Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information: Dynamic effects on the nonlinear optical properties of Donor Acceptor Stenhouse Adducts: insights from combined MD+QM simulations

Angela Dellai,[*,†] Carmelo Naim,[†,‡] Javier Cerezo,[¶] Giacomo Prampolini,[*,§] and Frédéric Castet[*,†]

†*Univ. Bordeaux, CNRS, Bordeaux INP, Institut des Sciences Moléculaires, UMR 5255, F-33400 Talence, France*

‡*Donostia International Physics Center (DIPC), Manuel Lardizabal Ibilbidea 4, 20018 Donostia, Euskadi, Spain*

¶*Departamento de Química and Institute for Advanced Research in Chemical Sciences (IAdChem), Universidad Autónoma de Madrid, 28049 Madrid, Spain*

§*Consiglio Nazionale delle Ricerche, CNR-ICCOM, Pisa, Italy*

E-mail: angela.dellai@u-bordeaux.fr; giacomo.prampolini@pi.iccom.cnr.it; frederic.castet@u-bordeaux.fr

Contents

1 QMD-FF parameters tables **S-3**

1.1 Open form S-3

1.2 Closed form S-9

2 Force Field validation **S-16**

3 Dynamic behavior and nonlinear optical properties **S-19**

3.1 Calculation of the β_{zxx}/β_{zzz} ratio S-24

1 QMD-FF parameters tables

1.1 Open form

Table S1: Intermolecular QMD-FF parameters of open DASA conformer: σ (Å), ϵ (kJ/mol) and q (e^-). Atom types are shown in Figure 3.

Atom type	σ^{inter}	ϵ^{inter}	q
C_{A1}	3.750	0.4393	0.2707
N_A	3.250	0.7113	0.0740
C_{A2}	3.750	0.4393	0.2338
C_{A3}	3.550	0.3180	-0.1145
O_{A1}	2.960	0.8786	-0.5024
O_{A2}	2.960	0.8786	-0.4986
C_{AN}	3.500	0.2761	-0.1498
H_C	2.500	0.1255	0.0946
C_{C1}	3.550	0.3180	-0.1258
H_{C1}	2.420	0.1255	0.1234
C_{C2}	3.500	0.2761	0.2437
O_H	3.120	0.7113	-0.5964
H_O	0.000	0.0000	0.4391
C_{C3}	3.550	0.3180	-0.3029
H_{C3}	2.420	0.1255	0.1957
C_{C4}	3.550	0.3180	-0.0868
H_{C4}	2.420	0.1255	0.1566
C_{C5}	3.550	0.3180	-0.1406
H_{C5}	2.420	0.1255	0.2217
N_C	3.250	0.7113	0.0330
C_{CN}	3.500	0.2761	-0.1111
C_{C6}	3.500	0.2761	-0.1455
H_{C6}	2.500	0.1255	0.1220
C_{B1}	3.550	0.2929	0.0582
C_{B2}	3.550	0.2929	-0.1165
C_{B3}	3.550	0.2929	-0.2309
C_{B4}	3.550	0.2929	-0.0893
H_{B2}	2.420	0.1255	0.1395
H_{B3}	2.420	0.1255	0.1724
H_{B4}	2.420	0.1255	0.1463

Table S2: QMD-FF stretching parameters for the open form: equilibrium distances r^0 and force constants k^s appearing in equation (5) are in Å and in kJ/mol Å^{-2}, respectively.

stretching	$\mathbf{r^0}$	$\mathbf{k^s}$	**stretching**	$\mathbf{r^0}$	$\mathbf{k^s}$
C_{A1}-N_A	1.388	2717.81	N_A-C_{A2}	1.390	2600.98
C_{A2}-C_{A3}	1.441	2406.97	C_{A1}-O_{A1}	1.222	6271.06
C_{A2}-O_{A2}	1.244	5624.38	N_A-C_{AN}	1.463	2477.31
C_{AN}-H_C	1.088	3297.62	C_{A3}-C_{C1}	1.406	2976.06
C_{C1}-C_{C2}	1.398	3402.90	C_{C2}-C_{C3}	1.400	3213.43
C_{C3}-C_{C4}	1.398	3482.42	C_{C4}-C_{C5}	1.392	3399.86
C_{C5}-N_C	1.325	4037.84	N_C-C_{CN}	1.457	2556.00
N_C-C_{C6}	1.457	2505.61	C_{C6}-C_{B1}	1.517	2158.76
C_{C2}-O_H	1.355	3570.57	O_H-H_O	0.995	2910.45
C_{C1}-H_{C1}	1.089	3409.33	C_{C3}-H_{C3}	1.090	3366.06
C_{C4}-H_{C4}	1.087	3459.06	C_{C5}-H_{C5}	1.092	3347.93
C_{CN}-H_C	1.098	3221.46	C_{C6}-H_{C6}	1.096	3183.75
C_{B1}-C_{B2}	1.398	3116.89	C_{B2}-C_{B3}	1.395	3371.12
C_{B3}-C_{B4}	1.396	3464.22	C_{B2}-H_{B2}	1.091	3339.49
C_{B3}-H_{B3}	1.089	3397.74	C_{B4}-H_{B4}	1.089	3398.19

Table S3: QMD-FF bending parameters for the open form: equilibrium angles θ^0 and force constants k^b appearing in equation (5) are in degrees and in kJ/mol rad^{-2}, respectively.

bending	$\theta^{\mathbf{0}}$	$\mathbf{k^b}$	**bending**	$\theta^{\mathbf{0}}$	$\mathbf{k^b}$
N_A-C_{A1}-N_A	117.1	474.01	C_{A1}-N_A-C_{A2}	124.6	474.01
N_A-C_{A2}-C_{A3}	117.3	248.81	C_{A2}-C_{A3}-C_{A2}	119.5	723.62
N_A-C_{A1}-O_{A1}	120.3	706.02	C_{A1}-N_A-C_{AN}	118.9	615.12
C_{A2}-N_A-C_{AN}	120.0	697.33	N_A-C_{A2}-O_{A2}	118.0	816.10
C_{A3}-C_{A2}-O_{A2}	124.7	474.06	C_{A2}-C_{A3}-C_{C1}	125.4	593.46
N_A-C_{AN}-H_C	108.1	446.93	H_C-C_{AN}-H_C	110.3	313.59
C_{A3}-C_{C1}-C_{C2}	134.2	485.26	C_{C1}-C_{C2}-C_{C3}	117.4	268.10
C_{C2}-C_{C3}-C_{C4}	123.8	739.16	C_{C3}-C_{C4}-C_{C5}	119.4	750.20
C_{C4}-C_{C5}-N_C	125.6	646.46	C_{C5}-N_C-C_{C6}	121.4	604.45
N_C-C_{C6}-C_{B1}	112.5	634.04	C_{C1}-C_{C2}-O_H	125.8	441.12
C_{C2}-O_H-H_O	107.5	692.60	O_H-C_{C2}-C_{C3}	116.8	239.70
C_{C5}-N_C-C_{CN}	120.7	545.24	C_{CN}-N_C-C_{C6}	117.8	694.32
N_C-C_{CN}-H_C	110.6	449.13	H_C-C_{CN}-H_C	109.1	297.87
C_{A3}-C_{C1}-H_{C1}	112.5	278.21	H_{C1}-C_{C1}-C_{C2}	113.3	312.56
C_{C2}-C_{C3}-H_{C3}	117.2	343.39	H_{C3}-C_{C3}-C_{C4}	119.0	324.17
C_{C3}-C_{C4}-H_{C4}	119.4	315.18	H_{C4}-C_{C4}-C_{C5}	121.2	276.11
C_{C4}-C_{C5}-H_{C5}	119.2	325.75	H_{C5}-C_{C5}-N_C	115.2	407.30
N_C-C_{C6}-H_{C6}	107.7	463.41	H_{C6}-C_{C6}-H_{C6}	107.9	337.84
H_{C6}-C_{C6}-C_{B1}	110.4	342.97	C_{B2}-C_{B1}-C_{B2}	119.3	733.26
C_{B1}-C_{B2}-C_{B3}	120.3	617.65	C_{B2}-C_{B3}-C_{B4}	120.2	722.18
C_{B3}-C_{B4}-C_{B3}	119.7	683.17	C_{C6}-C_{B1}-C_{B2}	121.0	689.87
C_{B1}-C_{B2}-H_{B2}	120.0	240.14	C_{B3}-C_{B2}-H_{B2}	119.7	344.29
C_{B2}-C_{B3}-H_{B3}	119.8	319.89	C_{B4}-C_{B3}-H_{B3}	120.0	325.85

Table S4: QMD-FF parameters for the stiff torsions described by equation (6) in the open form: equilibrium dihedral angles ϕ^0 are in degrees and force constants k^t in kJ/mol rad^{-2}.

dihedral	$\phi^{\mathbf{0}}$	$\mathbf{k^t}$	**dihedral**	$\phi^{\mathbf{0}}$	$\mathbf{k^t}$
C_{A1}-N_A-C_{A2}-C_{A3}	0.0	82.26	N_A -C_{A2}-C_{A3}-C_{A2}	0.0	82.26
N_A-C_{A1}-N_A-C_{A2}	0.0	82.26	O_{A1}-C_{A1}-N_A -C_{A2}	180.0	82.26
O_{A2}-C_{A2}-C_{A3}-C_{A2}	180.0	82.26	C_{A1}-N_A -C_{A2}-O_{A2}	180.0	82.26
N_A-C_{A1}-N_A-C_{AN}	180.0	82.26	C_{AN}-N_A -C_{A2}-C_{A3}	180.0	82.26
O_{A1}-C_{A1}-N_A-C_{AN}	0.0	82.26	O_{A2}-C_{A2}-C_{A3}-C_{C1}	0.0	82.26
C_{AN}-N_A-C_{A2}-O_{A2}	0.0	82.26	N_A -C_{A2}-C_{A3}-C_{C1}	180.0	82.26
C_{B1}-C_{B2}-C_{B3}-C_{B4}	0.0	86.50	C_{B2}-C_{B3}-C_{B4}-C_{B3}	0.0	86.50
C_{B2}-C_{B1}-C_{B2}-C_{B3}	0.0	86.50	C_{C6}-C_{B1}-C_{B2}-C_{B3}	180.0	86.50
C_{B2}-C_{B1}-C_{B2}-H_{B2}	180.0	50.49	H_{B2}-C_{B2}-C_{B3}-C_{B4}	180.0	50.49
C_{B1}-C_{B2}-C_{B3}-H_{B3}	180.0	50.49	H_{B3}-C_{B3}-C_{B4}-C_{B3}	180.0	50.49
C_{B2}-C_{B3}-C_{B4}-H_{B4}	180.0	50.49	H_{B2}-C_{B2}-C_{B3}-H_{B3}	0.0	50.49
C_{C6}-C_{B1}-C_{B2}-H_{B2}	0.0	50.49	H_{B3}-C_{B3}-C_{B4}-H_{B4}	0.0	50.49
C_{A1}-N_A-O_{A1}-N_A	0.0	82.26	C_{A2}-N_A -O_{A2}-C_{A3}	0.0	82.26
C_{A2}-C_{A3}-O_{A2}-N_A	0.0	82.26	N_A -C_{A1}-C_{A2}-C_{AN}	0.0	82.26
C_{A3}-C_{A2}-C_{A2}-C_{C1}	0.0	82.26	C_{C1}-C_{A3}-H_{C1}-C_{C2}	0.0	690.25
C_{C3}-C_{C1}-O_H-C_{C2}	0.0	330.40	C_{C4}-C_{C2}-H_{C3}-C_{C3}	0.0	544.30
C_{C5}-C_{C3}-H_{C4}-C_{C4}	0.0	369.33	N_C -C_{C4}-H_{C5}-C_{C5}	0.0	657.82
C_{C6}-C_{C5}-C_{CN}-N_C	0.0	216.36	C_{B1}-C_{C6}-C_{B2}-C_{B2}	0.0	86.50
H_{B2}-C_{B1}-C_{B3}-C_{B2}	0.0	50.49	H_{B3}-C_{B2}-C_{B4}-C_{B3}	0.0	50.49
H_{B4}-C_{B3}-C_{B3}-C_{B4}	0.0	50.49	C_{A3}-C_{C1}-C_{C2}-C_{C3} (δ_{C1})	180.0	95.26
C_{C3}-C_{C4}-C_{C5}-N_C (δ_{C4})	180.0	91.70			

Table S5: Intramolecular parameters for flexible torsions in open form: number of cosines n, γ (degrees) and force constants k^d in kJ/mol. All dihedral labels refer to Figure 3.b

dihedral	N_{cos}	n	k^d (kJ/mol)	γ (degr)
C_{A1}-N_A-C_{AN}-H_C (δ_1)	1	3	1.500	0.00
C_{C6}-N_C-C_{CN}-H_C (δ_2)	1	3	0.924	180.00
C_{A2}-C_{A3}-C_{C1}-C_{C2} (δ_{RA})	4	0	15.711	0.00
		2	-23.112	0.00
		4	5.331	0.00
		6	-0.641	0.00
C_{C1}-C_{C2}-O_H-H_O (δ_{OH})	4	0	9.912	0.00
		1	-23.116	0.00
		2	-1.788	0.00
		3	2.571	0.00
N_C-C_{C6}-C_{B1}-C_{B2} (δ_{RB})	4	0	28.812	0.00
		2	-0.647	0.00
		4	0.354	0.00
		6	0.532	0.00
C_{C1}-C_{C2}-C_{C3}-C_{C4} (δ_{C2})	6	0	14.406	0.00
		1	8.038	0.00
		2	-37.869	0.00
		3	4.355	0.00
		4	6.953	0.00
		5	-1.891	0.00
C_{C2}-C_{C3}-C_{C4}-C_{C5} (δ_{C3})	6	0	14.406	0.00
		1	1.651	0.00
		2	-34.927	0.00
		3	1.533	0.00
		4	5.008	0.00
		5	-0.093	0.00
C_{C4}-C_{C5}-N_C-C_{C6} (δ_{N1})	6	0	14.406	0.00
		1	5.015	0.00
		2	-30.065	0.00
		3	-3.151	0.00
		4	5.088	0.00
		5	0.303	0.00
C_{C5}-N_C-C_{C6}-C_{B1} (δ_{N2})	6	0	14.406	0.00
		1	-0.194	0.00
		2	4.591	0.00
		3	-4.062	0.00
		4	0.758	0.00
		5	-0.999	0.00

Table S6: Open form's QMD-FF parameters for the specific non-bonded intramolecular interactions accounted for in equation (8): σ^{intra} (Å) and ϵ^{intra} (kJ/mol). All labels refer to Figure 3.a.

Pair (ij)	σ_{ij}^{intra}	ϵ_{ij}^{intra}
O_{A2}-H_O	1.410	15.0000
H_{C3}-H_C	2.460	0.1255
H_{C4}-H_C	2.460	0.1255
H_{C6}-H_C	2.460	0.1255
H_{B2}-H_{C5}	2.460	0.1255
H_{B2}-H_C	2.460	0.1255

1.2 Closed form

Table S7: Intermolecular QMD-FF parameters of closed DASA conformer: σ (Å), ϵ (kJ/mol) and q (e^-) Atom types are shown in Figure 4

Atom type	σ^{inter}	ϵ^{inter}	q
C_{A1}	3.750	0.4393	0.3253
N_A	3.250	0.7113	0.0859
C_{A2}	3.750	0.4393	0.0992
C_{A3}	3.550	0.3180	-0.1625
O_{A1}	2.960	0.8786	-0.5918
O_{A2}	2.960	0.8786	-0.5030
C_{AN}	3.500	0.2761	-0.1020
H_C	2.500	0.1255	0.1619
C_{R1}	3.500	0.2761	-0.0032
H_{R1}	2.500	0.1255	0.0612
C_{R2}	3.750	0.4393	0.5957
O_R	2.960	0.8786	-0.5416
C_{R3}	3.550	0.3180	-0.3055
H_{R3}	2.420	0.1255	0.2082
C_{R4}	3.550	0.3180	-0.2318
H_{R4}	2.420	0.1255	0.2199
C_{R5}	3.500	0.2761	0.0044
H_{R5}	2.420	0.1255	0.1609
N_R	3.250	0.7113	-0.0138
H_{NR}	0.000	0.0000	0.3289
C_{CN}	3.500	0.2761	-0.3140
C_{C6}	3.500	0.2761	-0.0372
H_{C6}	2.500	0.1255	0.0850
C_{B1}	3.550	0.2929	0.0623
C_{B2}	3.550	0.2929	-0.0915
C_{B3}	3.550	0.2929	-0.2379
C_{B4}	3.550	0.2929	-0.0647
H_{B2}	2.420	0.1255	0.1188
H_{B3}	2.420	0.1255	0.1732
H_{B4}	2.420	0.1255	0.1440

Table S8: QMD-FF stretching parameters for the closed form: equilibrium distances r^0 and force constants k^s appearing in equation (5) are in Å and in kJ/mol Å^{-2}, respectively.

stretching	$\mathbf{r^0}$	$\mathbf{k^s}$	**stretching**	$\mathbf{r^0}$	$\mathbf{k^s}$
C_{A1}-N_A	1.377	2859.78	N_A-C_{A2}	1.413	2416.15
C_{A2}-C_{A3}	1.418	2839.20	C_{A1}-O_{A1}	1.230	5927.62
C_{A2}-O_{A2}	1.240	5029.42	N_A-C_{AN}	1.457	2529.66
C_{AN}-H_C	1.093	3264.68	C_{A3}-C_{R1}	1.491	2607.11
C_{R1}-H_{R1}	1.102	3064.97	C_{R1}-C_{R2}	1.525	1874.39
C_{R2}-O_R	1.209	7272.48	C_{R2}-C_{R3}	1.494	2014.50
C_{R3}-H_{R3}	1.088	3451.38	C_{R3}-C_{R4}	1.341	5154.49
C_{R4}-H_{R4}	1.089	3391.87	C_{R1}-C_{R5}	1.531	2007.31
C_{R4}-C_{R5}	1.504	2303.88	C_{R5}-H_{R5}	1.094	3207.08
C_{R5}-N_R	1.510	1692.34	N_R-H_{NR}	1.048	3029.60
N_R-C_{CN}	1.485	2290.03	N_R-C_{C6}	1.506	1859.39
C_{C6}-C_{B1}	1.507	2653.71	C_{CN}-H_C	1.093	3298.18
C_{C6}-H_{C6}	1.095	3231.91	C_{B1}-C_{B2}	1.398	3182.34
C_{B2}-C_{B3}	1.395	3380.41	C_{B3}-C_{B4}	1.395	3497.59
C_{B2}-H_{B2}	1.090	3344.46	C_{B3}-H_{B3}	1.089	3411.13

Table S9: QMD-FF bending parameters for the closed form: equilibrium angles θ^0 and force constants k^b appearing in equation (5) are in degrees and in kJ/mol rad^{-2}, respectively.

bending	$\theta^{\mathbf{0}}$	$\mathbf{k^b}$	**bending**	$\theta^{\mathbf{0}}$	$\mathbf{k^b}$
N_A-C_{A1}-N_A	117.3	502.38	C_{A1}-N_A-C_{A2}	123.8	502.38
N_A-C_{A2}-C_{A3}	115.9	248.81	C_{A2}-C_{A3}-C_{A2}	120.8	677.67
N_A-C_{A1}-O_{A1}	121.6	627.51	C_{A1}-N_A-C_{AN}	117.0	544.48
C_{A2}-N_A-C_{AN}	119.5	688.57	N_A-C_{A2}-O_{A2}	119.7	782.04
C_{A3}-C_{A2}-O_{A2}	124.3	613.94	C_{A2}-C_{A3}-C_{R1}	119.0	387.75
N_A-C_{AN}-H_C	109.5	441.97	H_C-C_{AN}-H_C	110.5	302.95
C_{A3}-C_{R1}-C_{R2}	121.2	405.19	C_{A3}-C_{R1}-C_{R5}	112.8	298.42
C_{R1}-C_{R2}-C_{R3}	106.4	167.94	C_{R1}-C_{R5}-C_{R4}	105.2	586.96
C_{R2}-C_{R3}-C_{R4}	110.5	726.45	C_{R3}-C_{R4}-C_{R5}	110.3	594.02
C_{R2}-C_{R1}-C_{R5}	102.8	644.12	C_{R1}-C_{R2}-O_R	127.1	530.78
O_R-C_{R2}-C_{R3}	126.3	611.07	C_{A3}-C_{R1}-H_{R1}	108.2	228.32
H_{R1}-C_{R1}-C_{R2}	103.4	358.32	H_{R1}-C_{R1}-C_{R5}	107.4	349.87
C_{R2}-C_{R3}-H_{R3}	122.8	301.78	H_{R3}-C_{R3}-C_{R4}	126.8	231.36
C_{R3}-C_{R4}-H_{R4}	125.4	244.08	H_{R4}-C_{R4}-C_{R5}	124.0	281.99
C_{R1}-C_{R5}-H_{R5}	108.5	395.21	C_{R4}-C_{R5}-H_{R5}	109.3	330.93
H_{R5}-C_{R5}-N_R	106.4	338.85	C_{R1}-C_{R5}-N_R	109.3	545.53
C_{R4}-C_{R5}-N_R	117.8	577.99	C_{R5}-N_R-C_{CN}	113.2	665.09
C_{R5}-N_R-C_{C6}	112.9	654.92	C_{CN}-N_R-C_{C6}	111.4	505.05
N_R-C_{C6}-C_{B1}	111.1	808.64	C_{R5}-N_R-H_{NR}	104.5	532.32
H_{NR}-N_R-C_{CN}	106.1	498.85	H_{NR}-N_R-C_{C6}	108.1	488.41
N_R-C_{CN}-H_C	108.9	474.58	H_C-C_{CN}-H_C	109.9	293.08
N_R-C_{C6}-H_{C6}	106.9	458.11	H_{C6}-C_{C6}-H_{C6}	109.3	317.34
H_{C6}-C_{C6}-C_{B1}	111.7	365.45	C_{B2}-C_{B1}-C_{B2}	119.4	517.72
C_{B1}-C_{B2}-C_{B3}	120.4	644.26	C_{B2}-C_{B3}-C_{B4}	119.9	650.60
C_{B3}-C_{B4}-C_{B3}	119.9	627.76	C_{C6}-C_{B1}-C_{B2}	120.5	648.94
C_{B1}-C_{B2}-H_{B2}	119.8	279.80	C_{B3}-C_{B2}-H_{B2}	119.8	345.73
C_{B2}-C_{B3}-H_{B3}	119.8	301.62	C_{B4}-C_{B3}-H_{B3}	120.2	327.30

Table S10: QMD-FF parameters for the stiff torsions described by equation (6) in the closed form: equilibrium dihedral angles ϕ^0 are in degrees and force constants k^t in kJ/mol rad^{-2}.

dihedral	$\phi^{\mathbf{0}}$	$\mathbf{k^t}$	**dihedral**	$\phi^{\mathbf{0}}$	$\mathbf{k^t}$
C_{A1}-N_A-C_{A2}-C_{A3}	-7.0	75.35	N_A -C_{A2}-C_{A3}-C_{A2}	15.0	75.35
N_A-C_{A1}-N_A-C_{A2}	-4.0	75.35	O_{A1}-C_{A1}-N_A -C_{A2}	-176.0	75.35
O_{A2}-C_{A2}-C_{A3}-C_{A2}	-163.0	75.35	C_{A1}-N_A -C_{A2}-O_{A2}	171.0	75.35
N_A-C_{A1}-N_A-C_{AN}	176.0	75.35	C_{AN}-N_A -C_{A2}-C_{A3}	180.0	75.35
O_{A1}-C_{A1}-N_A-C_{AN}	0.0	75.35	O_{A2}-C_{A2}-C_{A3}-C_{R1}	-5.0	75.35
C_{AN}-N_A-C_{A2}-O_{A2}	-3.0	75.35	N_A -C_{A2}-C_{A3}-C_{R1}	173.0	75.35
C_{B1}-C_{B2}-C_{B3}-C_{B4}	0.0	82.43	C_{B2}-C_{B3}-C_{B4}-C_{B3}	0.0	82.43
C_{B2}-C_{B1}-C_{B2}-C_{B3}	0.0	82.43	C_{C6}-C_{B1}-C_{B2}-C_{B3}	180.0	82.43
C_{B2}-C_{B1}-C_{B2}-H_{B2}	180.0	49.02	H_{B2}-C_{B2}-C_{B3}-C_{B4}	180.0	49.02
C_{B1}-C_{B2}-C_{B3}-H_{B3}	180.0	49.02	H_{B3}-C_{B3}-C_{B4}-C_{B3}	180.0	49.02
C_{B2}-C_{B3}-C_{B4}-H_{B4}	180.0	49.02	H_{B2}-C_{B2}-C_{B3}-H_{B3}	0.0	49.02
C_{C6}-C_{B1}-C_{B2}-H_{B2}	0.0	49.02	H_{B3}-C_{B3}-C_{B4}-H_{B4}	0.0	49.02
C_{R1}-C_{R2}-C_{R3}-C_{R4}	9.0	131.96	C_{R2}-C_{R3}-C_{R4}-C_{R5}	6.0	131.96
C_{R3}-C_{R4}-C_{R5}-C_{R1}	-18.0	131.96	C_{R2}-C_{R1}-C_{R5}-C_{R4}	21.0	131.96
C_{R5}-C_{R1}-C_{R2}-C_{R3}	-18.0	131.96	C_{A3}-C_{R1}-C_{R2}-O_R	39.0	54.60
C_{R5}-C_{R1}-C_{R2}-O_R	166.0	54.60	C_{A3}-C_{R1}-C_{R2}-C_{R3}	-145.0	54.60
H_{R1}-C_{R1}-C_{R2}-O_R	-82.0	54.60	H_{R1}-C_{R1}-C_{R2}-C_{R3}	93.0	54.60
C_{A3}-C_{R1}-C_{R5}-C_{R4}	153.5	20.89	C_{A3}-C_{R1}-C_{R5}-N_R	-79.0	20.89
C_{A3}-C_{R1}-C_{R5}-H_{R5}	38.0	20.89	H_{R1}-C_{R1}-C_{R5}-C_{R4}	-87.0	20.89
H_{R1}-C_{R1}-C_{R5}-H_{R5}	156.0	20.89	H_{R1}-C_{R1}-C_{R5}-N_R	40.0	20.89
C_{R2}-C_{R1}-C_{R5}-N_R	149.0	20.89	C_{R2}-C_{R1}-C_{R5}-H_{R5}	-95.0	20.89
C_{R1}-C_{R2}-C_{R3}-H_{R3}	-172.0	49.62	O_R -C_{R2}-C_{R3}-H_{R3}	3.0	49.62
O_R-C_{R2}-C_{R3}-C_{R4}	-176.0	49.62	C_{R2}-C_{R3}-C_{R4}-H_{R4}	180.0	53.64
H_{R3}-C_{R3}-C_{R4}-H_{R4}	0.0	53.64	H_{R3}-C_{R3}-C_{R4}-C_{R5}	-174.0	53.64
C_{R3}-C_{R4}-C_{R5}-N_R	-140.0	20.89	H_{R4}-C_{R4}-C_{R5}-N_R	46.0	20.89
H_{R4}-C_{R4}-C_{R5}-C_{R1}	168.0	20.89	C_{R3}-C_{R4}-C_{R5}-H_{R5}	99.0	20.89
H_{R4}-C_{R4}-C_{R5}-H_{R5}	-75.0	20.89	C_{A1}-N_A -O_{A1}-N_A	0.0	75.35
C_{A2}-N_A-O_{A2}-C_{A3}	0.0	75.35	C_{A2}-C_{A3}-O_{A2}-N_A	0.0	75.35
N_A-C_{A1}-C_{A2}-C_{AN}	5.0	75.35	C_{A3}-C_{A2}-C_{A2}-C_{R1}	-13.0	75.35
C_{R1}-C_{A3}-H_{R1}-C_{R2}	34.0	37.29	C_{R2}-C_{R1}-O_R -C_{R3}	-3.0	131.96
C_{R3}-C_{R2}-C_{R4}-H_{R3}	0.0	20.89	C_{R5}-C_{R3}-H_{R4}-C_{R4}	-4.0	20.89
C_{B1}-C_{C6}-C_{B2}-C_{B2}	0.0	82.43	H_{B2}-C_{B1}-C_{B3}-C_{B2}	0.0	49.02
H_{B3}-C_{B2}-C_{B4}-C_{B3}	0.0	49.02	H_{B4}-C_{B3}-C_{B3}-C_{B4}	0.0	49.02

Table S11: QMD-FF parameters of flexible torsions for DASA closed form: number of cosines n, γ (degrees) and force constants k^d, in kJ/mol, refer to equation (7). All dihedral labels refer to Figure 4.b.

dihedral	N_{cos}	n	k^d (kJ/mol)	γ (degr)
C_{A1}-N_A-C_{AN}-H_C (δ_1)	1	3	2.655	0.00
C_{R5}-N_R-C_{CN}-H_C (δ_2)	1	3	4.649	0.00
C_{A2}-C_{A3}-C_{R1}-C_{R2} (δ_{RA})	7	0	2.940	0.00
		1	-8.376	0.00
		2	-0.832	0.00
		3	8.060	0.00
		4	9.024	0.00
		5	1.548	0.00
		6	2.312	0.00
N_R-C_{C6}-C_{B1}-C_{B2} (δ_{RB})	7	0	2.940	0.00
		1	5.166	0.00
		2	1.653	0.00
		3	-5.120	0.00
		4	0.148	0.00
		5	0.330	0.00
		6	0.090	0.00
C_{R1}-C_{R5}-N_R-C_{C6} (δ_{N1})	7	0	2.940	0.00
		1	6.712	0.00
		2	2.771	0.00
		3	5.944	0.00
		4	4.444	0.00
		5	-1.897	0.00
		6	1.844	0.00
C_{CN}-N_R-C_{C6}-C_{B1} (δ_{N2})	7	0	2.940	0.00
		1	-1.428	0.00
		2	-0.372	0.00
		3	9.116	0.00
		4	1.610	0.00
		5	0.729	0.00
		6	-0.319	0.00

Table S12: Closed form's QMD-FF parameters for the specific non-bonded intramolecular interactions accounted for in equation (8): σ^{intra} (Å) and ϵ^{intra} (kJ/mol). All labels refer to Figure 3.a.

Ring A $\cdots$ Ring R

Pair (ij)	σ_{ij}^{intra}	ϵ_{ij}^{intra}	Pair (ij)	σ_{ij}^{intra}	ϵ_{ij}^{intra}
O_{A2}-H_{NR}	1.470	0.5000	O_{A2}-O_R	2.840	0.1000
O_{A2}-H_{R5}	2.080	0.1000			

Ring A $\cdots$ Methyl (M)

Pair (ij)	σ_{ij}^{intra}	ϵ_{ij}^{intra}	Pair (ij)	σ_{ij}^{intra}	ϵ_{ij}^{intra}
C_{A1}-C_{CN}	3.620	0.3483	C_{A1}-H_C	3.060	0.2348
C_{A2}-C_{CN}	3.340	0.3483	C_{A2}-H_C	2.570	0.2348
C_{A3}-C_{CN}	3.210	0.2963	C_{A3}-H_C	2.590	0.1998
N_A-C_{CN}	3.370	0.4432	N_A-H_C	2.850	0.2988
O_{A1}-C_{CN}	3.220	0.4926	O_{A1}-H_C	2.720	0.3321
O_{A2}-C_{CN}	3.160	0.4926	O_{A2}-H_C	2.260	0.3321
C_{AN}-C_{CN}	3.500	0.2761	C_{AN}-H_C	2.960	0.1862

Ring A $\cdots$ Ring B

Pair (ij)	σ_{ij}^{intra}	ϵ_{ij}^{intra}	Pair (ij)	σ_{ij}^{intra}	ϵ_{ij}^{intra}
C_{A1}-C_{B1}	3.650	0.3587	N_A-C_{B1}	3.400	0.4564
C_{A1}-C_{B2}	3.650	0.3587	N_A-C_{B2}	3.300	0.4564
C_{A1}-C_{B3}	3.330	0.3587	N_A-C_{B3}	3.360	0.4564
C_{A1}-C_{B4}	3.330	0.3587	N_A-C_{B4}	3.330	0.4564
C_{A2}-C_{B1}	3.370	0.3587	O_{A1}-C_{B1}	3.240	0.5073
C_{A2}-C_{B2}	3.450	0.3587	O_{A1}-C_{B2}	3.240	0.5073
C_{A2}-C_{B3}	3.510	0.3587	O_{A1}-C_{B3}	3.240	0.5073
C_{A2}-C_{B4}	3.650	0.3587	O_{A1}-C_{B4}	3.240	0.5073
C_{A3}-C_{B1}	3.420	0.3052	O_{A2}-C_{B1}	3.240	0.5073
C_{A3}-C_{B2}	3.430	0.3052	O_{A2}-C_{B2}	3.060	0.5073
C_{A3}-C_{B3}	3.550	0.3052	O_{A2}-C_{B3}	3.240	0.5073
C_{A3}-C_{B4}	3.550	0.3052	O_{A2}-C_{B4}	3.240	0.5073
C_{AN}-C_{B1}	3.520	0.2844	C_{AN}-C_{B3}	3.490	0.2844
C_{AN}-C_{B2}	3.520	0.2844	C_{AN}-C_{B4}	3.460	0.2844

Table S13: Closed form's QMD-FF parameters for the specific non-bonded intramolecular interactions accounted for in equation (8): σ^{intra} (Å) and ϵ^{intra} (kJ/mol). All labels refer to Figure 3.a.

Ring A $\cdots$ Ring B

Pair (ij)	σ_{ij}^{intra}	ϵ_{ij}^{intra}	Pair (ij)	σ_{ij}^{intra}	ϵ_{ij}^{intra}
O_{A2}-C_{C6}	3.240	0.1000	O_{A2}-H_{C6}	2.210	0.1000
C_{A1}-H_{B2}	3.010	0.1000	N_A-H_{B2}	2.800	0.1000
C_{A1}-H_{B3}	2.920	0.1000	N_A-H_{B3}	2.800	0.1000
C_{A1}-H_{B4}	3.010	0.1000	N_A-H_{B4}	2.800	0.1000
C_{A2}-H_{B2}	2.800	0.1000	O_{A1}-H_{B2}	2.680	0.1000
C_{A2}-H_{B3}	3.010	0.1000	O_{A1}-H_{B3}	2.680	0.1000
C_{A2}-H_{B4}	3.010	0.1000	O_{A1}-H_{B4}	2.680	0.1000
C_{A3}-H_{B2}	2.630	0.1000	O_{A2}-H_{B2}	2.590	0.1000
C_{A3}-H_{B3}	2.930	0.1000	O_{A2}-H_{B3}	2.680	0.1000
C_{A3}-H_{B4}	2.930	0.1000	O_{A2}-H_{B4}	2.680	0.1000
C_{AN}-H_{B2}	2.910	0.1000	C_{AN}-H_{B3}	2.910	0.1000
C_{AN}-H_{B4}	2.910	0.1000	H_C-C_{B1}	2.980	0.1917
H_C-C_{B2}	2.980	0.1917	H_C-H_{B2}	2.460	0.1000
H_C-C_{B3}	2.880	0.1917	H_C-H_{B3}	2.290	0.1000
H_C-C_{B4}	2.850	0.1917	H_C-H_{B4}	2.460	0.1000

Ring R $\cdots$ Ring B

Pair (ij)	σ_{ij}^{intra}	ϵ_{ij}^{intra}	Pair (ij)	σ_{ij}^{intra}	ϵ_{ij}^{intra}
H_{R1}-H_C	1.950	0.1000	H_{R5}-C_{B2}	2.440	0.1000
H_{R5}-H_{B2}	1.910	0.1000			

2 Force Field validation

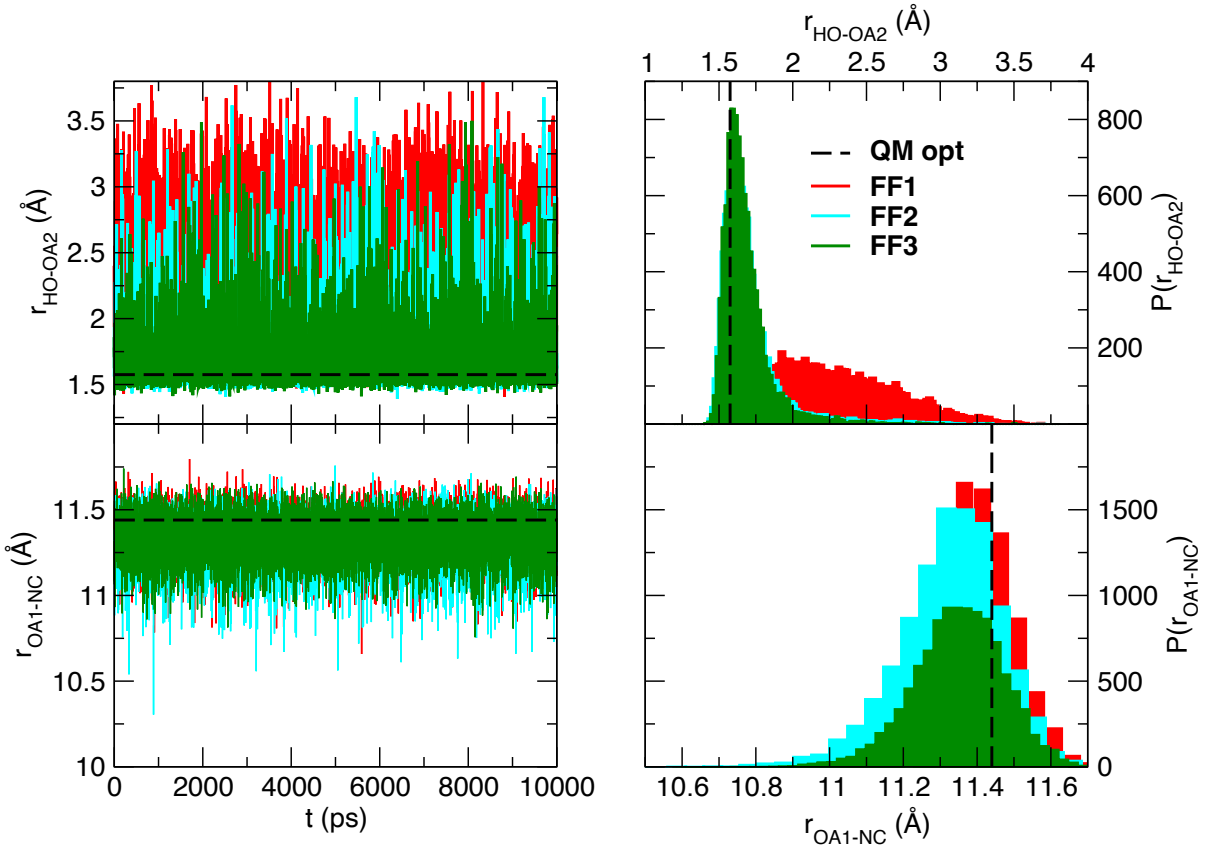

Figure S1: Time behaviour (left panels) and distributions (right panels) of the intramolecular HB distance r_{HO-OA2} (top) and the overal molecular elongation r_{OA1-NC} (bottom) for 100 structural snapshots taken every 10 picoseconds of the MD trajectory of the open form, computed with the FF1, FF2 and FF3 force fields. The values obtained form the QM optimized structures are also displayed for comparison with dashed black lines.

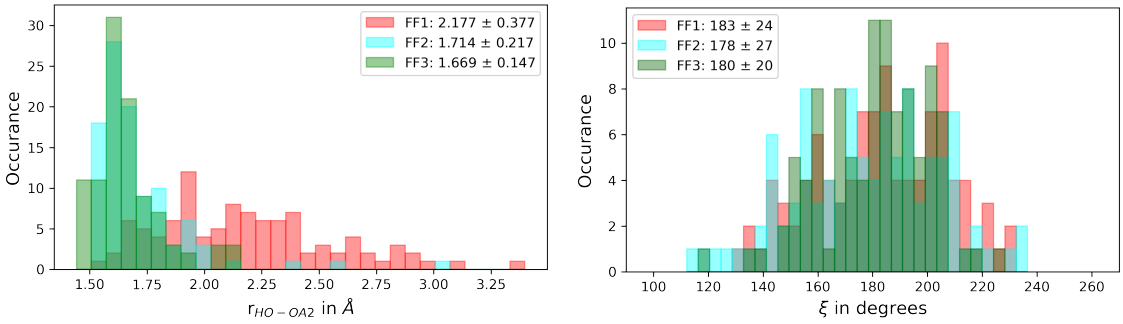

Figure S2: Distribution of r_{HO-OA2} (left) and ξ (right) for 100 structural snapshots taken every 10 ps of the MD trajectory of the open form, computed with FF1, FF2 and FF3 force fields. Average values and standard deviations are reported in the legend.

Table S14: Bond length alternation (BLA, Å), dihedral planarity (ξ, degrees), vertical excitation energy (ΔE_{01}, eV) and dynamic (λ = 1300 nm) and static HRS hyperpolarizability (β_{HRS}, a.u.) for the open form of BA4 (conformer 1) computed at the SMD:M06-2X/6-311+G(d) level in chloroform using the DFT equilibrium geometry, and using the MD+DFT scheme with the different force fields in chloroform.

	DFT	FF1/$CHCl_3$	FF2/$CHCl_3$	FF3/$CHCl_3$
BLA	-0.001	0.003±0.030	0.000±0.025	-0.001±0.025
ξ	180	183±24	178±27	180±20
ΔE_{01}	2.53	2.49±0.11	2.43±0.11	2.46±0.09
β_{HRS}^{dyn}	4860	12195±7286	11420±7632	10010±5349
β_{HRS}^{stat}	3669	6018±2646	5822±2642	5246±2059

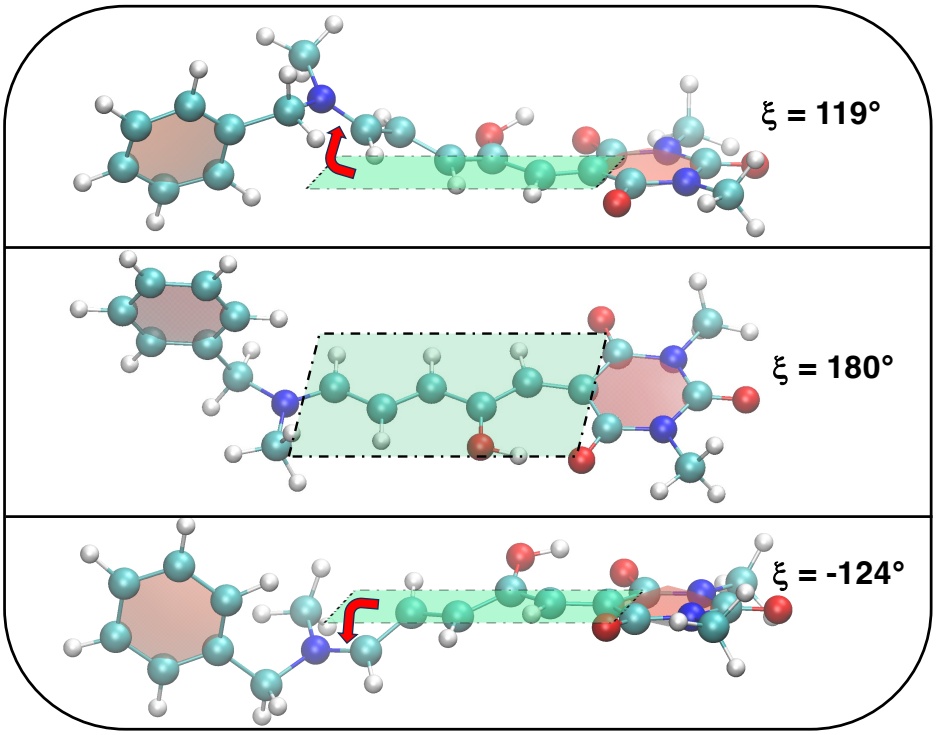

Figure S3: Selection of ξ-distorted geometries retrieved along the MD trajectory obtained with FF2. In the center panel, the QM optimized structure with $\xi = 180°$ is shown for comparison.

3 Dynamic behavior and nonlinear optical properties

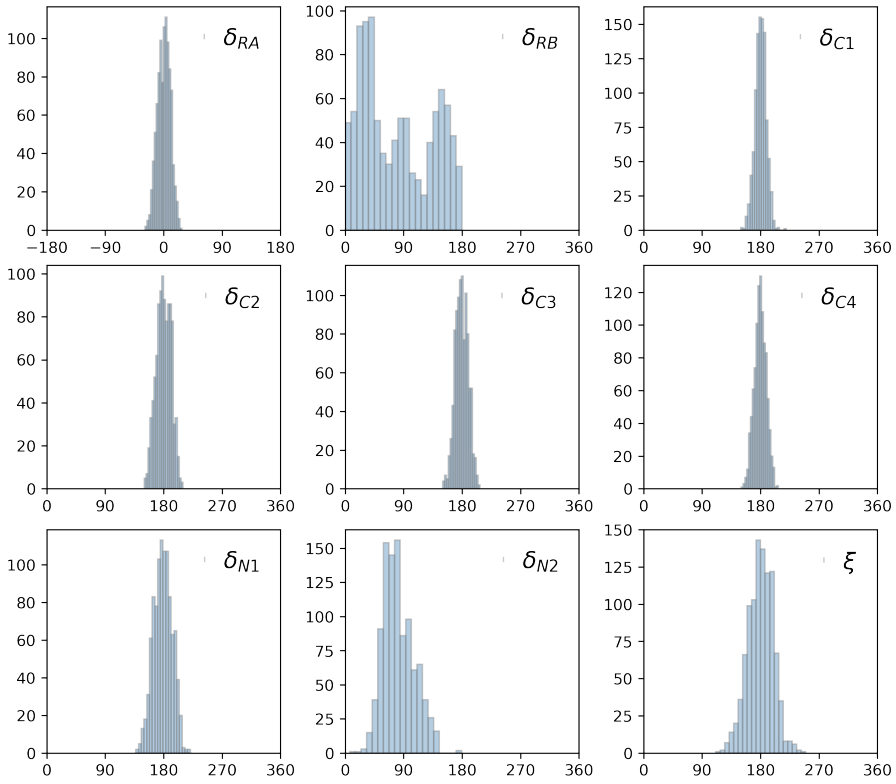

Figure S4: Statistical distributions of the geometrical parameters, extracted for 1000 structural snapshots along the MD trajectory starting from conformer 1 of the open form. All angles are in degrees.

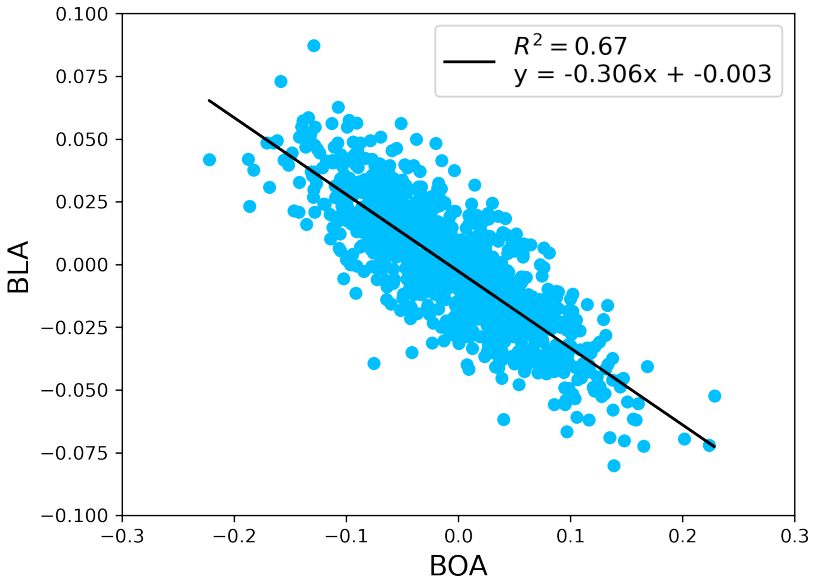

Figure S5: Correlation between bond length alternation (BLA, Å) and bond order alternation (BOA) in the open form, for 1000 snapshots extracted from the MD trajectory. BOA values were calculated at the SMD:M06-2X-D3/aug-cc-pVDZ level.

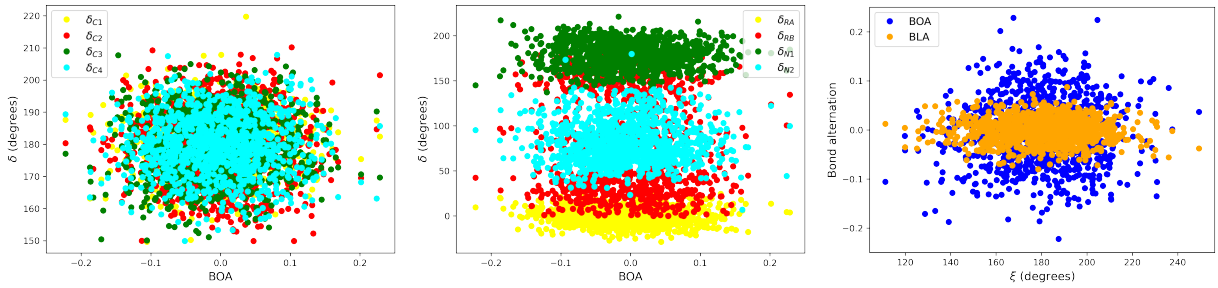

Figure S6: Variation of the torsional parameters δ_{C1-4} (left) and $\delta_{RA,RB,N1,N2}$ (middle) as a function of BOA (similar variation is also found when plotting the dihedral angles as a function of BLA). Variation of BOA and BLA with the dihedral planarity ξ (right).

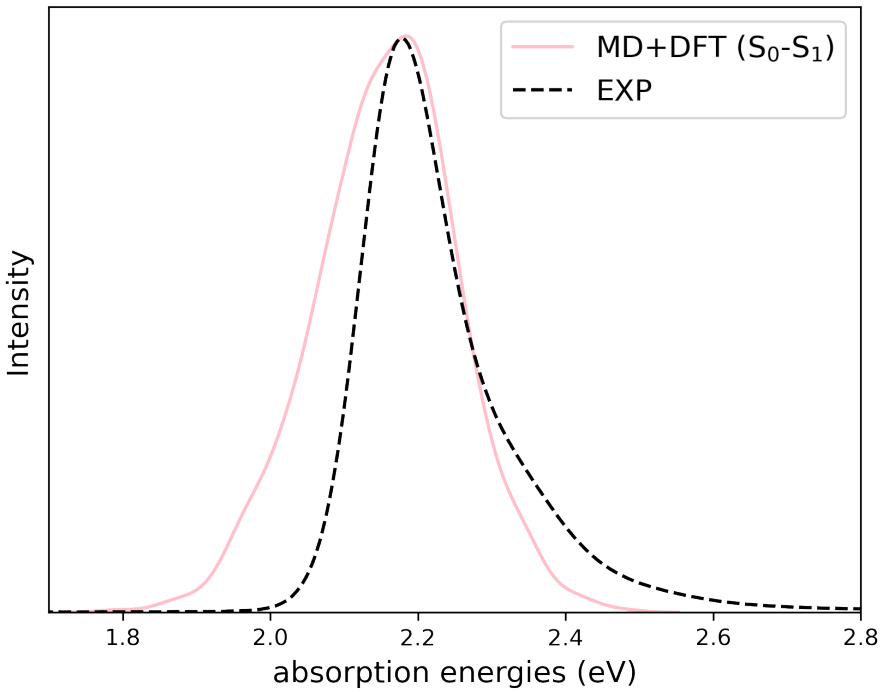

Figure S7: Absorption spectrum of the open form of BA4 measured in chloroform (black curve) and fitted distribution of the $S_0 \rightarrow S_1$ vertical excitation energies computed using the MD+DFT approach (red curve). To allow for straightforward comparison, the computed spectrum has been shifted to match the maximum in absorption of the measured spectrum.

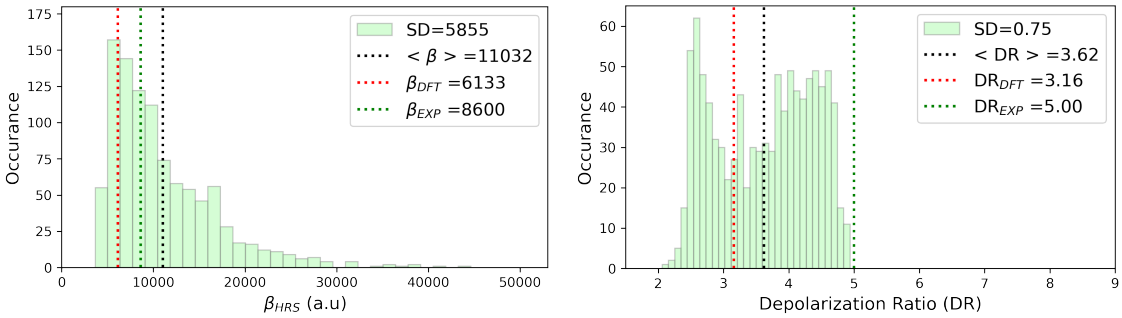

Figure S8: Statistical distributions of dynamic (1300 nm) HRS first hyperpolarizability and depolarization ratio, calculated using the MD+DFT scheme at the SMD:M06-2X/6-311+G(d) level for 1000 structural snapshots extracted from the MD trajectory starting from conformer 2 of the open form. Vertical dotted lines indicate either average values, values computed at the DFT level using the equilibrium geometry of the chromophore (conformer 2), or experimental values.

Table S15: Nonlinear optical properties (at 1300 nm) of the open form of BA4 in its conformers 1 and 2, and average properties computed accounting for to their Maxwell-Boltzmann statistical populations.

	Conformer 1		**Conformer 2**		**Averaged**	
	DFT	MD+DFT	DFT	MD+DFT	DFT	MD+DFT
β_{HRS}	4860	10969 ± 5999	6133	11032 ± 5855	5267	10989
DR	2.69	3.69 ± 0.77	3.16	3.62 ± 0.75	2.84	3.67

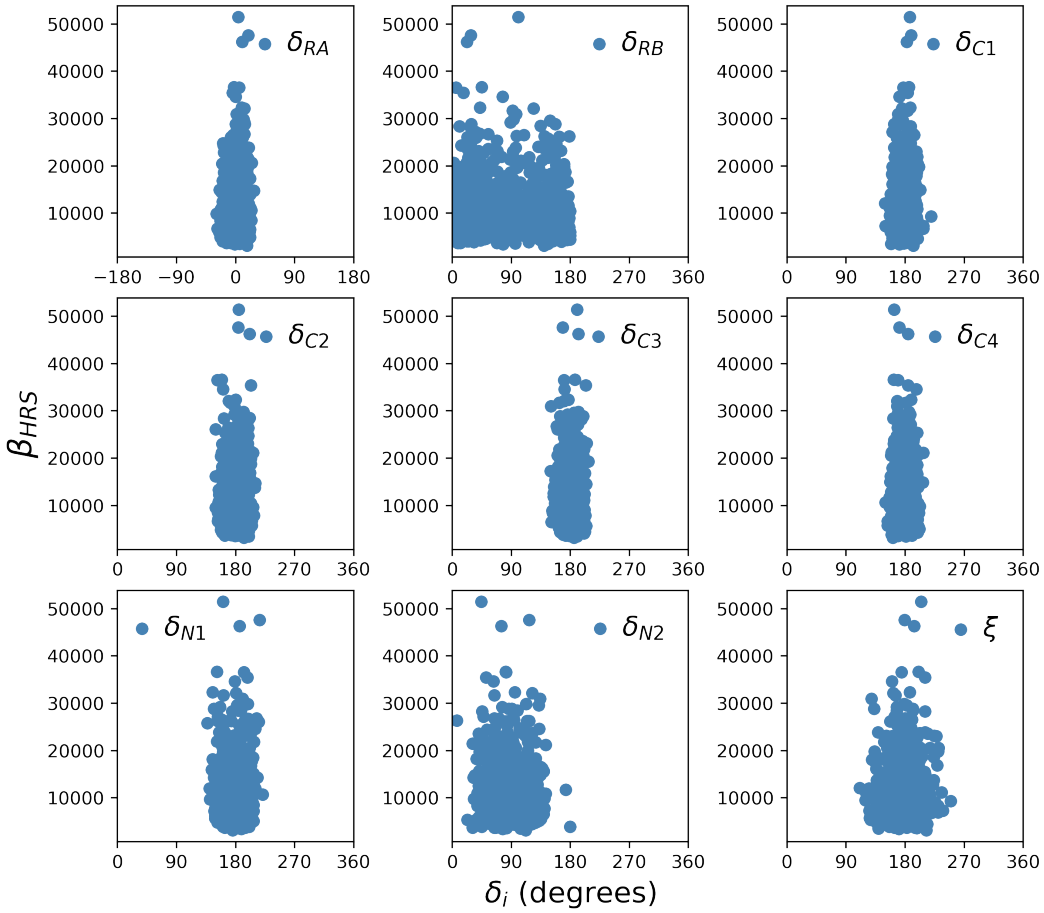

Figure S9: Variation of β_{HRS} with the geometrical parameters, as calculated using the MD+DFT scheme at the SMD:M06-2X/6-311+G(d) level for 1000 structural snapshots extracted from the MD trajectory starting from conformer 1 of the open form.

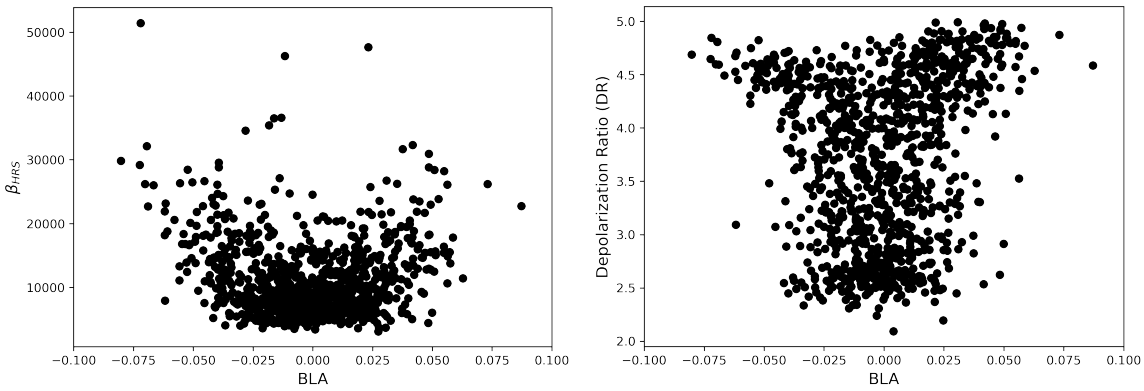

Figure S10: Correlation between BLA and β_{HRS} (left) and DR (right), as calculated using the MD+DFT scheme at the SMD:M06-2X/6-311+G(d) level for 1000 structural snapshots extracted from the MD trajectory starting from conformer 1 of the open form.

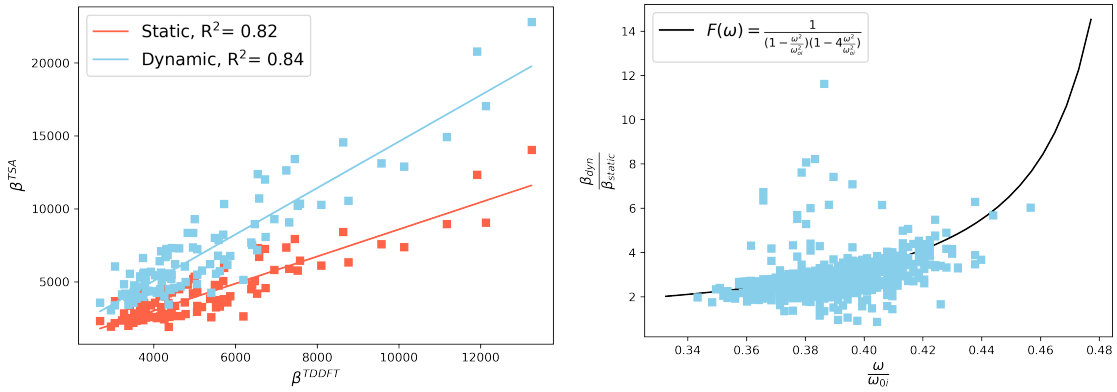

Figure S11: Left: Correlation between β_{HRS}^{TSA} and β_{HRS}^{TDDFT} in the open form. Values were calculated at the SMD:M06-2X/6-311+G(d) level for 100 snapshots extracted from the MD trajectory. Right: Frequency dispersion effects on the HRS hyperpolarizabilities of open DASAs. The black line represents the frequency dispersion factor evaluated using the 2-state approximation (equation 16 of the manuscript). The color points represent the frequency dispersion evaluated as the ratio between dynamic and static β_{HRS}^{TDDFT} values.

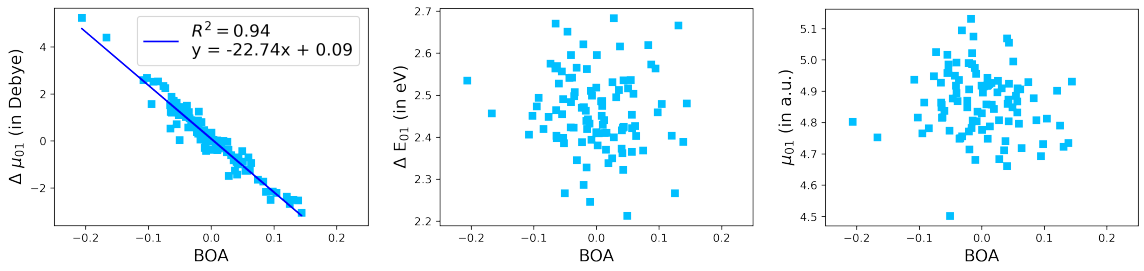

Figure S12: Evolution of $\Delta\mu_{01}$ (left), ΔE_{01}, (middle) and μ_{01} (right) of the open form as a function of the bond order alternation (BOA). The calculations have been performed for 100 structural snapshots taken every 10 picoseconds of the MD trajectory.

3.1 Calculation of the β_{zxx}/β_{zzz} ratio

The computation of $R = \beta_{zxx}/\beta_{zzz}$, involving two particular components of the molecular β tensor, poses the problem of the definition of the molecular frame. Since in this work molecular structures are extracted from MD trajectories, the Cartesian axes are defined arbitrarily. However, it is still possible to calculate R from the β tensor components expressed in the dipole orientation, as they are provided in Gaussian16 outputs. In this case, the dipole vector defines the z axis, and it is also parallel to the C_2 symmetry axis in the case of a pure C_{2v} symmetry. Even though the orientation of the x axis remains arbitrary, R can be calculated by using the z-component of the β vector, whose general expression for the SHG process is:

$$\beta_z = \sum_{i=x,y,z} (\beta_{zii} + 2\beta_{izi}) = 3\beta_{zzz} + \beta_{zxx} + 2\beta_{xzx} + \beta_{zyy} + 2\beta_{yzy} \quad (1)$$

Assuming Kleinman symmetry ($\beta_{ijk} \equiv \beta_{kij}$) and $\beta_{zyy} = 0$ simplifies the above expression into:

$$\beta_z = 3(\beta_{zzz} + \beta_{zxx}) \quad (2)$$

so that R can be defined solely from β components oriented along the z axis:

$$R = \frac{1}{3}\frac{\beta_z}{\beta_{zzz}} - 1 \quad (3)$$

In this study, the R ratios were computed using the general expression of β_z (equation 1) from the dynamic ($\lambda = 1300$ nm) β components, *i.e.* without considering Kleinman conditions. The results reported in Figure 14b, showing that the R ratio follows qualitatively the behavior expected for a planar C_{2v} symmetry, validates *a posteriori* the neglect of the β_{zyy} component in the expression of R given equation 3.