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Accessory Publication

The Role of Linear Alkyl and Alkoxy Side Chains in the Modulation of the Structure and Electrical Properties of Bithiophene:a Theoretical Study

Alkyl and Alkoxy derivatives of Bithiophene

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Table 1S. Selected geometrical parameters of BT in *trans* conformations obtained with B3LYP, M05-2X and PBE0 methods together with 6-31+G** and 6-311G** basis set, and mPW1PW91 and MP2 methods with 6-31G*, 6-31+G*, 6-31+G** and 6-311G** basis sets.

	B3LYP		M05-2X		PBE0		mPW1PW91				MP2			
	6-31+G**	6-311G**	6-31+G**	6-31G*	6-31+G*	6-31+G*	6-31G*	6-31+G*	6-31+G**	6-311G**	6-31G*	6-31+G*	6-31+G**	6-311G**
BOND LENGTH / Angstroms														
S_1-C_2	1.755	1.753	1.734	1.731	1.737	1.735	1.739	1.738	1.738	1.736	1.733	1.732	1.732	1.727
C_2-C_3	1.380	1.375	1.372	1.368	1.377	1.372	1.375	1.376	1.376	1.372	1.385	1.388	1.388	1.389
C_3-C_4	1.425	1.422	1.425	1.421	1.420	1.417	1.419	1.420	1.420	1.417	1.415	1.417	1.416	1.416
C_4-C_5	1.370	1.365	1.365	1.361	1.368	1.363	1.365	1.367	1.367	1.363	1.378	1.382	1.381	1.382
C_5-S_1	1.735	1.733	1.722	1.720	1.720	1.718	1.721	1.721	1.721	1.719	1.718	1.718	1.717	1.714
C_2-$C_{2'}$	1.453	1.451	1.456	1.454	1.450	1.448	1.448	1.450	1.450	1.448	1.450	1.453	1.450	1.454
C_3-H_6	1.084	1.082	1.082	1.080	1.085	1.083	1.084	1.084	1.083	1.082	1.087	1.087	1.082	1.085
C_4-H_7	1.084	1.082	1.081	1.079	1.084	1.083	1.083	1.084	1.083	1.081	1.085	1.086	1.081	1.084
C_5-H_8	1.081	1.079	1.078	1.070	1.082	1.080	1.081	1.081	1.080	1.079	1.083	1.084	1.080	1.082
BOND ANGLES / Degrees														
S_1-C_2-C_3	110.2	110.2	110.9	110.9	110.4	110.4	110.3	110.3	110.4	110.4	110.6	110.7	110.7	110.8
C_2-C_3-C_4	113.5	113.5	112.9	112.9	113.2	113.3	113.3	113.3	113.2	113.3	113.0	112.9	112.9	112.8
C_3-C_4-C_5	112.8	112.9	112.6	112.6	112.6	112.7	112.7	112.7	112.7	112.7	112.6	112.5	112.5	112.4
C_4-C_5-S_1	111.6	111.6	111.7	111.8	111.6	111.6	111.6	111.6	111.6	111.6	111.7	111.6	111.7	111.8
C_5-S_1-C_2	91.9	91.7	91.9	91.8	92.1	92.0	92.1	92.1	92.1	92.0	92.1	92.2	92.2	92.2
C_3-C_2-$C_{2'}$	129.0	129.1	128.6	128.6	128.9	128.9	129.0	128.9	128.9	128.9	128.5	128.4	128.4	128.2
C_2-C_3-H_6	122.8	122.7	122.8	122.7	122.8	122.6	122.8	122.8	122.8	122.7	122.4	122.4	122.4	122.3
C_3-C_4-H_7	123.8	123.8	124.0	124.0	124.0	124.0	123.9	123.9	124.0	124.0	124.3	124.4	124.4	124.5
C_4-C_5-H_8	128.5	128.7	128.2	128.3	128.4	128.6	128.4	128.3	128.4	128.6	128.1	128.1	128.0	128.2
DIHEDRAL ANGLE / Degrees														
S_1-C_2-C_3-C_4	0.5	0.5	0.5	0.6	0.5	0.5	0.5	0.5	0.5	0.5	0.4	0.6	0.6	0.4
C_2-C_3-C_4-C_5	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.4	0.3	0.3	0.6
C_3-C_4-C_5-S_1	-0.6	-0.8	-0.7	-0.8	-0.7	-0.8	-0.7	-0.7	-0.7	-0.7	-1.0	-1.1	-1.0	-1.3
C_4-C_5-S_1-C_2	0.8	0.9	0.8	0.9	0.8	0.9	0.8	0.8	0.8	0.9	1.1	1.2	1.2	1.3
C_5-S_1-C_2-C_3	-0.7	-0.8	-0.7	-0.9	-0.7	-0.8	-0.7	-0.8	-0.7	-0.8	-0.9	-1.0	-1.0	-1.0
S_1- C_2-$C_{2'}$-$S_{1'}$	155.8	150.7	151.5	147.2	154.4	151.3	155.7	153.6	154.0	150.8	141.5	133.5	134.2	137.5
C_3- C_2-$C_{2'}$-$C_{3'}$	156.1	151.4	151.7	148.1	154.7	152.0	156.4	153.9	154.3	151.3	143.2	138.4	135.5	139.2
H_6- C_3-C_4-C_5	-178.5	-178.2	-178.3	0.1	-178.4	-178.3	-178.4	-178.4	-178.4	-178.3	-178.1	-177.9	-179.9	-177.9
H_7- C_4-C_5-S_1	180.0	180.0	179.9	-178.2	180.0	180.0	180.0	180.0	180.0	180.0	-179.9	-180.0	-180.0	-179.8
H_8- C_5-S_1-C_2	-179.3	-179.2	179.4	179.9	-179.3	-179.3	-179.3	-179.3	-179.3	-179.3	-179.0	-179.1	-179.1	-179.1
Energy / Hartree														
	-1104.841	-1104.943	-1104.765	-1104.872	-1104.173	-1104.267	-1104.760	-1104.770	-1104.780	-1104.876	-1102.705	-1102.730	-1102.778	-1102.911

Table 2S. Selected geometrical parameters of BT in *cis* conformations obtained with B3LYP, M05-2X and PBE0 methods together with 6-31G*, 6-31+G*, 6-31+G** and 6-311G** basis sets.

	B3LYP				M05-2X				PBE0			
	6-31G*	6-31+G*	6-31+G**	6-311G**	6-31G*	6-31+G*	6-31+G**	6-311G**	6-31G*	6-31+G*	6-31+G**	6-311G**
BOND LENGTH / Angstroms												
S_1-C_2	1.755	1.755	1.754	1.752	1.735	1.734	1.734	1.732	1.734	1.737	1.737	1.735
C_2-C_3	1.378	1.380	1.380	1.375	1.370	1.372	1.372	1.368	1.375	1.377	1.377	1.372
C_3-C_4	1.424	1.425	1.425	1.422	1.424	1.425	1.425	1.421	1.419	1.420	1.420	1.417
C_4-C_5	1.368	1.371	1.370	1.365	1.363	1.366	1.366	1.361	1.366	1.368	1.368	1.364
C_5-S_1	1.735	1.734	1.734	1.732	1.722	1.722	1.722	1.720	1.720	1.719	1.719	1.718
C_2-$C_{2'}$	1.455	1.455	1.455	1.453	1.456	1.458	1.458	1.455	1.450	1.452	1.452	1.449
C_3-H_6	1.084	1.085	1.084	1.082	1.081	1.081	1.081	1.079	1.085	1.085	1.084	1.083
C_4-H_7	1.085	1.085	1.084	1.082	1.081	1.081	1.081	1.079	1.085	1.085	1.084	1.083
C_5-H_8	1.082	1.082	1.081	1.080	1.078	1.079	1.079	1.077	1.082	1.083	1.082	1.080
BOND ANGLES / Degrees												
S_1-C_2-C_3	110.2	110.2	110.2	110.2	110.8	110.9	110.9	110.9	110.3	110.4	110.4	110.4
C_2-C_3-C_4	113.5	113.5	113.5	113.5	113.0	112.9	112.9	113.0	113.3	113.2	113.2	113.2
C_3-C_4-C_5	112.9	112.8	112.8	112.9	112.6	112.6	112.6	112.6	112.7	112.6	112.6	112.7
C_4-C_5-S_1	111.6	111.6	111.6	111.6	111.7	111.8	111.7	111.8	111.6	111.6	111.6	111.6
C_5-S_1-C_2	91.8	91.9	91.9	91.7	91.8	91.9	91.9	91.8	92.1	92.1	92.1	92.0
C_3-C_2-$C_{2'}$	127.7	127.6	127.6	127.7	127.4	127.3	127.3	127.3	127.5	127.5	127.5	127.6
C_2-C_3-H_6	122.5	122.6	122.5	122.5	122.6	122.6	122.6	122.4	122.5	122.6	122.5	122.5
C_3-C_4-H_7	123.7	123.8	123.8	123.8	124.0	124.0	124.1	124.1	123.9	124.0	124.0	124.0
C_4-C_5-H_8	128.5	128.4	128.4	128.7	128.2	128.2	128.2	128.3	128.4	128.3	128.4	128.6
DIHEDRAL ANGLE / Degrees												
S_1-C_2-C_3-C_4	-0.1	-0.1	-0.1	-0.1	-0.1	0.0	0.0	0.0	-0.1	-0.1	-0.1	-0.1
C_2-C_3-C_4-C_5	-0.4	-0.5	-0.5	-0.4	-0.5	-0.5	-0.5	-0.5	-0.4	-0.4	-0.5	-0.5
C_3-C_4-C_5-S_1	0.8	0.8	0.8	0.7	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8
C_4-C_5-S_1-C_2	-0.8	-0.7	-0.7	-0.7	-0.7	-0.7	-0.7	-0.7	-0.7	-0.7	-0.7	-0.7
C_5-S_1-C_2-C_3	0.5	0.4	0.4	0.5	0.4	0.4	0.4	0.4	0.5	0.4	0.4	0.4
S_1- C_2-$C_{2'}$-$S_{1'}$	32.7	35.7	35.5	37.3	35.2	38.3	38.3	39.6	32.8	35.7	35.4	35.9
C_3- C_2-$C_{2'}$-$C_{3'}$	29.5	32.7	32.5	33.8	32.6	35.6	35.6	36.7	30.0	32.9	32.6	32.9
H_6- C_3-C_4-C_5	177.9	177.7	177.7	177.7	177.8	177.7	177.7	177.8	177.8	177.7	177.7	177.8
H_7- C_4-C_5-S_1	179.9	179.8	179.8	179.8	179.9	179.9	179.9	179.9	179.9	179.8	179.8	179.8
H_8- C_5-S_1-C_2	179.1	179.2	179.2	179.2	179.3	179.3	179.3	179.4	179.2	179.2	179.2	179.3
Energy / Hartree												
	-1104.816	-1104.830	-1104.840	-1104.942	-1104.743	-1104.754	-1104.764	-1104.871	-1104.751	-1104.162	-1104.172	-1104.266

Table 2S (cont.). Main geometrical parameters of BT in cis conformations obtained with MPW1PW91 and MP2 methods together with 6-31G*, 6-31+G*, 6-31+G** and 6-311+G** basis set.

	MPW1PW91				MP2			
	6-31G*	6-31+G*	6-31+G*	6-311G**	6-31G*	6-31+G*	6-31+G*	6-311G**
BOND LENGTH / Angstrons								
S_1-C_2	1.739	1.738	1.738	1.736	1.734	1.733	1.733	1.727
C_2-C_3	1.375	1.376	1.376	1.372	1.385	1.388	1.388	1.389
C_3-C_4	1.419	1.420	1.420	1.417	1.415	1.417	1.417	1.416
C_4-C_5	1.365	1.368	1.368	1.363	1.378	1.382	1.381	1.382
C_5-S_1	1.721	1.720	1.720	1.719	1.718	1.718	1.717	1.714
C_2-$C_{2'}$	1.450	1.452	1.452	1.450	1.452	1.455	1.455	1.455
C_3-H_6	1.083	1.084	1.083	1.081	1.086	1.087	1.082	1.085
C_4-H_7	1.083	1.084	1.083	1.081	1.085	1.086	1.081	1.084
C_5-H_8	1.081	1.081	1.080	1.079	1.083	1.084	1.079	1.082
BOND ANGLES / Degrees								
S_1-C_2-C_3	110.3	110.4	110.4	110.4	110.6	110.7	110.7	110.8
C_2-C_3-C_4	113.3	113.2	113.2	113.3	113.0	112.9	112.9	112.8
C_3-C_4-C_5	112.7	112.7	112.7	112.7	112.6	112.5	112.5	112.4
C_4-C_5-S_1	111.6	111.6	111.6	111.6	111.7	111.7	111.7	111.8
C_5-S_1-C_2	92.1	92.1	92.1	92.0	92.1	92.2	92.2	92.3
C_3-C_2-$C_{2'}$	127.6	127.5	127.5	127.6	127.2	127.2	127.2	126.9
C_2-C_3-H_6	122.5	122.6	122.5	122.5	122.2	122.2	122.2	122.1
C_3-C_4-H_7	123.9	124.0	124.0	124.0	124.3	124.8	124.4	124.5
C_4-C_5-H_8	128.4	128.3	128.4	128.6	128.2	128.1	128.1	128.2
DIHEDRAL ANGLE / Degrees								
S_1-C_2-C_3-C_4	-0.1	-0.1	-0.1	-0.1	0.1	0.0	0.0	0.2
C_2-C_3-C_4-C_5	-0.4	-0.4	-0.5	-0.5	-0.8	-0.7	-0.7	-1.0
C_3-C_4-C_5-S_1	0.7	0.8	0.8	0.8	1.1	1.1	1.1	1.3
C_4-C_5-S_1-C_2	-0.7	-0.7	-0.7	-0.7	-0.9	-0.9	-0.9	-1.0
C_5-S_1-C_2-C_3	0.4	0.4	0.4	0.4	0.4	0.6	0.6	0.4
S_1- C_2-$C_{2'}$-$S_{1'}$	33.6	36.2	36.0	36.7	43.9	54.2	53.7	47.9
C_3- C_2-$C_{2'}$-$C_{3'}$	30.9	33.4	33.2	33.6	41.3	50.1	49.5	45.2
H_6- C_3-C_4-C_5	177.8	177.7	177.7	177.8	177.8	178.0	178.0	177.8
H_7- C_4-C_5-S_1	179.9	179.8	179.8	179.8	179.8	179.8	179.8	179.8
H_8- C_5-S_1-C_2	179.3	179.2	179.2	179.3	179.3	179.2	179.2	179.5
Energy / Hartree								
	-1104.759	-1104.769	-1104.779	-1104.875	-1102.705	-1102.730	-1102.777	-1102.910

Table 3S. Stable conformers, relative energy and *cis-trans* torsional barrier height of BT calculated at mPW1PW91 M05-2X, PBE0 and MP2 with 6-31G*.

		Cis	*Trans*	ΔE_{cis}	ΔE_{trans}
mPW1PW91	C_3-C_2-$C_{2'}$-$C_{3'}$ /Degree	29.5	158.l	2.016	2.699
	Relative Energy /kcal mol^{-1}	-0.418	-1.101		
M05-2X	C_3-C_2-$C_{2'}$-$C_{3'}$ /Degree	30.9	156.4	1.898	2.562
	Relative Energy /kcal mol^{-1}	-0.481	-1.145		
PBE0	C_3-C_2-$C_{2'}$-$C_{3'}$ /Degree	32.6	154.2	1.910	2.524
	Relative Energy /kcal mol^{-1}	-0.615	-1.229		
MP2	C_3-C_2-$C_{2'}$-$C_{3'}$ /Degree	30	157.0	1.988	2.661
	Relative Energy /kcal mol^{-1}	-0.451	-1.124		

Table 4S. Full set of geometrical parameters of 3,4'ABT and 3,4'OABT obtained with B3LYP/6-31G*.

	3,4'ABT						3,4'OABT					
n	0	1	2	3	4	5	0	1	2	3	4	5
BOND LENGTH / Angstroms												
S_1-C_2	1.758	1.758	1.758	1.758	1.758	1.758	1.756	1.756	1.756	1.756	1.756	1.756
C_2-C_3	1.377	1.377	1.377	1.377	1.377	1.377	1.382	1.382	1.382	1.382	1.382	1.382
C_3-C_4	1.429	1.431	1.431	1.431	1.431	1.431	1.426	1.427	1.427	1.427	1.427	1.427
C_4-C_5	1.370	1.370	1.371	1.371	1.371	1.371	1.373	1.373	1.373	1.373	1.373	1.373
C_5-S_1	1.734	1.734	1.734	1.734	1.734	1.734	1.732	1.732	1.733	1.733	1.733	1.733
C_2-$C_{2'}$	1.455	1.458	1.458	1.458	1.458	1.458	1.445	1.446	1.446	1.446	1.446	1.446
$S_{1'}$-$C_{2'}$	1.760	1.760	1.760	1.760	1.760	1.760	1.756	1.757	1.757	1.757	1.757	1.757
$C_{2'}$-$C_{3'}$	1.384	1.384	1.384	1.384	1.384	1.384	1.386	1.387	1.387	1.387	1.387	1.387
$C_{3'}$-$C_{4'}$	1.431	1.433	1.433	1.433	1.433	1.433	1.430	1.430	1.430	1.430	1.430	1.430
$C_{4'}$-$C_{5'}$	1.365	1.365	1.365	1.365	1.365	1.365	1.366	1.366	1.366	1.366	1.366	1.366
$C_{5'}$-$S_{1'}$	1.731	1.731	1.731	1.731	1.731	1.731	1.732	1.731	1.731	1.731	1.731	1.731
C_3-X_6*	1.507	1.511	1.510	1.510	1.510	1.510	1.361	1.361	1.361	1.361	1.361	1.361
C_4-H_7	1.086	1.086	1.086	1.086	1.086	1.086	1.082	1.083	1.083	1.083	1.083	1.083
C_5-H_8	1.082	1.082	1.082	1.082	1.082	1.082	1.081	1.081	1.081	1.081	1.081	1.081
$C_{3'}$-$H_{6'}$	1.086	1.086	1.086	1.086	1.086	1.086	1.083	1.083	1.083	1.083	1.083	1.083
$C_{4'}$-$X_{7'}$*	1.506	1.510	1.509	1.509	1.509	1.509	1.365	1.365	1.365	1.365	1.365	1.365
$C_{5'}$-$H_{8'}$	1.082	1.082	1.083	1.083	1.083	1.083	1.080	1.080	1.080	1.080	1.080	1.080
BOND ANGLES / Degrees												
S_1-C_2-C_3	109.7	109.7	109.7	109.7	109.7	109.7	110.3	110.3	110.3	110.3	110.3	110.3
C_2-C_3-C_4	114.6	114.6	114.6	114.6	114.6	114.6	113.3	113.3	113.3	113.3	113.3	113.3
C_3-C_4-C_5	111.6	111.5	111.5	111.5	111.5	111.5	112.9	112.8	112.8	112.8	112.8	112.8
C_4-C_5-S_1	112.5	112.5	112.5	112.5	112.5	112.5	111.6	111.7	111.7	111.7	111.7	111.7
C_5-S_1-C_2	91.7	91.7	91.7	91.7	91.7	91.7	91.9	91.9	91.9	91.9	91.9	91.9
$S_{1'}$-$C_{2'}$-$C_{3'}$	110.8	110.9	110.9	110.9	110.9	110.9	109.5	109.5	109.5	109.5	109.5	109.5
$C_{2'}$-$C_{3'}$-$C_{4'}$	112.0	111.9	111.9	111.9	111.9	111.9	114.1	113.9	113.9	113.9	113.9	113.9
$C_{3'}$-$C_{4'}$-$C_{5'}$	114.0	114.1	114.1	114.1	114.1	114.1	112.3	112.3	112.4	112.4	112.4	112.4
$C_{4'}$-$C_{5'}$-$S_{1'}$	111.3	111.4	111.4	111.4	111.4	111.4	112.1	112.1	112.1	112.1	112.1	112.1
$C_{5'}$-$S_{1'}$-$C_{2'}$	91.8	91.8	91.8	91.8	91.8	91.8	92.2	92.1	92.1	92.1	92.1	92.1
C_3-C_2-$C_{2'}$	127.7	127.7	127.7	127.7	127.7	127.7	127.4	127.4	127.4	127.4	127.4	127.4
C_2-$C_{2'}$-$C_{3'}$	130.9	131.2	131.2	131.2	131.2	131.2	129.3	129.3	129.4	129.4	129.4	129.4
C_2-C_3-X_6	125.7	126.1	126.1	126.1	126.1	126.1	119.6	119.7	119.7	119.7	119.7	119.7
C_3-C_4-H_7	122.7	122.7	122.7	122.7	122.7	122.7	124.3	124.3	124.3	124.3	124.3	124.3
C_4-C_5-H_8	128.3	128.3	128.3	128.3	128.3	128.3	127.9	127.9	127.9	127.9	127.9	127.9
$C_{2'}$-$C_{3'}$-$H_{6'}$	122.3	122.1	122.1	122.1	122.1	122.1	122.7	122.7	122.7	122.7	122.7	122.7
$C_{3'}$-$C_{4'}$-$X_{7'}$	123.8	124.0	124.0	124.0	124.0	124.0	126.5	126.5	126.5	126.5	126.5	126.5
$C_{4'}$-$C_{5'}$-$H_{8'}$	127.7	127.7	127.7	127.7	127.7	127.7	127.2	127.2	127.2	127.2	127.2	127.2
DIHEDRAL ANGLE / Degrees												
S_1-C_2-C_3-C_4	0.4	0.7	0.7	0.7	0.7	0.7	0.0	0.0	0.0	0.0	0.0	0.0
C_2-C_3-C_4-C_5	0.0	-0.1	-0.1	-0.1	-0.1	-0.1	0.0	0.0	0.0	0.0	0.0	0.0
C_3-C_4-C_5-S_1	-0.4	-0.5	-0.5	-0.5	-0.5	-0.5	0.0	0.0	0.0	0.0	0.0	0.0
C_4-C_5-S_1-C_2	0.5	0.7	0.7	0.7	0.7	0.7	0.0	0.0	0.0	0.0	0.0	0.0
C_5-S_1-C2-C_3	-0.5	-0.8	-0.8	-0.8	-0.8	-0.8	0.0	0.0	0.0	0.0	0.0	0.0
S_1-C_2-$C_{2'}$-$S_{1'}$	145.4	137.8	137.7	138.1	137.6	138.4	180.0	180.0	179.9	-179.8	-179.1	-179.6
C_3-C_2-$C_{2'}$-$C_{3'}$	148.5	141.0	140.9	141.3	140.7	141.5	180.0	180.0	179.9	179.8	179.9	179.6
$S_{1'}$-$C_{2'}$-$C_{3'}$-$C_{4'}$	0.7	0.4	0.5	0.5	0.5	0.5	0.0	0.0	0.0	0.0	0.0	0.0
$C_{2'}$-$C_{3'}$-$C_{4'}$-$C_{5'}$	0.0	0.1	0.1	0.1	0.1	0.1	0.0	0.0	0.0	0.0	0.0	0.0
$C_{3'}$-$C_{4'}$-$C_{5'}$-$S_{1'}$	-0.6	-0.6	-0.6	-0.6	-0.6	-0.6	0.0	0.0	0.0	0.0	0.0	0.0
$C_{4'}$-$C_{5'}$-$S_{1'}$-$C_{2'}$	0.8	0.8	0.8	0.8	0.8	0.8	0.0	0.0	0.0	0.0	0.0	0.0
$C_{5'}$-$S_{1'}$-$C_{2'}$-$C_{3'}$	-0.8	-0.7	-0.7	-0.7	-0.7	-0.7	0.0	0.0	0.0	0.0	0.0	0.0
X_6-C_3-C_4-C_5	-179.8	-179.6	-179.6	-179.6	-179.6	-179.6	180.0	180.0	180.0	180.0	180.0	180.0
H_7-C_4-C_5-S_1	-179.1	-179.0	-179.1	-179.1	-179.1	-179.1	180.0	180.0	180.0	180.0	180.0	180.0
H_8-C_5-S_1-C_2	120.2	109.2	107.6	108.1	107.5	108.4	180.0	-179.4	179.9	-179.7	180.0	-179.7
$H_{6'}$-$C_{3'}$-$C_{4'}$-$C_{5'}$	86.8	103.1	102.5	102.5	102.7	102.3	180.0	179.9	180.0	179.8	180.0	179.7
$X_{7'}$-$C_{4'}$-$C_{5'}$-$S_{1'}$	-178.9	-179.2	-179.2	-179.2	-179.2	-179.2	180.0	180.0	180.0	180.0	180.0	180.0
$H_{8'}$-$C_{5'}$-$S_{1'}$-$C_{2'}$	-179.7	-178.9	-178.9	-178.9	-178.9	-178.9	180.0	180.0	180.0	180.0	180.0	180.0
C-X_6-C_3-C_2	-178.5	-178.6	-178.7	-178.7	-178.7	-178.7	180.0	180.0	180.0	180.0	180.0	180.0
C-$X_{7'}$-$C_{4'}$-$C_{5'}$	-179.2	-178.8	-178.8	-178.8	-178.8	-178.8	180.0	180.0	180.0	180.0	180.0	180.0

* X is a O atom for 3,4'OABT; C atom for 3,4'ABT

Table 5S. Full set of geometrical parameters of 3,4'ABT and 3,4'OABT obtained with B3LYP/6-31+G*

	3,4'ABT						3,4'OABT					
n	0	1	2	3	4	5	0	1	2	3	4	5
BOND LENGTH / Angstroms												
S_1-C_2	1.757	1.756	1.756	1.756	1.756	1.756	1.754	1.754	1.754	1.754	1.754	1.754
C_2-C_3	1.379	1.378	1.378	1.378	1.378	1.378	1.385	1.385	1.385	1.385	1.385	1.385
C_3-C_4	1.431	1.432	1.432	1.432	1.432	1.432	1.427	1.427	1.427	1.427	1.427	1.427
C_4-C_5	1.372	1.373	1.373	1.373	1.373	1.373	1.374	1.374	1.374	1.374	1.374	1.374
C_5-S_1	1.735	1.735	1.735	1.735	1.735	1.735	1.732	1.732	1.732	1.732	1.732	1.732
C_2-$C_{2'}$	1.458	1.460	1.460	1.460	1.460	1.460	1.447	1.447	1.447	1.447	1.447	1.447
$S_{1'}$-$C_{2'}$	1.758	1.759	1.759	1.759	1.759	1.759	1.756	1.756	1.756	1.756	1.756	1.756
$C_{2'}$-$C_{3'}$	1.386	1.385	1.385	1.385	1.385	1.385	1.388	1.388	1.388	1.388	1.388	1.388
$C_{3'}$-$C_{4'}$	1.432	1.434	1.434	1.434	1.434	1.434	1.430	1.430	1.430	1.430	1.430	1.430
$C_{4'}$-$C_{5'}$	1.368	1.368	1.368	1.368	1.368	1.368	1.369	1.369	1.369	1.369	1.369	1.369
$C_{5'}$-$S_{1'}$	1.730	1.731	1.730	1.730	1.730	1.730	1.731	1.731	1.731	1.731	1.731	1.731
C_3-X_6*	1.508	1.511	1.510	1.510	1.510	1.510	1.362	1.362	1.362	1.362	1.362	1.362
C_4-H_7	1.086	1.086	1.086	1.086	1.086	1.086	1.083	1.083	1.083	1.083	1.083	1.083
C_5-H_8	1.082	1.082	1.082	1.082	1.082	1.082	1.082	1.082	1.082	1.082	1.082	1.082
$C_{3'}$-$H_{6'}$	1.086	1.086	1.086	1.086	1.086	1.086	1.083	1.083	1.083	1.083	1.083	1.083
$C_{4'}$-$X_{7'}$*	1.506	1.510	1.510	1.510	1.510	1.510	1.366	1.366	1.366	1.366	1.366	1.366
$C_{5'}$-$H_{8'}$	1.083	1.083	1.083	1.083	1.083	1.083	1.081	1.081	1.081	1.081	1.081	1.081
BOND ANGLES / Degrees												
S_1-C_2-C_3	109.8	109.8	109.8	109.8	109.8	109.8	110.3	110.3	110.3	110.3	110.3	110.3
C_2-C_3-C_4	114.5	114.5	114.5	114.5	114.5	114.5	113.1	113.1	113.1	113.1	113.1	113.1
C_3-C_4-C_5	111.5	111.4	111.4	111.4	111.4	111.4	113.0	113.0	113.0	113.0	113.0	113.0
C_4-C_5-S_1	112.5	112.5	112.5	112.5	112.5	112.5	111.6	111.6	111.6	111.6	111.6	111.6
C_5-S_1-C_2	91.7	91.7	91.7	91.7	91.7	91.7	92.0	92.0	92.0	92.0	92.0	92.0
$S_{1'}$-$C_{2'}$-$C_{3'}$	110.9	111.0	111.0	111.0	111.0	111.0	109.5	109.5	109.5	109.5	109.5	109.5
$C_{2'}$-$C_{3'}$-$C_{4'}$	111.9	111.9	111.9	111.9	111.9	111.9	114.0	114.0	114.0	114.0	114.0	114.0
$C_{3'}$-$C_{4'}$-$C_{5'}$	113.9	114.0	114.0	114.0	114.0	114.0	112.2	112.2	112.2	112.2	112.2	112.2
$C_{4'}$-$C_{5'}$-$S_{1'}$	111.4	111.4	111.4	111.4	111.4	111.4	112.1	112.1	112.1	112.1	112.1	112.1
$C_{5'}$-$S_{1'}$-$C_{2'}$	91.8	91.8	91.8	91.8	91.8	91.8	92.2	92.2	92.2	92.2	92.2	92.2
C_3-C_2-$C_{2'}$	127.8	127.8	127.8	127.8	127.8	127.8	127.2	127.2	127.2	127.2	127.2	127.2
C_2-$C_{2'}$-$C_{3'}$	130.6	130.8	130.8	130.8	130.8	130.8	129.3	129.3	129.3	129.3	129.3	129.3
C_2-C_3-X_6	125.7	126.0	126.0	126.0	126.0	126.0	119.6	119.6	119.6	119.6	119.6	119.6
C_3-C_4-H_7	122.8	122.9	122.9	122.9	122.9	122.9	124.5	124.5	124.5	124.5	124.5	124.5
C_4-C_5-H_8	128.3	128.2	128.2	128.2	128.2	128.2	127.9	127.9	127.9	127.9	127.9	127.9
$C_{2'}$-$C_{3'}$-$H_{6'}$	122.3	122.1	122.1	122.1	122.1	122.1	122.7	122.7	122.7	122.7	122.7	122.7
$C_{3'}$-$C_{4'}$-$X_{7'}$	123.8	124.0	124.0	124.0	124.0	124.0	126.4	126.4	126.4	126.4	126.4	126.4
$C_{4'}$-$C_{5'}$-$H_{8'}$	127.7	127.6	127.6	127.6	127.6	127.6	127.3	127.3	127.3	127.3	127.3	127.3
DIHEDRAL ANGLE / Degrees												
S_1-C_2-C_3-C_4	0.6	0.8	0.8	0.8	0.8	0.8	0.0	0.0	0.0	0.0	0.0	0.0
C_2-C_3-C_4-C_5	-0.1	-0.2	-0.2	-0.2	-0.2	-0.2	0.0	0.0	0.0	0.0	0.0	0.0
C_3-C_4-C_5-S_1	-0.4	-0.5	-0.5	-0.5	-0.5	-0.5	0.0	0.0	0.0	0.0	0.0	0.0
C_4-C_5-S_1-C_2	0.7	0.8	0.8	0.8	0.8	0.8	0.0	0.0	0.0	0.0	0.0	0.0
C_5-S_1-C2-C_3	-0.7	-0.9	-0.9	-0.9	-0.9	-0.9	0.0	0.0	0.0	0.0	0.0	0.0
S_1-C_2-$C_{2'}$-$S_{1'}$	140.5	132.7	132.8	132.8	132.8	132.7	179.9	179.9	-179.8	180.0	-179.9	179.7
C_3-C_2-$C_{2'}$-$C_{3'}$	143.3	135.5	135.5	135.6	135.6	135.5	179.9	179.9	-179.8	180.0	-179.9	179.7
$S_{1'}$-$C_{2'}$-$C_{3'}$-$C_{4'}$	0.5	0.4	0.4	0.4	0.4	0.4	0.0	0.0	0.0	0.0	0.0	0.0
$C_{2'}$-$C_{3'}$-$C_{4'}$-$C_{5'}$	0.0	0.1	0.1	0.1	0.1	0.1	0.0	0.0	0.0	0.0	0.0	0.0
$C_{3'}$-$C_{4'}$-$C_{5'}$-$S_{1'}$	-0.6	-0.6	-0.7	-0.7	-0.7	-0.7	0.0	0.0	0.0	0.0	0.0	0.0
$C_{4'}$-$C_{5'}$-$S_{1'}$-$C_{2'}$	0.8	0.7	0.7	0.7	0.7	0.7	0.0	0.0	0.0	0.0	0.0	0.0
$C_{5'}$-$S_{1'}$-$C_{2'}$-$C_{3'}$	-0.8	-0.6	-0.7	-0.7	-0.7	-0.7	0.0	0.0	0.0	0.0	0.0	0.0
X_6-C_3-C_4-C_5	-179.8	-179.5	-179.5	-179.5	-179.5	-179.5	180.0	180.0	180.0	180.0	180.0	180.0
H_7-C_4-C_5-S_1	-179.1	-179.0	-179.0	-179.0	-179.0	-179.0	180.0	180.0	180.0	180.0	180.0	180.0
H_8-C_5-S_1-C_2	120.2	109.2	107.8	107.7	107.5	107.4	180.0	179.9	-179.9	180.0	180.0	180.0
$H_{6'}$-$C_{3'}$-$C_{4'}$-$C_{5'}$	87.9	104.5	103.7	103.8	103.8	103.8	180.0	180.0	179.8	180.0	-179.9	180.0
$X_{7'}$-$C_{4'}$-$C_{5'}$-$S_{1'}$	-178.2	-179.3	-179.3	-179.3	-179.3	-179.3	180.0	180.0	180.0	180.0	180.0	180.0
$H_{8'}$-$C_{5'}$-$S_{1'}$-$C_{2'}$	-179.7	-179.1	-179.0	-179.0	-179.0	-179.0	180.0	180.0	180.0	180.0	180.0	180.0
C-X_6-C_3-C_2	-178.6	-178.8	-178.9	-178.9	-178.9	-178.9	180.0	180.0	180.0	180.0	180.0	180.0
C-$X_{7'}$-$C_{4'}$-$C_{5'}$	-179.0	-178.5	-179.6	-179.6	-179.6	-179.6	180.0	180.0	180.0	180.0	180.0	180.0

* X is a O atom for 3,4'OABT; C atom for 3,4'ABT

Table 6S. Calculated optical bandgap energies (eV) for BT, 3,4'ABT and 3,4'OABT at TD-B3LYP/6-31G* level.

n	0	1	2	3	4	5
BT			4.12			
3,4'ABT	4.17	4.25	4.24	4.24	4.24	4.24
3,4'OABT	3.68	3.67	3.67	3.67	3.67	3.67

Table 7S. Calculated optical bandgap energies (eV) of BT TD-PBE0 and TD-M05-2X in combination with 6-31G* and 6-31+G* basis sets

TD-PBE0		TD-M05-2X/6-31G*	
6-31G*	6-31+G*	6-31G*	6-31+G*
4.26	4.14	4.59	4.47

Table 8S. Optimized structural parameters of BT^{+} and their differences respect to the neutral state at B3LYP/6-31+G* level.

	B3LYP/6-31+G*		M05-2X/6-31+G*		PBE0/6-31+G*	
	Value	Difference*	Value	Difference*	Value	Difference*
BOND LENGTH / Angstroms						
S_1-C_2	1.770	0.015	1.749	0.015	1.751	0.014
C_2-C_3	1.417	0.037	1.415	0.043	1.414	0.037
C_3-C_4	1.392	-0.033	1.387	-0.038	1.388	-0.032
C_4-C_5	1.397	0.027	1.394	0.029	1.394	0.026
C_5-S_1	1.715	-0.020	1.702	-0.020	1.702	-0.018
C_2-$C_{2'}$	1.408	-0.045	1.402	-0.054	1.404	-0.046
C_3-H_6	1.085	0.000	1.082	0.000	1.085	0.000
C_4-H_7	1.084	-0.001	1.080	-0.001	1.084	-0.001
C_5-H_8	1.084	0.002	1.080	0.001	1.085	0.002
BOND ANGLES / Degrees						
S_1-C_2-C_3	110.2	0.0	110.6	-0.3	110.4	0.0
C_2-C_3-C_4	113.2	-0.3	112.8	-0.1	113.0	-0.2
C_3-C_4-C_5	112.4	-0.4	112.1	-0.5	112.2	-0.4
C_4-C_5-S_1	113.3	1.7	113.5	1.8	113.3	1.7
C_5-S_1-C_2	90.9	-1.0	91.0	-0.9	91.1	-1.0
C_3-C_2-$C_{2'}$	128.1	-0.9	127.6	-0.9	127.9	-1.0
C_2-C_3-H_6	122.9	0.1	123.0	0.1	123.0	0.2
C_3-C_4-H_7	124.6	0.8	124.8	0.8	124.8	2.0
C_4-C_5-H_8	127.0	-1.4	126.8	-1.4	127.0	3.0
DIHEDRAL ANGLE / Degrees						
S_1-C_2-C_3-C_4	0.0	-0.5	0.0	-0.5	0.0	-0.5
C_2-C_3-C_4-C_5	0.0	-0.1	0.0	-0.1	0.0	-0.1
C_3-C_4-C_5-S_1	0.0	0.6	0.0	0.7	0.0	0.7
C_4-C_5-S_1-C_2	0.0	-0.8	0.0	-0.8	0.0	-0.8
C_5-S_1-C_2-C_3	0.0	0.7	0.0	0.7	0.0	0.7
S_1- C_2-$C_{2'}$-$S_{1'}$	180.0	24.5	180.0	28.7	180.0	25.8
C_3- C_2-$C_{2'}$-$C_{3'}$	180.0	24.2	180.0	28.5	180.0	25.6
H_6- C_3-C_4-C_5	180.0	-0.6	180.0	-0.7	180.0	-0.6
H_7- C_4-C_5-S_1	180.0	0.0	180.0	0.1	180.0	0.0
H_8- C_5-S_1-C_2	180.0	-0.7	180.0	-0.6	180.0	-0.7

* Difference = $X_{Polaronic} - X_{Neutral}$

Table 9S. Main geometrical parameters of 3,4'ABT^{+} obtained with B3LYP/6-31+G

n	0	1	2	3	4	5	0	1	2	3	4	5
	Value						Difference*					
BOND LENGTH / Angstroms												
S_1-C_2	1.771	1.771	1.771	1.771	1.771	1.771	0.014	0.015	0.015	0.015	0.015	0.015
C_2-C_3	1.417	1.418	1.418	1.418	1.418	1.418	0.038	0.040	0.040	0.040	0.040	0.040
C_3-C_4	1.398	1.396	1.397	1.397	1.397	1.397	-0.033	-0.036	-0.035	-0.035	-0.035	-0.035
C_4-C_5	1.402	1.404	1.404	1.404	1.404	1.404	0.030	0.031	0.031	0.031	0.031	0.031
C_5-S_1	1.716	1.714	1.715	1.715	1.715	1.715	-0.019	-0.021	-0.020	-0.020	-0.020	-0.020
C_2-$C_{2'}$	1.409	1.411	1.411	1.411	1.411	1.411	-0.049	-0.049	-0.049	-0.049	-0.049	-0.049
$S_{1'}$-$C_{2'}$	1.775	1.777	1.777	1.777	1.777	1.777	0.017	0.018	0.018	0.018	0.018	0.018
$C_{2'}$-$C_{3'}$	1.432	1.432	1.432	1.432	1.432	1.432	0.046	0.047	0.047	0.047	0.047	0.047
$C_{3'}$-$C_{4'}$	1.403	1.405	1.406	1.406	1.406	1.406	-0.029	-0.029	-0.028	-0.028	-0.028	-0.028
$C_{4'}$-$C_{5'}$	1.388	1.386	1.385	1.385	1.385	1.385	0.020	0.018	0.017	0.017	0.017	0.017
$C_{5'}$-$S_{1'}$	1.712	1.712	1.713	1.713	1.713	1.713	-0.018	-0.019	-0.017	-0.017	-0.017	-0.017
C_3-X_6*	1.500	1.506	1.503	1.503	1.503	1.503	-0.008	-0.005	-0.007	-0.007	-0.007	-0.007
C_4-H_7	1.084	1.084	1.085	1.085	1.085	1.085	-0.002	-0.002	-0.001	-0.001	-0.001	-0.001
C_5-H_8	1.084	1.084	1.084	1.084	1.084	1.084	0.002	0.002	0.002	0.002	0.002	0.002
$C_{3'}$-$H_{6'}$	1.085	1.085	1.085	1.085	1.085	1.085	-0.001	-0.001	-0.001	-0.001	-0.001	-0.001
$C_{4'}$-$X_{7'}$*	1.503	1.507	1.505	1.505	1.505	1.505	-0.003	-0.003	-0.005	-0.005	-0.005	-0.005
$C_{5'}$-$H_{8'}$	1.085	1.085	1.085	1.085	1.085	1.085	0.002	0.002	0.002	0.002	0.002	0.002
BOND ANGLES / Degrees												
S_1-C_2-C_3	109.6	109.4	109.4	109.4	109.4	109.4	0.2	0.4	0.4	0.4	0.4	0.4
C_2-C_3-C_4	114.7	114.9	114.9	114.9	114.9	114.9	-0.9	-0.8	-0.9	-0.9	-0.9	-0.9
C_3-C_4-C_5	110.6	110.6	110.5	110.5	110.5	110.5	1.8	1.7	1.7	1.7	1.7	1.7
C_4-C_5-S_1	114.3	114.2	114.2	114.2	114.2	114.2	-0.9	-0.7	-0.7	-0.7	-0.7	-0.7
C_5-S_1-C_2	90.8	91.0	91.0	91.0	91.0	91.0	-0.3	-0.5	-0.4	-0.4	-0.4	-0.4
$S_{1'}$-$C_{2'}$-$C_{3'}$	110.6	110.5	110.6	110.6	110.6	110.6	-0.5	-0.6	-0.6	-0.6	-0.6	-0.6
$C_{2'}$-$C_{3'}$-$C_{4'}$	111.4	111.3	111.3	111.3	111.3	111.3	0	0	0.1	0.1	0.1	0.1
$C_{3'}$-$C_{4'}$-$C_{5'}$	113.9	114.0	114.1	114.1	114.1	114.1	1.7	1.6	1.6	1.6	1.6	1.6
$C_{4'}$-$C_{5'}$-$S_{1'}$	113.1	113.0	113.0	113.0	113.0	113.0	-0.8	-0.7	-0.7	-0.7	-0.7	-0.7
$C_{5'}$-$S_{1'}$-$C_{2'}$	91.0	91.1	91.1	91.1	91.1	91.1	-1.2	-1.5	-1.5	-1.5	-1.5	-1.5
C_3-C_2-$C_{2'}$	126.6	126.3	126.3	126.3	126.3	126.3	-0.1	0.5	0.5	0.5	0.5	0.5
C_2-$C_{2'}$-$C_{3'}$	130.5	131.3	131.3	131.3	131.3	131.3	0.1	0.3	0.3	0.3	0.3	0.3
C_2-C_3-X_6	125.9	127.1	127.1	127.1	127.1	127.1	0.6	0.4	0.3	0.3	0.3	0.3
C_3-C_4-H_7	123.4	123.3	123.2	123.2	123.2	123.2	-1.3	-1.1	-1.1	-1.1	-1.1	-1.1
C_4-C_5-H_8	127.0	127.1	127.1	127.1	127.1	127.1	0.2	0.4	0.4	0.4	0.4	0.4
$C_{2'}$-$C_{3'}$-$H_{6'}$	122.4	122.4	122.4	122.4	122.4	122.4	1.5	1.6	1.6	1.6	1.6	1.6
$C_{3'}$-$C_{4'}$-$X_{7'}$	125.3	125.6	125.6	125.6	125.6	125.6	-1.3	-1.1	-1.1	-1.1	-1.1	-1.1
$C_{4'}$-$C_{5'}$-$H_{8'}$	126.4	126.5	126.5	126.5	126.5	126.5	0.2	1.1	1.1	1.1	1.1	1.1
DIHEDRAL ANGLE / Degrees												
S_1-C_2-C_3-C_4	0.0	0.2	0.1	0.1	-178.2	-178.2	-0.6	-0.6	-0.7	-0.7	-179	-179
C_2-C_3-C_4-C_5	0.0	-0.2	-0.1	-0.1	179.7	179.7	0.1	0	0.1	0.1	179.9	179.9
C_3-C_4-C_5-S_1	0.0	0.1	0.1	0.1	178.2	178.2	0.4	0.6	0.6	0.6	178.7	178.7
C_4-C_5-S_1-C_2	0.0	0.0	0.0	0.0	179.9	179.9	-0.7	-0.8	-0.8	-0.8	179.1	179.1
C_5-S_1-C2-C_3	0.0	-0.1	-0.1	-0.1	-179.9	-179.9	0.7	0.8	0.8	0.8	-179	-179
S_1-C_2-$C_{2'}$-$S_{1'}$	180.0	178.7	178.7	178.8	178.8	178.8	39.5	46	45.9	46	46	46.1
C_3-C_2-$C_{2'}$-$C_{3'}$	180.0	178.4	178.4	178.5	178.5	178.5	36.7	42.9	42.9	42.9	42.9	43
$S_{1'}$-$C_{2'}$-$C_{3'}$-$C_{4'}$	0.0	0.1	0.0	0.0	0.0	0.0	-0.5	-0.3	-0.4	-0.4	-0.4	-0.4
$C_{2'}$-$C_{3'}$-$C_{4'}$-$C_{5'}$	0.0	-0.2	-0.1	-0.1	-0.1	-0.1	0	-0.3	-0.2	-0.2	-0.2	-0.2
$C_{3'}$-$C_{4'}$-$C_{5'}$-$S_{1'}$	0.0	0.2	0.1	0.1	0.1	0.1	0.6	0.8	0.8	0.8	0.8	0.8
$C_{4'}$-$C_{5'}$-$S_{1'}$-$C_{2'}$	0.0	-0.1	-0.1	-0.1	-0.1	-0.1	-0.8	-0.8	-0.8	-0.8	-0.8	-0.8
$C_{5'}$-$S_{1'}$-$C_{2'}$-$C_{3'}$	0.0	0.0	0.0	0.0	0.0	0.0	0.8	0.6	0.7	0.7	0.7	0.7
X_6-C_3-C_4-C_5	180.0	-179.6	179.9	179.9	179.9	179.9	359.8	-0.1	359.4	359.4	359.4	359.4
H_7-C_4-C_5-S_1	180.0	-179.9	-179.9	-179.9	-179.9	-179.9	359.1	-0.9	-0.9	-0.9	-0.9	-0.9
H_8-C_5-S_1-C_2	0.0	83.6	84.9	84.6	84.6	88.1	-120.2	-25.6	-22.9	-23.1	-22.9	-19.3
$H_{6'}$-$C_{3'}$-$C_{4'}$-$C_{5'}$	60.0	87.0	87.0	87.0	87.0	87.0	-27.9	-17.5	-16.7	-16.8	-16.8	-16.8
$X_{7'}$-$C_{4'}$-$C_{5'}$-$S_{1'}$	180.0	179.7	179.7	179.7	179.7	179.7	358.2	359	359	359	359	359
$H_{8'}$-$C_{5'}$-$S_{1'}$-$C_{2'}$	180.0	-178.4	-178.2	-178.2	-178.2	-178.2	359.7	0.7	0.8	0.8	0.8	0.8
C-X_6-C_3-C_2	180.0	179.7	179.7	179.7	179.7	179.7	358.6	358.5	358.6	358.6	358.6	358.6
C-$X_{7'}$-$C_{4'}$-$C_{5'}$	180.0	178.3	178.2	178.2	178.2	178.2	359	356.8	357.8	357.8	357.8	357.8

* Difference = $X_{Polaronic} - X_{Neutral}$

Table 10S. Main geometrical parameters of 3,4'OABT^{+} obtained with B3LYP/6-31+G

n	0	1	2	3	4	5	0	1	2	3	4	5
	Value						Difference*					
BOND LENGTH / Angstroms												
S_1-C_2	1.781	1.781	1.781	1.781	1.781	1.781	0.027	0.027	0.027	0.027	0.027	0.027
C_2-C_3	1.407	1.406	1.406	1.406	1.406	1.406	0.022	0.021	0.021	0.021	0.021	0.021
C_3-C_4	1.401	1.402	1.402	1.402	1.402	1.402	-0.026	-0.025	-0.025	-0.025	-0.025	-0.025
C_4-C_5	1.416	1.417	1.417	1.417	1.417	1.417	0.042	0.043	0.043	0.043	0.043	0.043
C_5-S_1	1.706	1.707	1.707	1.707	1.707	1.707	-0.026	-0.025	-0.025	-0.025	-0.025	-0.025
C_2-$C_{2'}$	1.407	1.407	1.407	1.407	1.407	1.407	-0.040	-0.040	-0.040	-0.040	-0.040	-0.040
$S_{1'}$-$C_{2'}$	1.762	1.763	1.763	1.763	1.763	1.763	0.006	0.007	0.007	0.007	0.007	0.007
$C_{2'}$-$C_{3'}$	1.427	1.428	1.428	1.428	1.428	1.428	0.039	0.040	0.040	0.040	0.040	0.040
$C_{3'}$-$C_{4'}$	1.417	1.418	1.418	1.418	1.418	1.418	-0.013	-0.012	-0.012	-0.012	-0.012	-0.012
$C_{4'}$-$C_{5'}$	1.375	1.374	1.374	1.374	1.374	1.374	0.006	0.005	0.005	0.005	0.005	0.005
$C_{5'}$-$S_{1'}$	1.726	1.726	1.726	1.726	1.726	1.726	-0.005	-0.005	-0.005	-0.005	-0.005	-0.005
C_3-X_6*	1.083	1.083	1.083	1.083	1.083	1.083	0.000	0.000	0.000	0.000	0.000	0.000
C_4-H_7	1.330	1.328	1.328	1.328	1.328	1.328	-0.036	-0.038	-0.038	-0.038	-0.038	-0.038
C_5-H_8	1.083	1.083	1.083	1.083	1.083	1.083	0.002	0.002	0.002	0.002	0.002	0.002
$C_{3'}$-$H_{6'}$	1.328	1.326	1.326	1.326	1.326	1.326	-0.034	-0.036	-0.036	-0.036	-0.036	-0.036
$C_{4'}$-$X_{7'}$*	1.082	1.082	1.082	1.082	1.082	1.082	-0.001	-0.001	-0.001	-0.001	-0.001	-0.001
$C_{5'}$-$H_{8'}$	1.084	1.084	1.084	1.084	1.084	1.084	0.002	0.002	0.002	0.002	0.002	0.002
BOND ANGLES / Degrees												
S_1-C_2-C_3	110.8	110.8	110.8	110.8	110.8	110.8	0.5	0.5	0.5	0.5	0.5	0.5
C_2-C_3-C_4	112.8	112.9	112.9	112.9	112.9	112.9	-0.3	-0.2	-0.2	-0.2	-0.2	-0.2
C_3-C_4-C_5	112.5	112.3	112.3	112.3	112.3	112.3	-0.5	-0.7	-0.7	-0.7	-0.7	-0.7
C_4-C_5-S_1	113.1	113.1	113.1	113.1	113.1	113.1	1.5	1.5	1.5	1.5	1.5	1.5
C_5-S_1-C_2	90.9	90.9	90.9	90.9	90.9	90.9	-1.1	-1.1	-1.1	-1.1	-1.1	-1.1
$S_{1'}$-$C_{2'}$-$C_{3'}$	109.7	109.7	109.7	109.7	109.7	109.7	0.2	0.2	0.2	0.2	0.2	0.2
$C_{2'}$-$C_{3'}$-$C_{4'}$	113.4	113.2	113.2	113.2	113.2	113.2	-0.6	-0.8	-0.8	-0.8	-0.8	-0.8
$C_{3'}$-$C_{4'}$-$C_{5'}$	111.7	111.8	111.8	111.8	111.8	111.8	-0.5	-0.4	-0.4	-0.4	-0.4	-0.4
$C_{4'}$-$C_{5'}$-$S_{1'}$	114.1	114.4	114.4	114.4	114.4	114.4	2	2.3	2.3	2.3	2.3	2.3
$C_{5'}$-$S_{1'}$-$C_{2'}$	91.2	91.2	91.2	91.2	91.2	91.2	-1.0	-1.0	-1.0	-1.0	-1.0	-1.0
C_3-C_2-$C_{2'}$	127.2	127.2	127.2	127.2	127.2	127.2	0.0	0.0	0.0	0.0	0.0	0.0
C_2-$C_{2'}$-$C_{3'}$	128.4	128.5	128.5	128.5	128.5	128.5	-0.9	-0.8	-0.8	-0.8	-0.8	-0.8
C_2-C_3-X_6	122.8	122.8	122.8	122.8	122.8	122.8	0.1	0.1	0.1	0.1	0.1	0.1
C_3-C_4-H_7	129.0	129.1	129.1	129.1	129.1	129.1	2.6	2.7	2.7	2.7	2.7	2.7
C_4-C_5-H_8	125.4	125.4	125.4	125.4	125.4	125.4	-1.9	-1.9	-1.9	-1.9	-1.9	-1.9
$C_{2'}$-$C_{3'}$-$H_{6'}$	119.0	119.2	119.2	119.2	119.2	119.2	-0.6	-0.4	-0.4	-0.4	-0.4	-0.4
$C_{3'}$-$C_{4'}$-$X_{7'}$	124.9	124.9	124.9	124.9	124.9	124.9	0.4	0.4	0.4	0.4	0.4	0.4
$C_{4'}$-$C_{5'}$-$H_{8'}$	126.7	126.7	126.7	126.7	126.7	126.7	-1.2	-1.2	-1.2	-1.2	-1.2	-1.2
DIHEDRAL ANGLE / Degrees												
S_1-C_2-C_3-C_4	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
C_2-C_3-C_4-C_5	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
C_3-C_4-C_5-S_1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
C_4-C_5-S_1-C_2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
C_5-S_1-C2-C_3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
S_1-C_2-$C_{2'}$-$S_{1'}$	180.0	180.0	180.0	179.9	179.9	179.9	0.1	0.1	0.1	-0.1	0.1	0.2
C_3-C_2-$C_{2'}$-$C_{3'}$	180.0	180.0	180.0	179.9	179.9	179.9	0.1	0.1	0.1	-0.1	0.1	0.2
$S_{1'}$-$C_{2'}$-$C_{3'}$-$C_{4'}$	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
$C_{2'}$-$C_{3'}$-$C_{4'}$-$C_{5'}$	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
$C_{3'}$-$C_{4'}$-$C_{5'}$-$S_{1'}$	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
$C_{4'}$-$C_{5'}$-$S_{1'}$-$C_{2'}$	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
$C_{5'}$-$S_{1'}$-$C_{2'}$-$C_{3'}$	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
X_6-C_3-C_4-C_5	180.0	180.0	180.0	180.0	180.0	180.0	0.0	0.0	0.0	0.0	0.0	0.0
H_7-C_4-C_5-S_1	180.0	180.0	180.0	180.0	180.0	180.0	0.0	0.0	0.0	0.0	0.0	0.0
H_8-C_5-S_1-C_2	180.0	180.0	180.0	179.9	179.9	179.9	0.0	0.1	0.1	-0.1	0.1	0.2
$H_{6'}$-$C_{3'}$-$C_{4'}$-$C_{5'}$	180.0	180.0	180.0	180.0	180.0	180.0	0.0	0.0	0.2	0.0	0.1	0.2
$X_{7'}$-$C_{4'}$-$C_{5'}$-$S_{1'}$	180.0	180.0	180.0	180.0	180.0	180.0	0.0	0.0	0.0	0.0	0.0	0.0
$H_{8'}$-$C_{5'}$-$S_{1'}$-$C_{2'}$	180.0	180.0	180.0	180.0	180.0	180.0	0.0	0.0	0.0	0.0	0.0	0.0
C-X_6-C_3-C_2	180.0	180.0	180.0	180.0	180.0	180.0	0.0	0.0	0.0	0.0	0.0	0.0
C-$X_{7'}$-$C_{4'}$-$C_{5'}$	180.0	180.0	180.0	180.0	180.0	180.0	0.0	0.0	0.0	0.0	0.0	0.0

* Difference = $X_{Polaronic} - X_{Neutral}$

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Table 11S. Vertical (VIP) and adiabatic (AIP) ionization potential and reorganization energy for BT calculated at M05-2X/6-31+G* and PBE0/6-31+G* levels.

	λ_1	λ_2	λ	AIP / eV	VIP / eV
M05-2X	0.2450	0.3195	0.5644	7.5775	7.8970
PBE0	0.1931	0.2573	0.4504	7.3539	7.6112

Figure 1S. C_2-C_3-$C_{2'}$-$C_{3'}$ Rotational barriers calculated at selected levels of theory mPW1PW91/6-31G*, M05-2X/6-31G*, PBE0/6-31G* and MP2/6-31G* levels corresponding to a rotation around C_2-C_3-$C_{2'}$-$C_{3'}$.

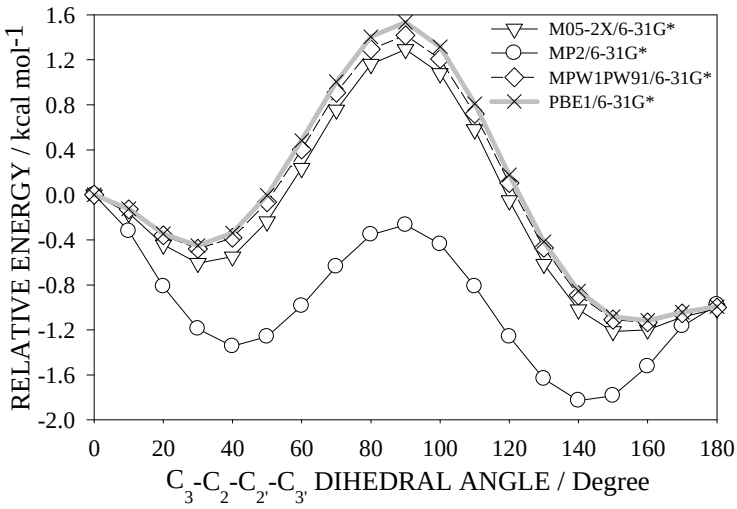
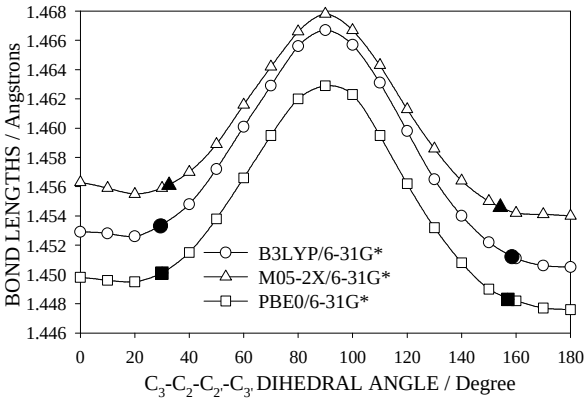
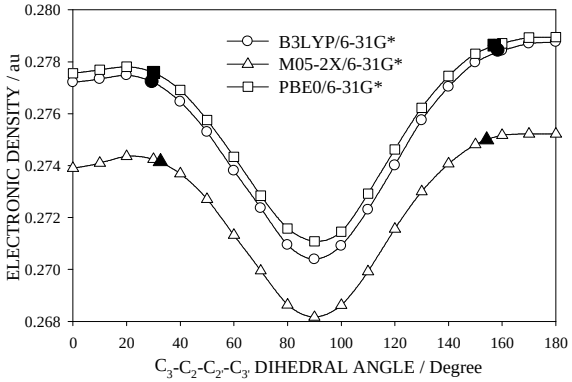


Figure 2S. Variation of (a) C_2-$C_{2'}$ bond length, (b) electronic density of C_2-$C_{2'}$ bond and (c) π (C_2-C_3) → π^* ($C_{2'}$-$C_{3'}$) charge transference as a function of the C_2-C_3-$C_{2'}$-$C_{3'}$ dihedral angle at PBE0/6-31G* and M05-2X/6-31G*.

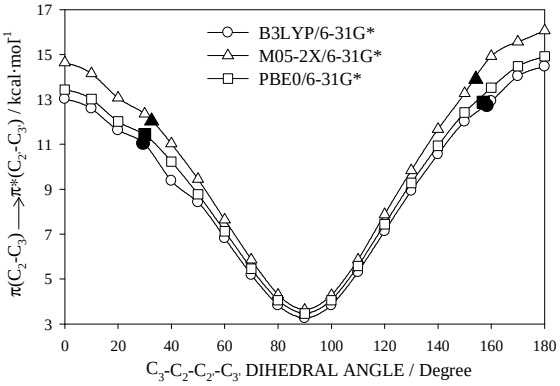
a)



b)



c)



Filled symbols represent the position of the optimized minima