,14}$ - $\beta_{20,15,16}$ - $\beta_{21,16,15}$ + $\beta_{21,16,17}$ - $2\beta_{22,17,16}$ + $2\beta_{22,17,18}$ - $\beta_{23,18,27}$ + $\beta_{23,18,19}$ + $\beta_{24,19,18}$ - $\beta_{24,19,14}$	A	$\delta(CH)_1$
S_{37}	$\beta_{8,3,2}$ - $\beta_{8,3,4}$ - $\beta_{9,4,3}$ + $\beta_{9,4,5}$ - $2\beta_{10,5,4}$ + $2\beta_{10,5,6}$ - $\beta_{11,6,5}$ + $\beta_{11,6,7}$+ $\beta_{12,7,6}$ - $\beta_{12,7,2}$ - $\beta_{20,15,14}$ + $\beta_{20,15,16}$ + $\beta_{21,16,15}$ - $\beta_{21,16,17}$ + $2\beta_{22,17,16}$ - $2\beta_{22,17,18}$ + $\beta_{23,18,27}$ - $\beta_{23,18,19}$ - $\beta_{24,19,18}$ + $\beta_{24,19,14}$	B	$\delta(CH)_2$
S_{38}	$\beta_{8,3,2}$ - $\beta_{8,3,4}$ - $\beta_{9,4,3}$ + $\beta_{9,4,5}$ + $2\beta_{10,5,4}$ - $2\beta_{10,5,6}$ - $\beta_{11,6,5}$ + $\beta_{11,6,7}$+ $\beta_{12,7,6}$ - $\beta_{12,7,2}$ + $\beta_{20,15,14}$ - $\beta_{20,15,16}$ - $\beta_{21,16,15}$ + $\beta_{21,16,17}$ + $2\beta_{22,17,16}$- $2\beta_{22,17,18}$ - $\beta_{23,18,27}$ + $\beta_{23,18,19}$ + $\beta_{24,19,18}$ - $\beta_{24,19,14}$	A	$\delta(CH)_3$
S_{39}	$\beta_{8,3,2}$ - $\beta_{8,3,4}$ - $\beta_{9,4,3}$ + $\beta_{9,4,5}$ + $2\beta_{10,5,4}$ - $2\beta_{10,5,6}$ - $\beta_{11,6,5}$ + $\beta_{11,6,7}$ + $\beta_{12,7,6}$ - $\beta_{12,7,2}$ - $\beta_{20,15,14}$ + $\beta_{20,15,16}$ + $\beta_{21,16,15}$	B	$\delta(CH)_4$

	- $\beta_{21,16,17}$ - $2\beta_{22,17,16}$ + $2\beta_{22,17,18}$ + $\beta_{23,18,27}$ - $\beta_{23,18,19}$ - $\beta_{24,19,18}$ + $\beta_{24,19,14}$		
S_{40}	$\beta_{8,3,2}$ - $\beta_{8,3,4}$ + $\beta_{9,4,3}$ - $\beta_{9,4,5}$ + $\beta_{11,6,5}$ - $\beta_{11,6,7}$ + $\beta_{12,7,6}$ - $\beta_{12,7,2}$ + $\beta_{20,15,14}$- $\beta_{20,15,16}$ + $\beta_{21,16,15}$ - $\beta_{21,16,17}$ + $\beta_{23,18,27}$ - $\beta_{23,18,19}$ + $\beta_{24,19,18}$ - $\beta_{24,19,14}$	A	$\delta(CH)_5$
S_{41}	$\beta_{8,3,2}$ - $\beta_{8,3,4}$ + $\beta_{9,4,3}$ - $\beta_{9,4,5}$ + $\beta_{11,6,5}$ - $\beta_{11,6,7}$ + $\beta_{12,7,6}$ - $\beta_{12,7,2}$ - $\beta_{20,15,14}$ + $\beta_{20,15,16}$ - $\beta_{21,16,15}$ + $\beta_{21,16,17}$ - $\beta_{23,18,27}$ + $\beta_{23,18,19}$ - $\beta_{24,19,18}$ + $\beta_{24,19,14}$	B	$\delta(CH)_6$
S_{42}	$\beta_{8,3,2}$ - $\beta_{8,3,4}$ + $\beta_{9,4,3}$ - $\beta_{9,4,5}$ - $\beta_{11,6,5}$ + $\beta_{11,6,7}$ - $\beta_{12,7,6}$ + $\beta_{12,7,2}$ + $\beta_{20,15,14}$- $\beta_{20,15,16}$ + $\beta_{21,16,15}$ - $\beta_{21,16,17}$ - $\beta_{23,18,27}$ + $\beta_{23,18,19}$ - $\beta_{24,19,18}$ + $\beta_{24,19,14}$	A	$\delta(CH)_7$
S_{43}	$\beta_{8,3,2}$ - $\beta_{8,3,4}$ + $\beta_{9,4,3}$ - $\beta_{9,4,5}$ - $\beta_{11,6,5}$ + $\beta_{11,6,7}$ - $\beta_{12,7,6}$ + $\beta_{12,7,2}$ - $\beta_{20,15,14}$ + $\beta_{20,15,16}$ - $\beta_{21,16,15}$ + $\beta_{21,16,17}$ + $\beta_{23,18,27}$ - $\beta_{23,18,19}$ + $\beta_{24,19,18}$ - $\beta_{24,19,14}$	B	$\delta(CH)_8$
S_{44}	$\beta_{8,3,2}$ - $\beta_{8,3,4}$ - $\beta_{9,4,3}$ + $\beta_{9,4,5}$ + $\beta_{11,6,5}$ - $\beta_{11,6,7}$ - $\beta_{12,7,6}$ + $\beta_{12,7,2}$ - $\beta_{20,15,14}$ + $\beta_{20,15,16}$ + $\beta_{21,16,15}$ - $\beta_{21,16,17}$ - $\beta_{23,18,27}$ + $\beta_{23,18,19}$ + $\beta_{24,19,18}$ - $\beta_{24,19,14}$	B	$\delta(CH)_9$
S_{45}	$\beta_{8,3,2}$ - $\beta_{8,3,4}$ - $\beta_{9,4,3}$ + $\beta_{9,4,5}$ + $\beta_{11,6,5}$ - $\beta_{11,6,7}$ - $\beta_{12,7,6}$ + $\beta_{12,7,2}$ + $\beta_{20,15,14}$ - $\beta_{20,15,16}$ - $\beta_{21,16,15}$ + $\beta_{21,16,17}$ + $\beta_{23,18,27}$ - $\beta_{23,18,19}$ - $\beta_{24,19,18}$ + $\beta_{24,19,14}$	A	$\delta(CH)_{10}$
S_{46}	$\tau_{2,1,13,14}$	A	τ(CNNC)
S_{47}	$\tau_{13,1,2,3}$ + $\tau_{13,1,2,7}$ + $\tau_{1,13,14,15}$ + $\tau_{1,13,14,19}$	A	τ(NNCC)
S_{48}	$\tau_{13,1,2,3}$ + $\tau_{13,1,2,7}$ - $\tau_{1,13,14,15}$ - $\tau_{1,13,14,19}$	B	τ(NNCC)
S_{49}	$\tau_{7,2,3,4}$ - $\tau_{2,3,4,5}$ + $\tau_{3,4,5,6}$ - $\tau_{4,5,6,7}$ + $\tau_{5,6,7,2}$ - $\tau_{6,7,2,3}$ + $\tau_{19,14,15,16}$ - $\tau_{14,15,16,17}$ + $\tau_{15,16,17,18}$ - $\tau_{16,17,18,19}$ + $\tau_{17,18,19,14}$ - $\tau_{18,19,14,15}$	A	τ(ring1)
S_{50}	$\tau_{7,2,3,4}$ - $\tau_{2,3,4,5}$ + $\tau_{3,4,5,6}$ - $\tau_{4,5,6,7}$ + $\tau_{5,6,7,2}$ - $\tau_{6,7,2,3}$ - $\tau_{19,14,15,16}$ + $\tau_{14,15,16,17}$ - $\tau_{15,16,17,18}$ + $\tau_{16,17,18,19}$ - $\tau_{17,18,19,14}$ + $\tau_{18,19,14,15}$	B	τ(ring2)
S_{51}	$\tau_{7,2,3,4}$ - $\tau_{3,4,5,6}$ + $\tau_{4,5,6,7}$ - $\tau_{6,7,2,3}$ + $\tau_{19,14,15,16}$ - $\tau_{15,16,17,18}$ + $\tau_{16,17,18,19}$ - $\tau_{18,19,14,15}$	A	τ(ring3)
S_{52}	$\tau_{7,2,3,4}$ - $\tau_{3,4,5,6}$ + $\tau_{4,5,6,7}$ - $\tau_{6,7,2,3}$ - $\tau_{19,14,15,16}$ + $\tau_{15,16,17,18}$ - $\tau_{16,17,18,19}$ + $\tau_{18,19,14,15}$	B	τ(ring4)
S_{53}	- $\tau_{7,2,3,4}$ + $2\tau_{2,3,4,5}$ - $\tau_{3,4,5,6}$ - $\tau_{4,5,6,7}$ + $2\tau_{5,6,7,2}$ - $\tau_{6,7,2,3}$ - $\tau_{19,14,15,16}$ + $2\tau_{14,15,16,17}$ - $\tau_{15,16,17,18}$ - $\tau_{16,17,18,19}$	A	τ(ring5)

	$+ 2\tau_{17,18,19,14} - \tau_{18,19,14,15}$		
S_{54}	$- \tau_{7,2,3,4} + 2\tau_{2,3,4,5} - \tau_{3,4,5,6} - \tau_{4,5,6,7} + 2\tau_{5,6,7,2} - \tau_{6,7,2,3}$ $+ \tau_{19,14,15,16} - 2\tau_{14,15,16,17} + \tau_{15,16,17,18} + \tau_{16,17,18,19}$ $- 2\tau_{17,18,19,14} + \tau_{18,19,14,15}$	B	τ(ring6)
S_{55}	$\tau_{1,3,2,7} + \tau_{13,15,14,19}$	A	γ(NC)
S_{56}	$\tau_{1,3,2,7} - \tau_{13,15,14,19}$	B	γ(NC)
S_{57}	$2\tau_{12,2,7,6} - 3\tau_{11,7,6,5} + 2\tau_{10,6,5,4} - 3\tau_{9,5,4,3} + 2\tau_{8,4,3,2}$ $+ 2\tau_{24,14,19,18} - 3\tau_{23,19,18,17} + 2\tau_{22,18,17,16}$ $- 3\tau_{21,17,16,15} + 2\tau_{20,16,15,14}$	A	$\gamma(CH)_1$
S_{58}	$2\tau_{12,2,7,6} - 3\tau_{11,7,6,5} + 2\tau_{10,6,5,4} - 3\tau_{9,5,4,3} + 2\tau_{8,4,3,2}$ $- 2\tau_{24,14,19,18} + 3\tau_{23,19,18,17} - 2\tau_{22,18,17,16}$ $+ 3\tau_{21,17,16,15} - 2\tau_{20,16,15,14}$	B	$\gamma(CH)_2$
S_{59}	$\tau_{12,2,7,6} + \tau_{11,7,6,5} + \tau_{10,6,5,4} + \tau_{9,5,4,3} + \tau_{8,4,3,2} + \tau_{24,14,19,18}$ $+ \tau_{23,19,18,17} + \tau_{22,18,17,16} + \tau_{21,17,16,15} + \tau_{20,16,15,14}$	A	$\gamma(CH)_3$
S_{60}	$\tau_{12,2,7,6} + \tau_{11,7,6,5} + \tau_{10,6,5,4} + \tau_{9,5,4,3} + \tau_{8,4,3,2} - \tau_{24,14,19,18}$ $- \tau_{23,19,18,17} - \tau_{22,18,17,16} - \tau_{21,17,16,15} - \tau_{20,16,15,14}$	B	$\gamma(CH)_4$
S_{61}	$\tau_{12,2,7,6} + \tau_{11,7,6,5} - \tau_{9,5,4,3} - \tau_{8,4,3,2} + \tau_{24,14,19,18} + \tau_{23,19,18,17}$ $- \tau_{21,17,16,15} - \tau_{20,16,15,14}$	A	$\gamma(CH)_5$
S_{62}	$\tau_{12,2,7,6} + \tau_{11,7,6,5} - \tau_{9,5,4,3} - \tau_{8,4,3,2} - \tau_{24,14,19,18} - \tau_{23,19,18,17}$ $+ \tau_{21,17,16,15} + \tau_{20,16,15,14}$	B	$\gamma(CH)_6$
S_{63}	$\tau_{12,2,7,6} - \tau_{11,7,6,5} + \tau_{9,5,4,3} - \tau_{8,4,3,2} + \tau_{24,14,19,18} - \tau_{23,19,18,17}$ $+ \tau_{21,17,16,15} - \tau_{20,16,15,14}$	A	$\gamma(CH)_7$
S_{64}	$\tau_{12,2,7,6} - \tau_{11,7,6,5} + \tau_{9,5,4,3} - \tau_{8,4,3,2} - \tau_{24,14,19,18} + \tau_{23,19,18,17}$ $- \tau_{21,17,16,15} + \tau_{20,16,15,14}$	B	$\gamma(CH)_8$
S_{65}	$\tau_{12,2,7,6} - 2\tau_{10,6,5,4} + \tau_{8,4,3,2} + \tau_{24,14,19,18} - 2\tau_{22,18,17,16}$ $+ \tau_{20,16,15,14}$	A	$\gamma(CH)_9$
S_{66}	$\tau_{12,2,7,6} - 2\tau_{10,6,5,4} + \tau_{8,4,3,2} - \tau_{24,14,19,18} + 2\tau_{22,18,17,16}$ $- \tau_{20,16,15,14}$	B	$\gamma(CH)_{10}$

[a] Atom numbering is shown in Figure S1; $r_{i,j}$ is the distance between atoms A_i and A_j; $\beta_{i,j,k}$ is the angle between vectors A_kA_i and A_kA_j; $\tau_{i,j,k,l}$ is the dihedral angle between the plane defined by A_i, A_j, A_k and the plane defined by A_j, A_k, A_l atoms; ν - stretching, δ - in-plane bending, γ - out-of-plane bending, τ - torsion; normalization constants not given.

Table S7: Changes in the vibrational spectra (Max $\Delta\nu$), expected to occur in E-AB molecule undergoing the zero-point vibrations along the τNNCC coordinates.[a]

E-C_2 (-3°)		E-C_{2h} (0°)		E-C_i (8.5°)		Max. $\Delta\nu$
Freq.	Int.	Freq.	Int.	Freq.	Int.	
20.31	0.08	14.80	0.03	25.10	0.12	10.30
59.24	1.35	60.89	1.41	57.03	1.38	3.87
78.22	1.91	82.27	1.89	86.84	1.80	8.62
99.16	0.04	94.84	0.00	99.79	0.00	4.95
216.44	0.00	217.13	0.00	216.82	0.00	0.69
239.90	0.24	239.02	0.00	240.52	0.00	1.50
292.71	0.34	295.18	0.62	295.93	1.16	3.23
301.93	0.28	299.61	0.00	300.25	0.00	2.32
403.13	0.00	402.65	0.00	402.44	0.27	0.69
406.68	0.06	406.15	0.00	405.94	0.00	0.74
471.49	0.16	471.35	0.00	472.41	0.00	1.07
514.96	23.52	514.51	23.49	515.30	21.90	0.78
531.22	5.94	532.11	6.25	529.81	8.13	2.30
541.75	13.20	541.30	13.67	542.75	12.77	1.44
606.20	0.00	606.79	0.00	607.56	0.00	1.36
612.57	0.62	613.25	0.65	613.95	0.60	1.38
664.47	0.00	664.71	0.00	664.97	0.00	0.49
682.25	0.12	681.66	0.00	682.25	0.00	0.59
686.00	76.74	685.25	76.76	685.72	77.59	0.75
759.96	0.33	759.14	0.00	758.56	0.00	1.40
780.50	48.44	779.96	48.34	779.42	49.68	1.08
819.22	0.58	819.67	0.57	819.70	0.68	0.47
832.63	0.05	831.34	0.04	830.89	0.97	1.74
834.11	0.06	832.83	0.00	832.36	0.00	1.75
913.01	0.11	913.53	0.00	910.23	0.00	3.30
922.30	0.08	921.74	0.00	924.51	0.00	2.77
928.60	7.23	927.64	7.25	927.05	8.32	1.55
963.05	0.00	961.94	0.00	960.72	0.72	2.33
963.81	0.07	962.71	0.00	961.59	0.00	2.21
980.14	0.08	979.35	0.00	978.29	0.00	1.85
980.65	0.45	979.82	0.42	978.58	1.31	2.06
993.46	3.22	993.43	3.39	993.65	3.05	0.22
993.47	0.00	993.45	0.00	993.66	0.00	0.21
1016.56	13.50	1017.07	13.51	1017.75	12.87	1.19
1017.46	0.00	1017.81	0.00	1018.56	0.00	1.10
1067.92	0.04	1068.55	0.00	1069.03	0.00	1.12
1072.38	15.17	1072.93	15.24	1073.43	15.31	1.05
1125.25	0.00	1125.47	0.00	1125.91	0.00	0.66
1139.69	31.50	1139.64	32.13	1140.23	29.27	0.60
1149.56	0.00	1149.90	0.00	1150.15	0.00	0.59
1149.67	0.36	1149.94	0.45	1150.25	0.35	0.58
1176.80	0.00	1176.86	0.00	1177.12	0.00	0.32
1224.84	20.33	1225.11	20.38	1224.70	18.63	0.41
1295.41	1.77	1295.23	1.69	1295.38	1.58	0.19
1298.70	0.00	1298.84	0.00	1298.56	0.00	0.28
1352.21	6.47	1352.63	6.52	1353.04	6.02	0.82
1355.19	0.01	1355.67	0.00	1356.06	0.00	0.87
1419.50	0.02	1419.60	0.00	1421.61	0.00	2.11
1445.58	13.04	1445.97	13.10	1446.71	12.75	1.12
1457.33	0.02	1457.74	0.00	1458.30	0.00	0.96
1471.96	9.57	1472.78	9.41	1473.28	9.56	1.32
1482.95	0.00	1483.14	0.00	1483.94	0.00	0.99
1577.42	3.92	1577.63	3.82	1578.09	3.73	0.67
1581.47	0.00	1581.57	0.00	1581.55	0.00	0.10
1594.13	5.98	1594.80	6.17	1595.40	5.80	1.28
1597.60	0.00	1598.22	0.00	1598.88	0.00	1.29
3103.99	4.76	3103.81	5.01	3104.05	4.79	0.24
3104.06	0.01	3103.88	0.00	3104.12	0.00	0.25
3114.16	17.29	3113.91	16.99	3113.87	17.10	0.29
3114.17	0.05	3113.94	0.00	3113.88	0.00	0.29
3124.15	30.52	3123.91	30.57	3124.13	30.19	0.24
3124.22	0.01	3123.96	0.00	3124.20	0.00	0.26
3133.55	39.66	3133.31	40.48	3133.33	39.66	0.23
3133.76	0.03	3133.54	0.00	3133.53	0.00	0.23
3141.79	14.46	3142.48	13.87	3141.69	14.14	0.79
3141.82	0.03	3142.51	0.00	3141.73	0.00	0.78

[a] Middle column (E-C_{2h}) –geometry at the minimum, left (E-C_2) and right (E-C_i) columns – geometries corresponding to the geometric limits of the zero-point vibrations along the τNNCC coordinates

Table S8: Changes in the vibrational spectra (Max $\Delta\nu$), expected to occur in Z-AB molecule undergoing the zero-point vibrations along the τNNCC coordinates.[a]

Z-C_2 (42.2°)		Z-C_2 (49.3°)		Z-C_2 (57.2°)		Max. $\Delta\nu$
Freq.	Int.	Freq.	Int.	Freq.	Int.	
46.55	1.40	50.37	1.41	54.63	1.45	8.07
51.22	0.02	50.78	0.01	47.79	0.00	3.42
73.28	0.48	68.18	0.48	63.17	0.47	10.11
154.46	4.63	151.43	3.91	146.80	2.93	7.66
180.31	0.15	171.04	0.19	159.94	0.24	20.37
270.46	5.88	265.02	0.23	259.28	0.22	11.18
271.22	0.23	278.54	5.74	287.22	5.61	16.00
398.07	3.77	397.20	4.44	395.86	4.84	2.21
403.43	0.02	400.30	0.05	397.29	0.08	6.14
410.59	2.85	418.29	3.16	426.65	3.52	16.06
444.10	6.91	438.84	4.84	431.81	2.79	12.29
495.83	5.06	494.90	4.68	493.65	4.39	2.18
527.40	0.09	531.77	0.23	535.68	0.47	8.28
590.75	5.49	592.44	5.15	594.03	4.45	3.28
611.61	0.03	612.25	0.04	612.77	0.06	1.16
613.92	0.12	615.87	0.29	618.48	0.53	4.56
686.61	39.33	686.99	31.26	685.46	3.01	1.53
687.65	18.43	688.21	19.56	689.57	20.50	1.92
696.10	58.15	691.69	67.78	689.05	95.74	7.05
748.18	0.03	746.08	0.03	742.78	0.21	5.40
761.64	38.69	760.20	32.06	758.20	26.00	3.45
768.27	11.25	768.51	12.42	768.33	14.23	0.24
822.39	7.87	820.78	5.62	820.80	4.38	1.61
824.26	1.43	822.95	1.50	822.35	1.36	1.91
829.11	2.47	831.57	2.82	833.26	1.71	4.15
903.71	0.17	901.35	0.32	899.75	0.64	3.95
907.88	21.70	906.22	20.45	906.08	18.77	1.80
950.55	0.74	947.99	0.35	946.72	0.26	3.82
950.77	0.27	948.52	0.28	946.83	0.22	3.93
968.79	0.60	967.52	0.60	966.60	0.69	2.19
968.84	0.05	967.68	0.05	966.78	0.05	2.06
992.29	0.41	992.62	0.38	992.91	0.32	0.62
992.81	1.09	993.27	1.18	993.69	1.31	0.88
1023.73	4.41	1024.25	4.52	1024.86	4.92	1.14
1024.38	2.06	1024.80	2.17	1025.27	2.29	0.89
1074.91	13.05	1074.74	13.31	1074.66	13.32	0.25
1076.57	1.49	1076.51	1.15	1076.81	0.84	0.30
1108.07	0.06	1112.68	0.19	1116.78	0.50	8.71
1133.70	2.16	1134.99	1.84	1135.64	1.27	1.94
1150.56	0.00	1150.68	0.03	1150.90	0.09	0.34
1150.87	0.19	1150.85	0.14	1150.95	0.09	0.10
1170.91	0.65	1170.19	0.76	1169.66	0.83	1.26
1172.22	0.17	1171.00	0.18	1169.87	0.29	2.35
1296.67	1.90	1296.26	1.95	1295.90	1.86	0.77
1300.69	0.12	1301.34	0.06	1302.18	0.01	1.49
1340.87	1.72	1340.50	2.34	1340.32	2.46	0.55
1348.55	0.02	1347.14	0.05	1345.89	0.06	2.66
1439.07	8.48	1438.64	7.37	1437.93	6.63	1.14
1445.17	4.09	1445.44	3.01	1445.51	2.13	0.34
1462.07	0.65	1463.36	1.51	1464.77	2.80	2.70
1469.79	5.32	1469.71	4.85	1469.88	4.88	0.17
1512.98	51.47	1520.25	47.36	1528.20	40.64	15.22
1570.34	4.33	1571.00	4.83	1572.25	5.53	1.92
1576.76	0.46	1578.19	0.50	1580.22	0.51	3.46
1590.72	1.54	1590.78	2.22	1590.61	3.49	0.17
1595.62	3.42	1596.13	4.13	1596.29	4.97	0.67
3105.89	2.15	3105.96	1.94	3106.02	1.81	0.13
3106.03	0.62	3106.07	0.61	3106.07	0.59	0.03
3113.70	9.09	3113.48	8.33	3113.25	7.88	0.45
3113.78	1.39	3113.56	0.85	3113.32	0.52	0.47
3124.37	14.92	3123.85	13.91	3123.48	12.76	0.89
3124.41	4.77	3123.93	5.03	3123.59	5.57	0.82
3131.93	36.49	3131.05	33.06	3130.35	30.92	1.58
3132.17	0.53	3131.27	0.23	3130.55	0.26	1.62
3136.59	6.96	3135.76	10.61	3135.56	12.17	1.04
3136.75	4.31	3135.86	5.54	3135.62	6.43	1.13

[a] Middle column (49.3°) –geometry at the minimum, left (42.2°) and right (57.2°) columns – geometries corresponding to the geometric limits of the zero-point vibrations along the τNNCC coordinates

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