Supporting Information

Characteristics and long-term kinetics of an azobenzene derivative and a donor-acceptor Stenhouse adduct as orthogonal photoswitches

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1. Synthesis

The synthesis and purification of Azo and DASA are described elsewhere.[1]

2. Sample preparation

For sample preparation, toluene (Uvasol grade), acetonitrile (Uvasol grade), toluene-d_8 (99.6 % D) and acetonitrile-d_3 (≥99.8 % D) were purchased from Merck KGaA. All chemicals were used without further purification.

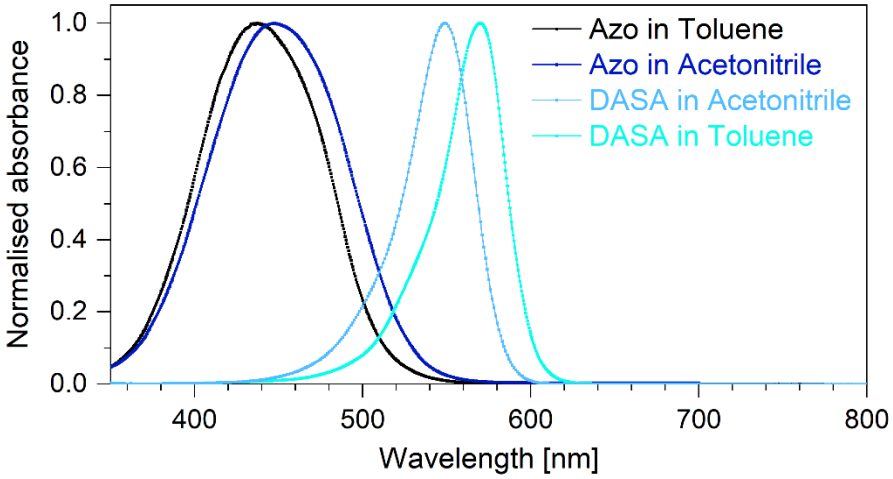
2.1. UV/VIS absorption measurements

Azo (1.3 mg, 2.0 µmol) was dissolved in toluene (650 µl) and sonicated for several minutes to ensure a homogeneous stock solution. Part of the stock solution (30 µl) was subsequently further diluted with toluene (3.000 ml).
DASA (1.0 mg, 3.3 µmol) was dissolved in toluene (1.000 ml) and sonicated for several minutes to ensure a homogeneous stock solution. Part of the stock solution (20 µl) was subsequently further diluted with toluene (3.000 ml).
For the equimolar mixtures of Azo and DASA, part of the above specified Azo stock solution (21 µl) and DASA stock solution (20 µl) was mixed and further diluted with toluene (2980 µl).

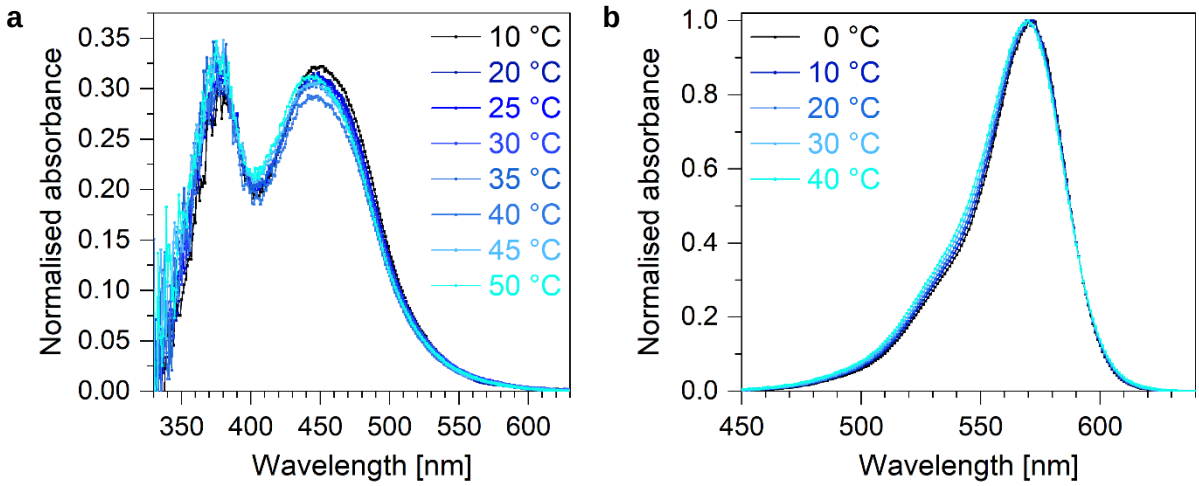
2.2. IR absorption measurements

DASA (1.0 mg, 3.3 µmol) was dissolved in toluene or acetonitrile (200 µl) and sonicated for several minutes to ensure a homogeneous solution.

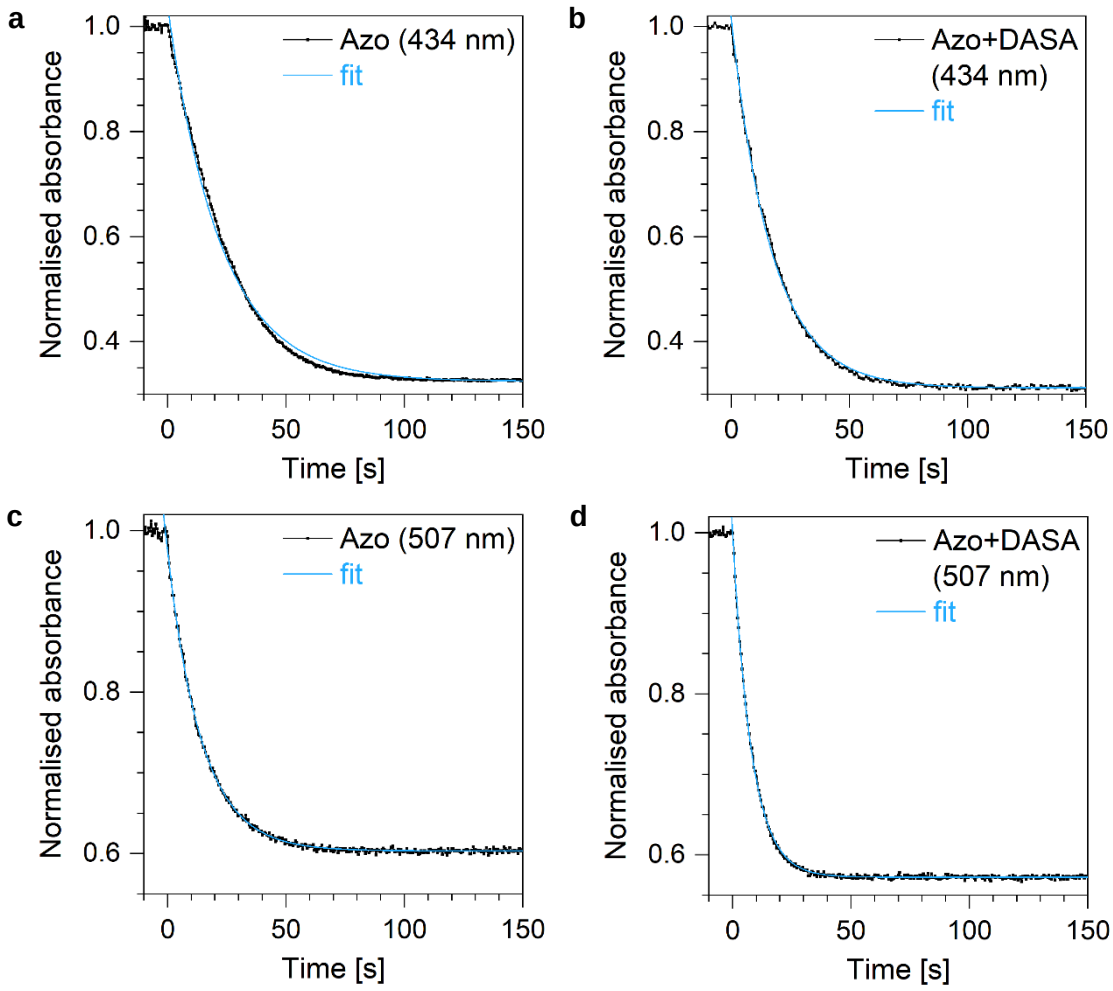
3. UV/VIS absorption data



Supplementary Figure S1 Shift of the absorption spectra of Azo and DASA in different environments due to solvatochromism.



Supplementary Figure S2 Hypsochromic shifts of the absorption maxima of (a) *Z*-Azo and *E*-Azo as well as (b) *Z*-DASA upon increasing temperature.



Supplementary Figure S3 Temporal evolution of the absorption of *E*-Azo at its maximum absorption wavelength in toluene upon *E*-to-*Z* photoisomerisation and their respective monoexponential fit curves. The photoisomerisation of a (a) pure Azo solution and an (b) equimolar Azo+DASA solution using blue light for orthogonal switching (434 nm) as well as of a (c) pure Azo solution and an (b) equimolar Azo+DASA solution using green light for simultaneous switching wavelength (507 nm) is studied.

The effective cross section σ is calculated based on the lifetime τ and the photon dose n_p per time t and area A according to equation 1. The photon dose n_p for a circular spot is thereby determined according to equation 2 using the Planck's quantum of action h, the speed of light in vacuum c_{vac}, the applied wavelength λ and the radius r.

$$\sigma = \frac{1}{\tau\, n_p} \tag{1}$$

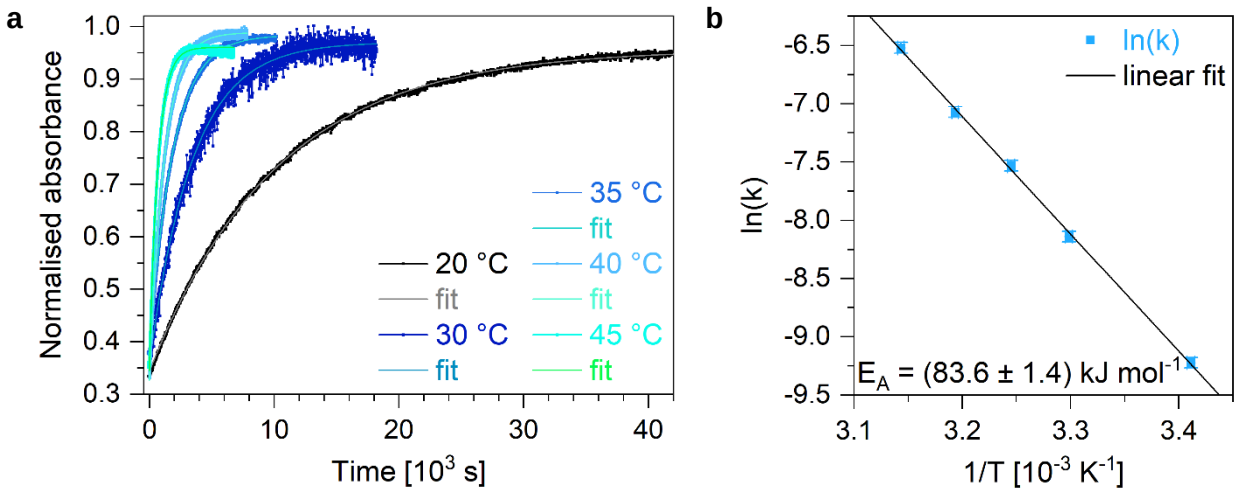
$$n_p(t, A) = \frac{P(t)}{E_p\, A} = \frac{P(t)\, \lambda}{h\, c_{vac}\, \pi\, r^2} \tag{2}$$

Supplementary Table S1 Lifetimes τ of Azo in toluene upon photochemically initiated *E*-to-*Z* isomerisation, applied photon doses n_p and wavelengths λ for orthogonally addressing Azo or simultaneously addressing Azo and DASA as well as the resulting effective cross sections σ of Azo.

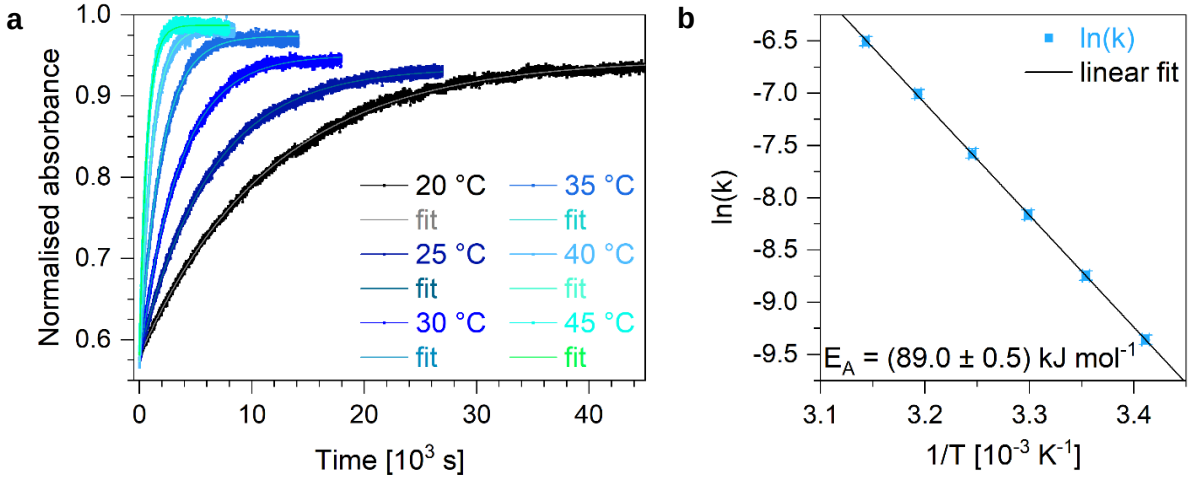
	Azo orthogonally	Azo+DASA orthogonally	Azo simultaneously	Azo+DASA simultaneously
τ [s]	22.41 ± 0.10	17.20 ± 0.09	14.39 ± 0.05	7.95 ± 0.03
n_p [10^{15} s^{-1} cm^{-2}]	8.6 ± 0.4	8.6 ± 0.4	72 ± 4	72 ± 4
λ [nm]	434	434	507	507
σ [10^{-18} cm^2]	5.21 ± 0.26	6.79 ± 0.34	0.97 ± 0.05	1.74 ± 0.09

Supplementary Table S2 Determined lifetimes of Azo in toluene upon thermally activated *Z*-to-*E* backswitching in different environments regarding DASA.

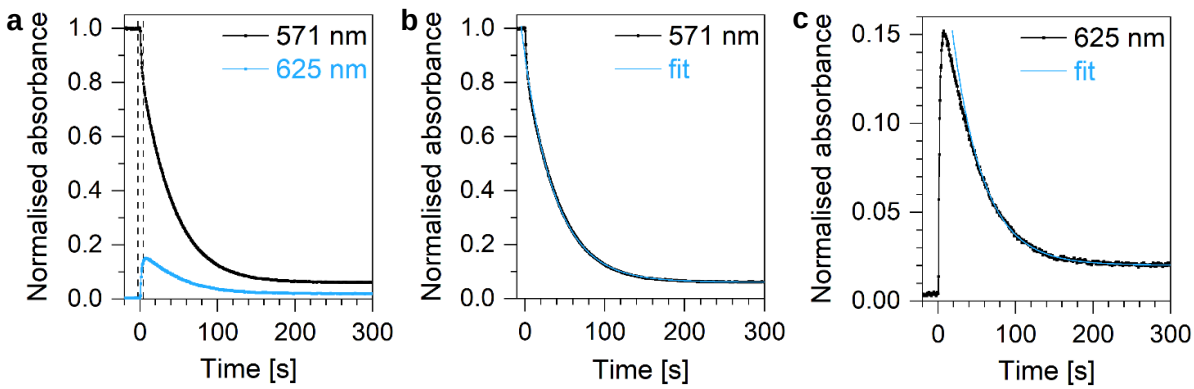
Temperature [°C]	Lifetime [s]		
	Azo	Azo+*Z*-DASA	Azo+DASA simultaneous thermal backswitching
20	-	10121.5 ± 12.1	11608.3 ± 12.7
25	-	-	6281.4 ± 5.7
30	2994.2 ± 1.9	3423.1 ± 17.9	3507.1 ± 4.2
35	-	1866.3 ± 2.0	1951.9 ± 2.2
40	1105.9 ± 1.9	1178.8 ± 0.4	1106.2 ± 0.9
45	-	679.7 ± 0.5	667.0 ± 0.8
50	382.6 ± 0.7	-	-
60	138.8 ± 0.3	-	-



Supplementary Figure S4 (a) Temporal evolution of the absorption of *E*-Azo at its maximum absorption wavelength upon thermally activated *Z*-to-*E* isomerisation in the presence of *Z*-DASA within an equimolar Azo+DASA mixture in toluene at different temperatures with the respective monoexponential fit curves. Using the fitted lifetimes, the corresponding rate constants are calculated and an (b) Arrhenius plot is applied to extract the activation energy of the *Z*-to-*E* isomerisation of Azo.



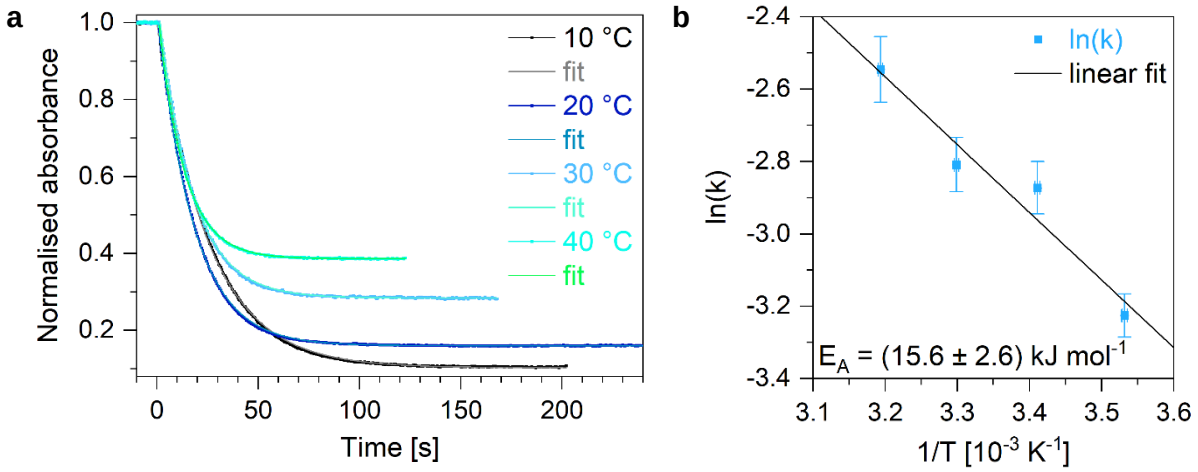
Supplementary Figure S5 (a) Temporal evolution of the absorption of *E*-Azo at its maximum absorption wavelength upon thermally activated *Z*-to-*E* isomerisation in an equimolar Azo+DASA mixture in toluene with simultaneous closed-to-linear isomerisation of DASA at different temperatures with the respective monoexponential fit curves. Using the fitted lifetimes, the corresponding rate constants are calculated and an (b) Arrhenius plot is applied to extract the activation energy of the thermally initiated *Z*-to-*E* isomerisation of Azo.



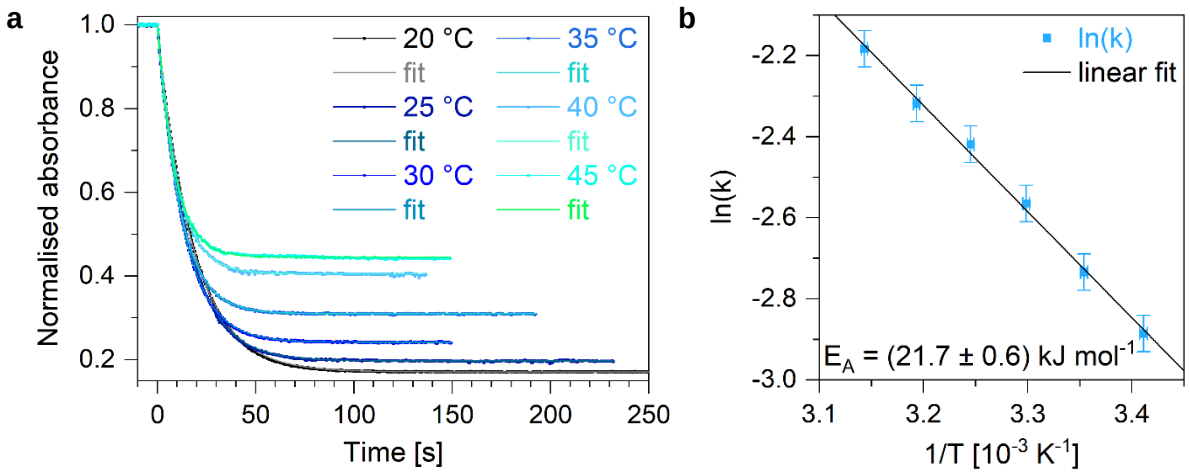
Supplementary Figure S6 Temporal evolution of the absorption of *Z*-DASA at 571 nm and of *E*-DASA at 625 nm at 0 °C. (a) Since the rise of the absorption feature of *E*-DASA is orders of magnitude faster than the decay time, the decay of the *Z*-DASA absorption feature is pseudo monoexponential and can be used to describe the ring closure and opening which is verified by the same decay times fitted by monoexponential fit curves to the decay of (b) *Z*-DASA and (c) *E*-DASA.

Supplementary Table S3 Determined lifetimes of DASA in toluene upon thermally activated linear-to-closed switching in different environments regarding Azo.

Temperature [°C]	Lifetime [s]		
	DASA	DASA+*E*-Azo	DASA+Azo simultaneous switching
0	39.43 ± 0.11	-	-
10	30.87 ± 0.12	25.17 ± 0.05	-
20	22.87 ± 0.09	17.68 ± 0.03	17.91 ± 0.02
25	-	-	15.39 ± 0.02
30	18.97 ± 0.06	16.59 ± 0.04	13.00 ± 0.02
35	-	-	11.23 ± 0.01
40	17.17 ± 0.04	12.75 ± 0.02	10.15 ± 0.03
45	-	-	8.87 ± 0.03



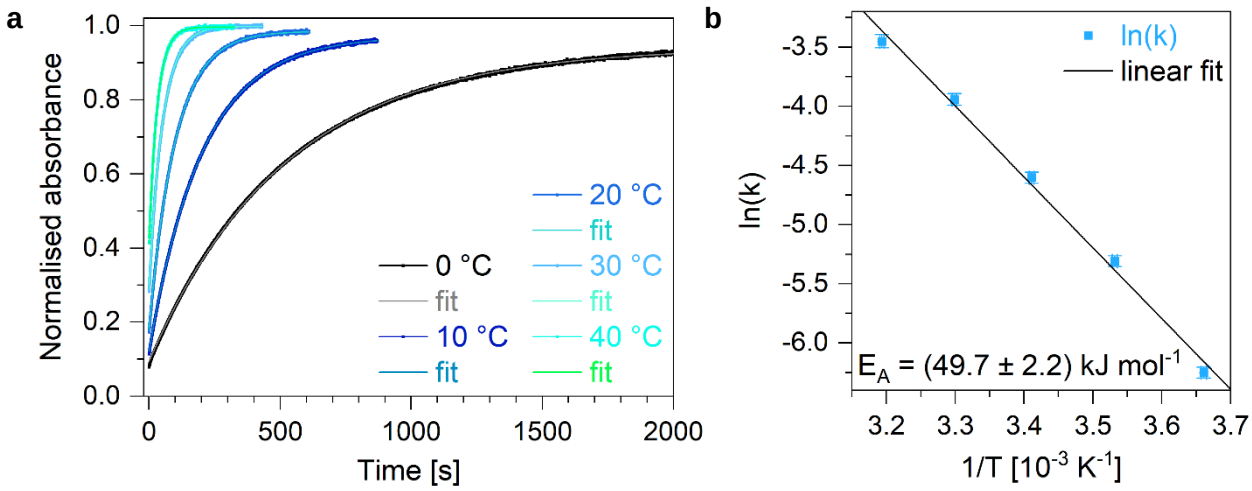
Supplementary Figure S7 (a) Temporal evolution of the absorption of *Z*-DASA at its maximum absorption wavelength upon linear-to-closed switching in an equimolar Azo+DASA mixture in toluene in the presence of *E*-Azo at different temperatures with the respective monoexponential fit curves. Using the fitted lifetimes, the corresponding rate constants are calculated and an (b) Arrhenius plot is applied to extract the activation energy of the thermally activated ring closure of DASA.



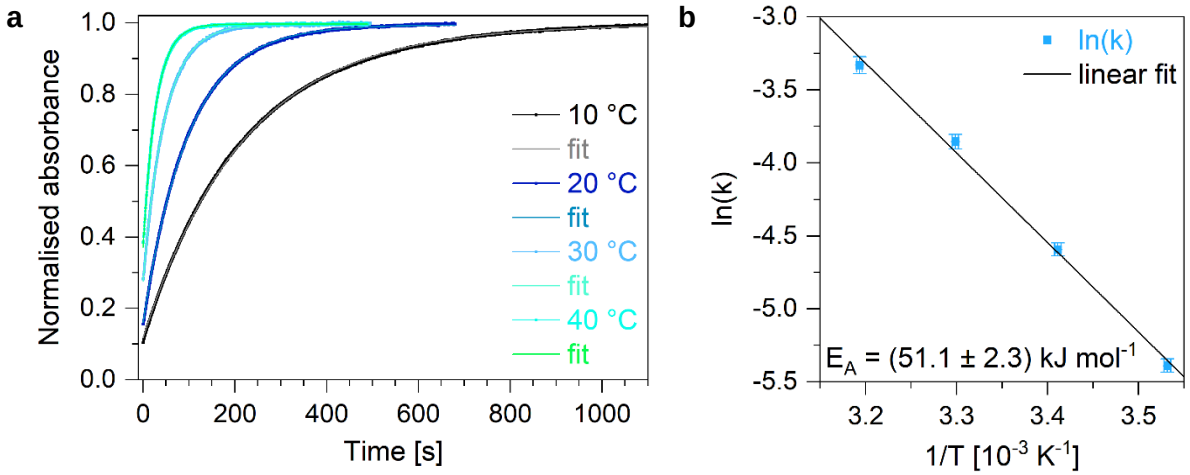
Supplementary Figure S8 (a) Temporal evolution of the absorption of *Z*-DASA at its maximum absorption wavelength upon linear-to-closed switching in an equimolar DASA+Azo mixture in toluene while Azo undergoes simultaneous *E*-to-*Z* isomerisation at different temperatures with the respective monoexponential fit curves. Using the fitted lifetimes, the corresponding rate constants are calculated and an (b) Arrhenius plot is applied to extract the activation energy of the thermally activated ring closure of DASA.

Supplementary Table S4 Effective cross sections σ of DASA in toluene upon open-to-closed isomerisation based on the lifetimes τ of DASA of **Supplementary Table 3**, applied photon dose n_p and wavelength λ for orthogonally addressing DASA or simultaneously addressing DASA and Azo.

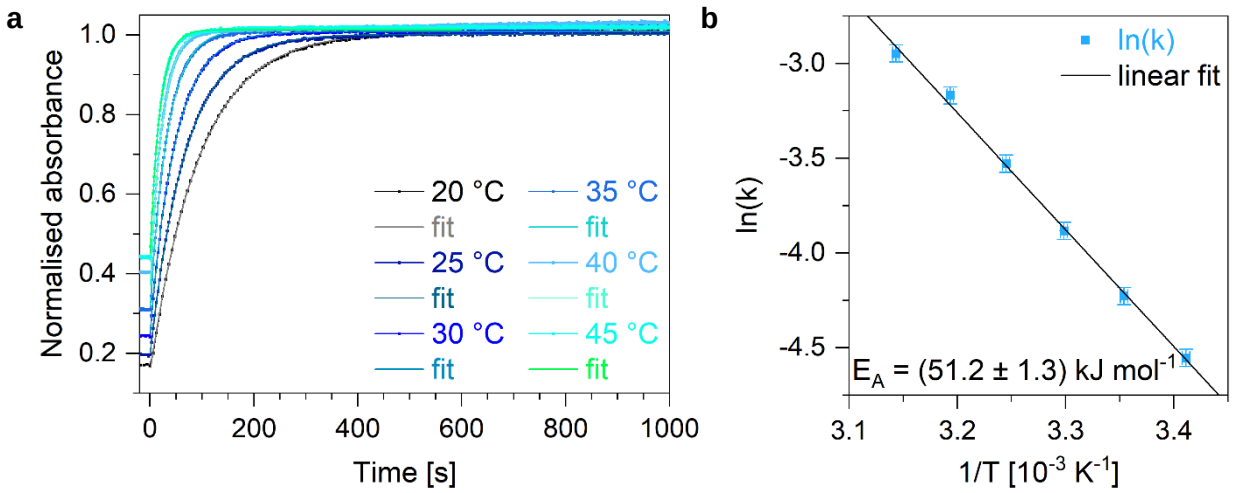
Temperature [°C]	Effective cross section σ [10^{-18} cm^2] Based on λ = 594 nm and n_p = (20 ± 1) · 10^{15} s^{-1} cm^{-2} or λ = 507 nm and n_p = (72 ± 4) · 10^{15} s^{-1} cm^{-2} for simultaneous switching		
	DASA	DASA+*E*-Azo	DASA+Azo simultaneous switching
0	1.24 ± 0.06	-	-
10	1.58 ± 0.08	1.94 ± 0.10	-
20	2.14 ± 0.11	2.77 ± 0.14	0.77 ± 0.04
25	-	-	0.90 ± 0.05
30	2.58 ± 0.13	2.95 ± 0.15	1.07 ± 0.05
35	-	-	1.23 ± 0.06
40	2.85 ± 0.14	3.83 ± 0.19	1.36 ± 0.07
45	-	-	1.56 ± 0.08



Supplementary Figure S9 (a) Temporal evolution of the absorption of *Z*-DASA at its maximum absorption wavelength upon closed-to-linear backswitching of DASA in toluene at different temperatures with the respective monoexponential fit curves. Using the fitted lifetimes, the corresponding rate constants are calculated and an (b) Arrhenius plot is applied to extract the activation energy for the thermally activated ring opening of DASA.



Supplementary Figure S10 (a) Temporal evolution of the absorption of *Z*-DASA at its maximum absorption wavelength upon closed-to-linear backswitching of DASA in an equimolar DASA+Azo mixture in toluene while *E*-Azo is present at different temperatures with the respective monoexponential fit curves. Using the fitted lifetimes, the corresponding rate constants are calculated and an (b) Arrhenius plot is applied to extract the activation energy for the thermally activated ring opening of DASA.

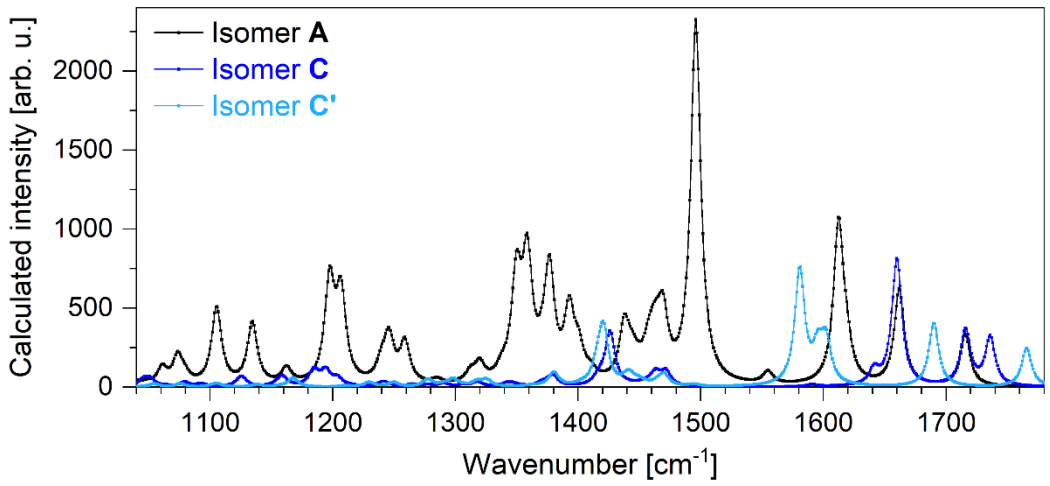


Supplementary Figure S11 (a) Temporal evolution of the first 1000 s of the absorption of *Z*-DASA at its maximum absorption wavelength upon closed-to-linear backswitching of DASA in an equimolar Azo+DASA mixture in toluene at different temperatures with the respective monoexponential fit curves. Using the fitted lifetimes, the corresponding rate constants are calculated and an (b) Arrhenius plot is applied to extract the activation energy for the thermally activated ring opening of DASA.

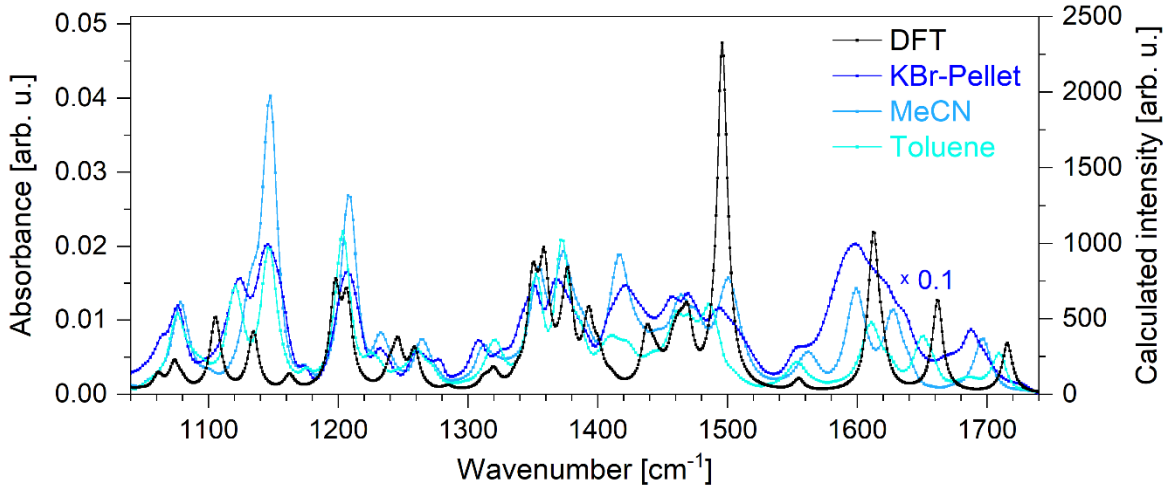
Supplementary Table S5 Determined lifetimes of DASA in toluene upon thermally activated closed-to-open isomerisation in different environments regarding Azo.

Temperature [°C]	Lifetime [s]		
	DASA	DASA+*E*-Azo	DASA+Azo simultaneous switching
0	518.63 ± 0.26	-	-
10	202.17 ± 0.10	218.98 ± 0.14	-
20	99.71 ± 0.06	98.76 ± 0.07	94.97 ± 0.21
25	-	-	68.51 ± 0.15
30	51.53 ± 0.05	47.15 ± 0.04	48.58 ± 0.09
35	-	-	34.09 ± 0.14
40	31.53 ± 0.04	27.97 ± 0.03	23.78 ± 0.11
45	-	-	19.06 ± 0.07

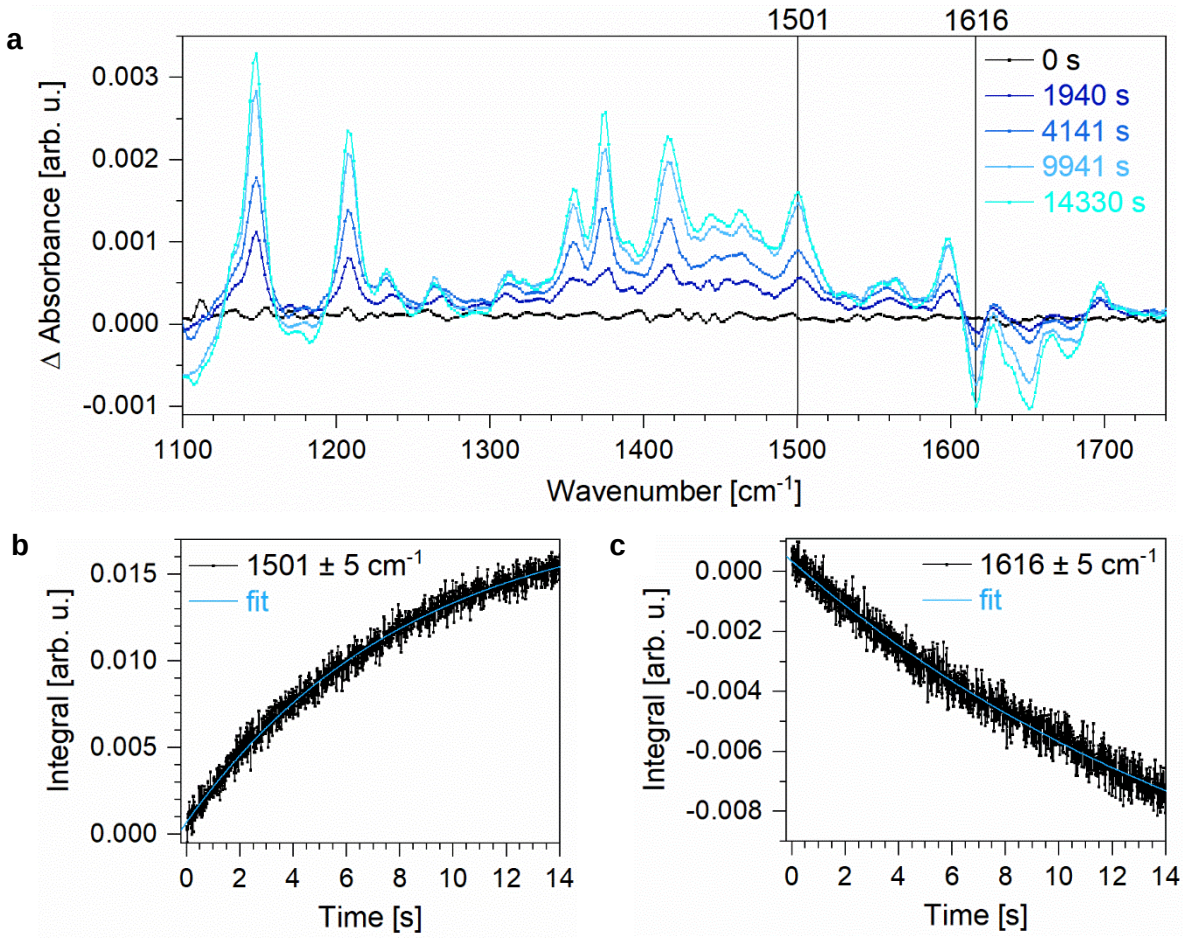
4. IR absorption data



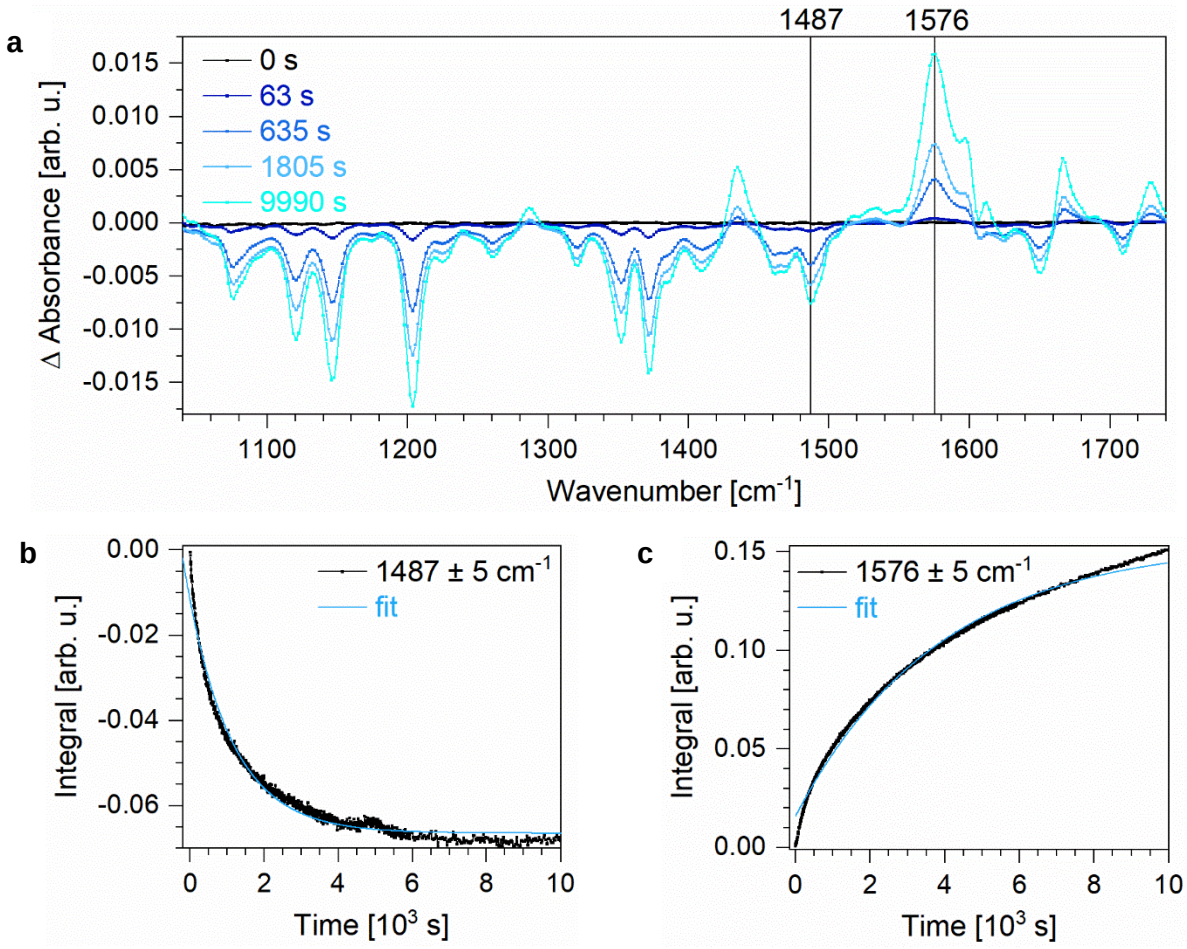
Supplementary Figure S12 IR absorption spectra calculated by density functional theory (DFT) using the B3LYP functional, the 6-311G(d,p) basis set, a scaling factor of 0.9682 and applying a FWHM of 5 cm^{-1}.



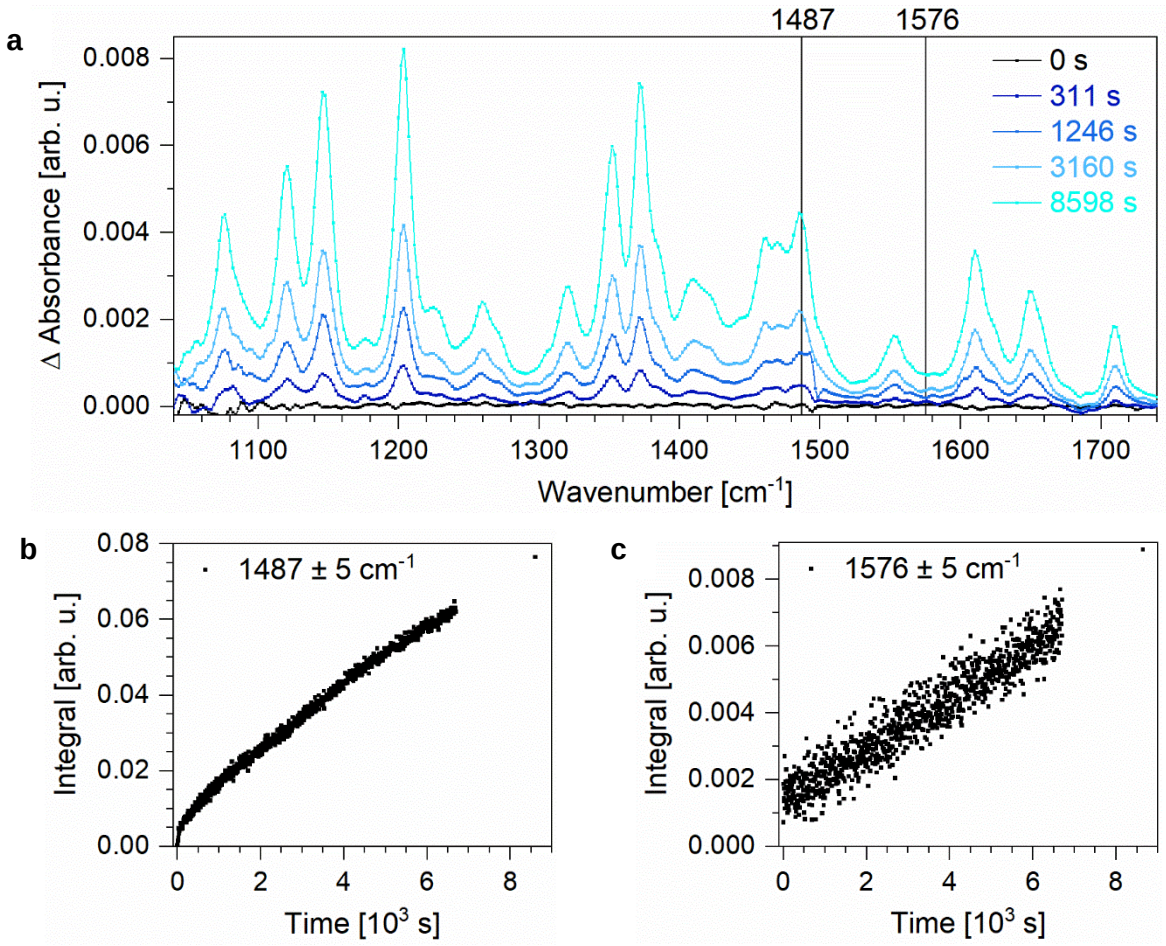
Supplementary Figure S13 Comparison of the IR absorption spectra of *Z*-DASA in different environments and the calculated absorption bands considering a scaling factor of 0.9682. Small shifts are observed but the absorption bands can be related to each other in order to assign the observed modes to the underlying vibrations.



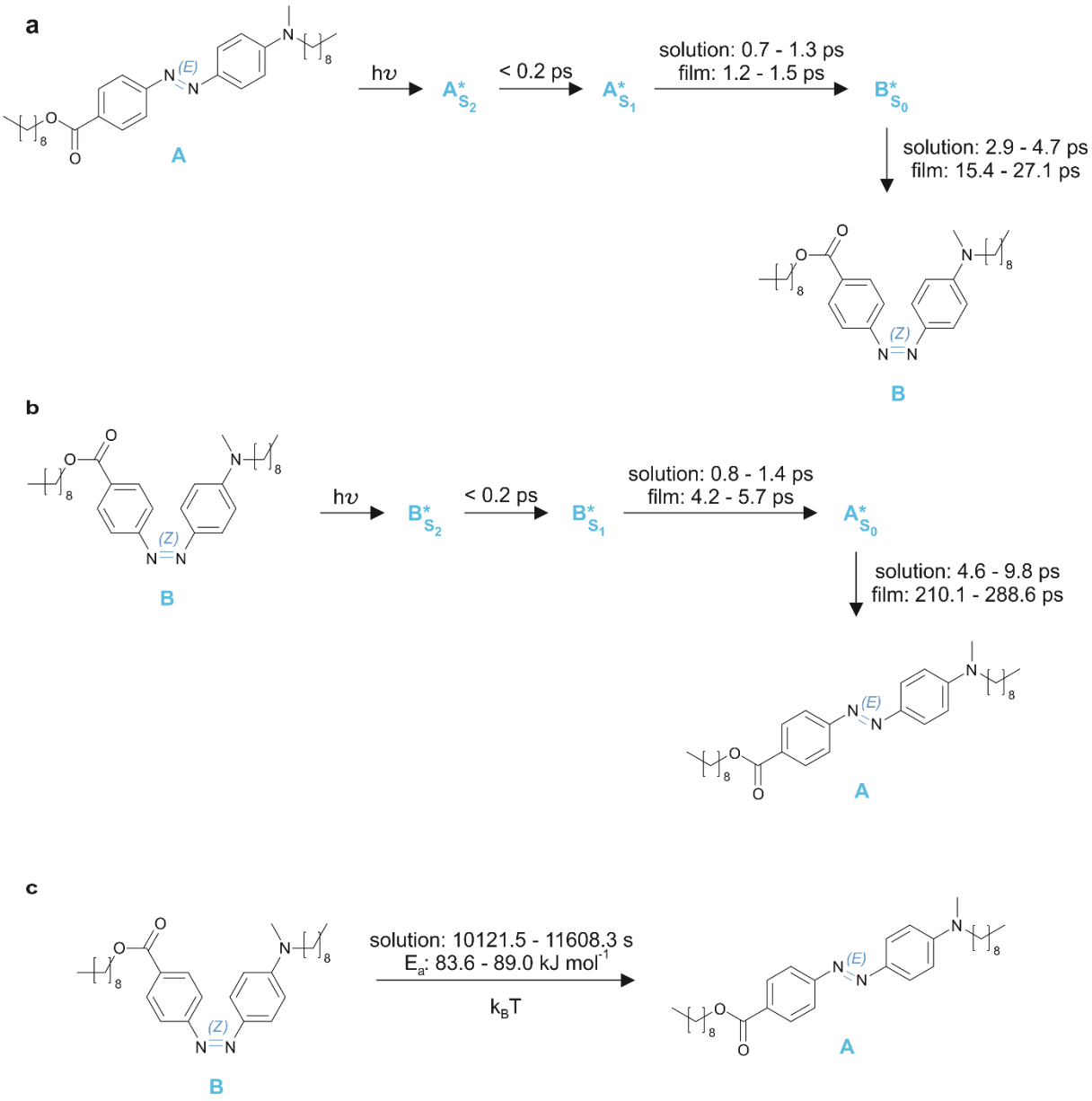
Supplementary Figure S14 (a) Changes in IR absorption upon closed-to-linear backswitching of DASA in acetonitrile-d_3 at room temperature. IR absorption bands related to the closed zwitterionic C' isomer, e.g. at (b) 1616 cm^{-1}, disappear while new absorption bands of the linear *Z*-DASA isomer, e.g. at (c) 1501 cm^{-1}, emerge.



Supplementary Figure S15 (a) Changes in IR absorption upon linear-to-closed switching of DASA in toluene-d_8 at room temperature. IR absorption bands related to the linear species, e.g. at (b) 1487 cm^{-1}, disappear while new absorption bands of the closed isomers C and C', e.g. at (c) 1576 cm^{-1}, emerge.



Supplementary Figure S16 (a) Changes in IR absorption upon closed-to-linear backswitching of DASA in toluene-d_8. IR absorption bands related to the closed zwitterionic isomer C', e.g. at (b) 1576 cm^{-1}, and new absorption bands of the linear *Z*-DASA isomer, e.g. at (c) 1487 cm^{-1}, grow linearly in intensity.

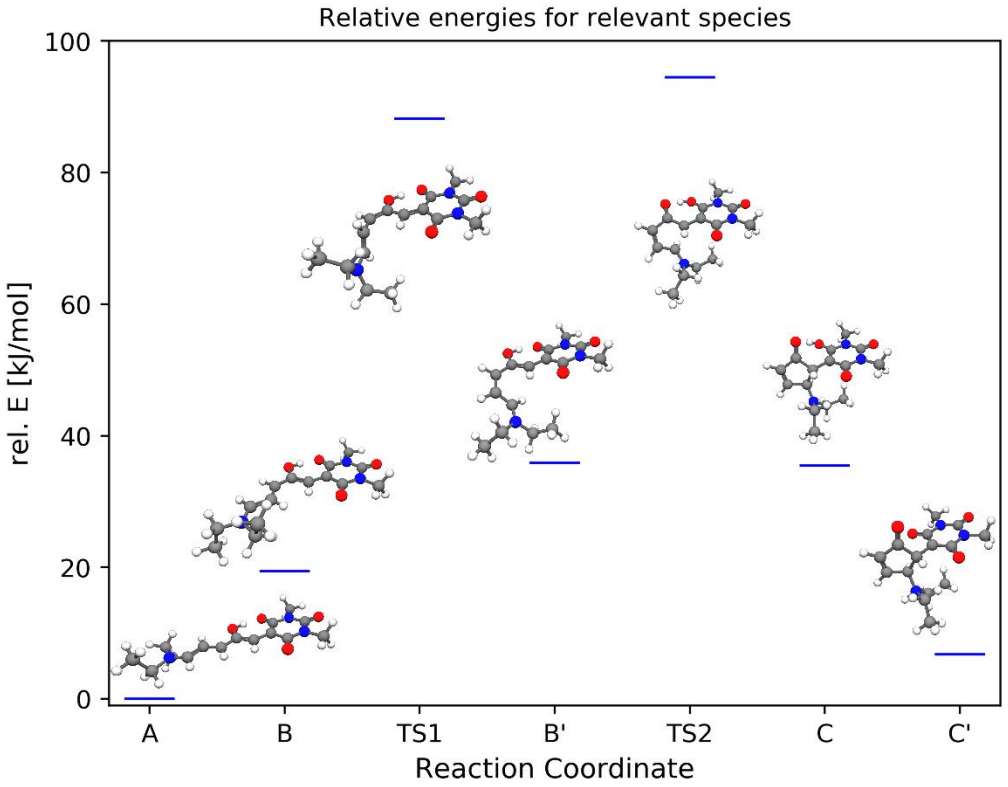


Supplementary Figure S17 Complete switching scheme of the (a) *E*-to-*Z*, (b) photoinitiated *Z*-to-*E* and (c) thermally activated *Z*-to-*E* switching of Azo including the determined lifetimes and activation energies found for pure Azo solutions and in an equimolar mixture of Azo+DASA in different environments, namely toluene solutions, acetonitrile solutions and thin PMMA blend films. The lifetimes in the picosecond range were determined within our former study of the ultrafast kinetics[2] while the longer lifetimes and activation energies are provided by this study.

5. Theory

The optimised geometries shown in **Fehler! Verweisquelle konnte nicht gefunden werden.** demonstrate the good agreement between the reaction coordinates along which the isomerisation of DASA isomer B to DASA isomer B' happens and along which the ring closure from DASA isomer B' to DASA isomer C takes place.
The calculated geometries of the DASA isomers and transition states are listed in the

Supplementary Table **S1** - Supplementary Table Supplementary **Table 7** whereas the Azo isomers and transition states are listed in the Supplementary Table 8 - Supplementary Table Supplementary **Table 10**.



Supplementary Figure 18 Relative energies of all explicitly considered species relative to the DASA isomer A.

Supplementary Table S1 Optimised geometry of the DASA isomer A using DFT theory, the range-separated hybrid exchange-correlation (xc)-functional ωB97X-D3 and the 6-311G(d,p) basis-set.

No.	Atom	x	y	z
1	C	4.9130533446	-0.0687760176	-0.0548768356
2	N	4.3449725069	1.1760882271	0.1017562016
3	C	2.9659589075	1.4206729865	0.1647477830
4	C	2.0960974368	0.2696358663	0.0436331581
5	C	2.6588877076	-1.0336352853	-0.1213431245
6	N	4.0445950318	-1.1410160054	-0.1627327303
7	C	0.7082235339	0.5531667153	0.1032257330
8	C	-0.4378814633	-0.2116466589	0.0122757004
9	O	-0.5027944291	-1.5543859874	-0.1731904304
10	O	2.5688880722	2.5726314345	0.3134040378
11	O	2.0145246238	-2.0910131763	-0.2297494757
12	C	5.2763885885	2.2964294761	0.2074342028
13	C	4.6089078688	-2.4784956811	-0.3350742254
14	O	6.1230887190	-0.2078459566	-0.0979837325
15	C	-1.6719362484	0.4624090811	0.1106983734
16	C	-2.9063388287	-0.1497767826	0.0239386155
17	C	-4.0609687754	0.6327430309	0.1325954662
18	N	-5.3055095284	0.2218655874	0.0549551046
19	C	-5.6540102739	-1.1856080549	-0.1668591626
20	C	-5.6834013237	-1.9782216414	1.1343688078
21	C	-6.4149102021	1.1745112257	0.1929751605
22	C	-6.9570461213	1.6242610179	-1.1570991606
23	H	0.4250655726	-1.8931918410	-0.2122279496
24	H	-7.7921758297	2.3116683273	-1.0051174272
25	H	-7.3176634726	0.7770337946	-1.7457381783
26	H	-6.1823849348	2.1413423462	-1.7286593813
27	H	-7.1927982031	0.6852294193	0.7842533516
28	H	-6.0532768195	2.0276368615	0.7689206867
29	H	-5.9563795804	-3.0149184113	0.9256394277
30	H	-4.7053840679	-1.9719452865	1.6212972835
31	H	-6.4190693549	-1.5624362473	1.8273620450
32	H	-6.6329280147	-1.2012628926	-0.6486453908
33	H	-4.9421429862	-1.6124852332	-0.8755207283
34	H	-3.9417673856	1.7008794064	0.3019332188
35	H	-2.9626129641	-1.2208635374	-0.1241970629
36	H	-1.6298683288	1.5373748158	0.2616252376
37	H	0.5104651704	1.6101787001	0.2483334058
38	H	5.9088828147	2.1785726706	1.0881213645
39	H	4.6884968911	3.2047176163	0.2921633455
40	H	5.6890460171	-2.3828156950	-0.3753379346
41	H	4.2378968159	-2.9196596516	-1.2601165728
42	H	4.3222932302	-3.1162397440	0.5016212522
43	H	5.9067922839	2.3413992272	-0.6809497595
Absolute energy = 1049.42790355860 Eh				

Supplementary Table 2 Optimised geometry of the DASA isomer B using DFT theory, the range-separated hybrid exchange-correlation (xc)-functional ωB97X-D3 and the 6-311G(d,p) basis-set.

No.	Atom	x	y	z
1	C	4.9455644884	0.2306075196	0.0888037260
2	N	4.2842884171	1.4235241609	0.2790783773
3	C	2.8904851631	1.5737450772	0.2601058304
4	C	2.1105572849	0.3807978876	0.0053761504
5	C	2.7716891207	-0.8705198806	-0.1971325985
6	N	4.1619418064	-0.8838904865	-0.1518056616
7	C	0.7049535008	0.5743221568	-0.0056776204
8	C	-0.3821143501	-0.2417037802	-0.2291021968
9	O	-0.3370412502	-1.5721166268	-0.5296198864
10	O	2.4065572360	2.6854974763	0.4551683807
11	O	2.2121675846	-1.9598021326	-0.4071486674
12	C	5.1262357554	2.5906946416	0.5274756756
13	C	4.8257647334	-2.1695829528	-0.3594362369
14	O	6.1622404502	0.1712254418	0.1315896410
15	C	-1.6976904637	0.2784417888	-0.1685926988
16	C	-2.1355701955	1.5575091712	0.1091520655
17	C	-3.5135710513	1.7992084847	0.1014953870
18	N	-4.1193105189	2.9368546594	0.3522722099
19	C	-3.3844103698	4.1638853250	0.6761551730
20	C	-2.9392048493	4.9054269831	-0.5784558513
21	C	-5.5851764435	3.0216177260	0.3105352938
22	C	-6.2064081720	2.8893194878	1.6942500726
23	H	0.6103732523	-1.8473441302	-0.5121247904
24	H	-7.2925283169	2.9774745457	1.6176341101
25	H	-5.8499554736	3.6710058422	2.3696818518
26	H	-5.9672845983	1.9162768026	2.1303233640
27	H	-5.8440670515	3.9798728585	-0.1461792512
28	H	-5.9461056290	2.2345955247	-0.3533713562
29	H	-2.4120686953	5.8196399258	-0.2976589588
30	H	-2.2658624360	4.2905086120	-1.1804481894
31	H	-3.7999327371	5.1797047073	-1.1935040432
32	H	-4.0492356058	4.7873085476	1.2760809693
33	H	-2.5338209712	3.9056190958	1.3094200754
34	H	-4.1770991224	0.9707517777	-0.1362737888
35	H	-1.4420638046	2.3599243142	0.3281122517
36	H	-2.4669150989	-0.4650216961	-0.3765884201
37	H	0.4472403076	1.6063869199	0.2051673371
38	H	5.6871052739	2.4619642542	1.4542343975
39	H	4.4735685154	3.4538496156	0.6080597179
40	H	5.8974339734	-2.0006958882	-0.3353646508
41	H	4.5332590607	-2.5838430677	-1.3240376974
42	H	4.5416359078	-2.8695480404	0.4270263355
43	H	5.8269653727	2.7277773505	-0.2962458292
Absolute energy =1049.41982182549 Eh				

Supplementary Table 3 Optimised geometry of the transition state TS1 using DFT theory, the range-separated hybrid exchange-correlation (xc)-functional ωB97X-D3 and the 6-311G(d,p) basis-set.

No.	Atom	x	y	z
1	C	4.2134615330	0.4283503592	0.7950128360
2	N	3.3491024929	1.4809081837	1.0411626205
3	C	2.0317665463	1.5414289252	0.6148734598
4	C	1.5321298746	0.3736808744	-0.1530905874
5	C	2.4335989550	-0.7542974651	-0.4071146996
6	N	3.7155051562	-0.6573134149	0.0761020108
7	C	0.2382125237	0.4690379686	-0.5580825137
8	C	-0.6929260242	-0.3894750322	-1.2631851583
9	O	-0.3836271981	-1.6348850899	-1.6847033577
10	O	1.3392549275	2.5073765983	0.8713814291
11	O	2.1163025007	-1.7678745959	-1.0232319599
12	C	3.9046579248	2.5939962509	1.8135322251
13	C	4.6120285440	-1.7866475611	-0.1844342960
14	O	5.3552247204	0.4553597602	1.1945425883
15	C	-1.9488898837	0.0748535461	-1.4687588962
16	C	-2.4468057612	1.4277135048	-1.1400605836
17	C	-3.1798733306	1.6716014836	-0.0372422905
18	N	-3.7437701485	2.8573308385	0.3569755019
19	C	-3.4875280961	4.0613209809	-0.4216772624
20	C	-4.3885785783	4.1681448800	-1.6488680730
21	C	-4.0007129281	3.0241312079	1.7842297787
22	C	-2.7547003494	3.3854949200	2.5908098191
23	H	0.5606734573	-1.8130570828	-1.4855335534
24	H	-2.9985402237	3.4882094169	3.6516591047
25	H	-2.3263468151	4.3322187694	2.2489419505
26	H	-1.9901869584	2.6094747220	2.4863971207
27	H	-4.7671916182	3.7954334155	1.9028298862
28	H	-4.4309979804	2.0902545617	2.1577265936
29	H	-4.1557117161	5.0748925037	-2.2138040891
30	H	-4.2602361027	3.3122134705	-2.3156018229
31	H	-5.4380880677	4.2100846968	-1.3459800749
32	H	-3.6606391570	4.9202600489	0.2307231506
33	H	-2.4294228383	4.1010589985	-0.7182613393
34	H	-3.3752397830	0.8525906910	0.6531994231
35	H	-2.2247475517	2.2197715450	-1.8503958899
36	H	-2.6236663707	-0.6246121289	-1.9639114317
37	H	-0.2287749202	1.4049543980	-0.2660733874
38	H	4.2619072273	2.2303591743	2.7764598809
39	H	3.1127526304	3.3210634158	1.9604921851
40	H	5.5759069111	-1.5587153216	0.2573935128
41	H	4.7169159403	-1.9303288818	-1.2595712685
42	H	4.1989924416	-2.6910228400	0.2617764800
43	H	4.7323331053	3.0480979059	1.2689866684
Absolute energy = 1049.39565425714 Eh				

Supplementary Table 4 Optimised geometry of the DASA isomer B' using DFT theory, the range-separated hybrid exchange-correlation (xc)-functional ωB97X-D3 and the 6-311G(d,p) basis-set.

No.	Atom	x	y	z
1	C	5.1114206276	0.0125973088	-0.2090774504
2	N	4.5590038141	1.2658047068	-0.3527283329
3	C	3.1838999723	1.5391435382	-0.3096841874
4	C	2.3046048759	0.4132033380	-0.1169686892
5	C	2.8466823928	-0.8938073816	0.0431453446
6	N	4.2308922437	-1.0346350114	-0.0102867752
7	C	0.9167042819	0.7359819006	-0.0349682879
8	C	-0.2331168301	-0.0208561147	0.0113976533
9	O	-0.2981118212	-1.3695367964	-0.1337339893
10	O	2.8021360568	2.7037262471	-0.4293084067
11	O	2.1872560446	-1.9331998710	0.2326142326
12	C	5.5009810904	2.3628025493	-0.5559329908
13	C	4.7755623743	-2.3804668101	0.1567424956
14	O	6.3190763368	-0.1527782994	-0.2553086109
15	C	-1.5053666397	0.6187201769	0.0944132901
16	C	-1.7809984956	1.8370315884	0.6608747131
17	C	-0.8827857552	2.4628739428	1.5557545631
18	N	-0.9119632430	3.7108179427	1.9411861435
19	C	-1.8479635195	4.6929123949	1.3814638285
20	C	-3.1353677644	4.7724132935	2.1928663640
21	C	0.0529805580	4.1941834021	2.9409433145
22	C	1.2910902600	4.7824764672	2.2780065928
23	H	0.6239014876	-1.7177821762	-0.0429331712
24	H	1.9891008435	5.1241841515	3.0452774988
25	H	1.0353142035	5.6360786481	1.6453140775
26	H	1.7919038324	4.0320842285	1.6605032843
27	H	-0.4588321774	4.9357660593	3.5577939701
28	H	0.3153505544	3.3541114526	3.5852098111
29	H	-3.7884990021	5.5372964770	1.7677790842
30	H	-3.6683695474	3.8187825158	2.1818885609
31	H	-2.9262213285	5.0396336200	3.2315908594
32	H	-1.3351384437	5.6564245343	1.3764616675
33	H	-2.0468303811	4.4247003030	0.3426171856
34	H	-0.1133444252	1.8525804020	2.0221310838
35	H	-2.7468669327	2.2923146395	0.4749340405
36	H	-2.3320074633	0.0646819947	-0.3461402021
37	H	0.7481062847	1.8040999079	-0.1015663521
38	H	6.1724682544	2.4450073945	0.2995595483
39	H	4.9221385668	3.2747903748	-0.6609323666
40	H	5.8579633554	-2.3094011708	0.1253878071
41	H	4.4224762323	-3.0303002332	-0.6447057439
42	H	4.4549441422	-2.7929737706	1.1132676200
43	H	6.0912450835	2.1885021345	-1.4560890783
Absolute energy = 1049.41711599953 Eh				

Supplementary Table 5 Optimised geometry of the transition state TS2 using DFT theory, the range-separated hybrid exchange-correlation (xc)-functional ωB97X-D3 and the 6-311G(d,p) basis-set.

No.	Atom	x	y	z
1	C	2.7512993700	1.3850583835	-0.0348497181
2	N	1.6701272678	1.7560114152	-0.8014731947
3	C	0.5742541391	0.9303232812	-1.0917481591
4	C	0.5855408542	-0.3838198059	-0.4992130053
5	C	1.6867060019	-0.7686753647	0.2397585816
6	N	2.7355911244	0.0913074361	0.4595238384
7	C	-0.6101220927	-1.1956463143	-0.7131668788
8	C	-0.6934334200	-2.6132172247	-0.6186946771
9	O	0.2704617892	-3.4054008297	-0.3695374549
10	O	-0.3322841326	1.3527855316	-1.8044497420
11	O	1.8438787318	-1.9407161337	0.7876510134
12	C	1.7014825404	3.1134805925	-1.3396217186
13	C	3.8890605544	-0.3801675927	1.2276857479
14	O	3.6726013667	2.1521956133	0.1838258688
15	C	-2.0712478934	-3.0764018173	-0.6991759170
16	C	-2.9505269199	-2.1988531643	-0.1848551024
17	C	-2.3750308422	-1.0557835921	0.5262585121
18	N	-2.9998567559	0.1273796193	0.5718505870
19	C	-3.8227691845	0.5952490408	-0.5412084252
20	C	-5.3160747844	0.5732262014	-0.2342214934
21	C	-2.7038945662	1.0784111697	1.6426207351
22	C	-1.4758508490	1.9399446309	1.3777909887
23	H	1.2091878778	-2.6356226341	0.3048388100
24	H	-1.3638465879	2.6830899169	2.1711047371
25	H	-1.5576153810	2.4641820417	0.4227213334
26	H	-0.5729310988	1.3249689537	1.3543876839
27	H	-3.5890806532	1.7066776859	1.7682262979
28	H	-2.5839104732	0.5140809101	2.5705557464
29	H	-5.8758723024	0.9535442062	-1.0922629379
30	H	-5.6579201639	-0.4427840950	-0.0214175354
31	H	-5.5527130473	1.2028883355	0.6273605660
32	H	-3.5025389927	1.6105543279	-0.7973577399
33	H	-3.6051235440	-0.0317496583	-1.4100471469
34	H	-1.7848389403	-1.2826708738	1.4084720943
35	H	-4.0295894452	-2.3056766265	-0.2541044647
36	H	-2.3310424147	-4.0558555092	-1.0835684754
37	H	-1.2714733449	-0.7489588009	-1.4437093081
38	H	1.7652235805	3.8349382721	-0.5248164741
39	H	0.7845251225	3.2626608945	-1.9007412861
40	H	4.6202470269	0.4213541716	1.2424639739
41	H	4.3122968493	-1.2645959449	0.7526794443
42	H	3.5882580159	-0.6262404031	2.2460110605
43	H	2.5643960376	3.2372602939	-1.9948944055
Absolute energy = 1049.39375489300 Eh				

Supplementary Table 6 Optimised geometry of the DASA isomer C using DFT theory, the range-separated hybrid exchange-correlation (xc)-functional ωB97X-D3 and the 6-311G(d,p) basis-set.

No.	Atom	x	y	z
1	C	2.6497251830	1.3340702394	-0.0451373666
2	N	1.5993264010	1.7317103410	-0.8431216511
3	C	0.4748168529	0.9501615784	-1.1357922969
4	C	0.4016489182	-0.3341380848	-0.4801429435
5	C	1.4829647088	-0.7514160021	0.2356104877
6	N	2.5732943467	0.0472767833	0.4638499648
7	C	-0.8729154324	-1.1075727176	-0.6245996894
8	C	-0.7669189991	-2.5941980518	-0.9054023940
9	O	0.2366900846	-3.1745400907	-1.2938735524
10	O	-0.3848154563	1.3764126871	-1.8982114484
11	O	1.5965478112	-1.9508978792	0.8042300208
12	C	1.7019366127	3.0722764912	-1.4153624866
13	C	3.7082965754	-0.4738313712	1.2305173331
14	O	3.5962145234	2.0659596783	0.1782552874
15	C	-2.0352308242	-3.2143368731	-0.5091521470
16	C	-2.6744118140	-2.3733930200	0.3081807017
17	C	-1.9355316293	-1.0743805010	0.5394148254
18	N	-2.8391864209	0.0400445888	0.6783739910
19	C	-3.4471461183	0.5164270652	-0.5579983667
20	C	-4.7564820822	1.2620139900	-0.3311945604
21	C	-2.5101215747	1.0407548830	1.6854354775
22	C	-1.4133295038	2.0514792482	1.3454732934
23	H	1.1685493457	-2.6073050566	0.2268857936
24	H	-1.3542859443	2.8130471466	2.1283968110
25	H	-1.6096755716	2.5574659824	0.3963396375
26	H	-0.4359246871	1.5673383704	1.2793203671
27	H	-3.4303332681	1.5814612943	1.9256684288
28	H	-2.2355676422	0.5017711889	2.5980197113
29	H	-5.2360767648	1.4684518739	-1.2914389608
30	H	-5.4402088997	0.6619108704	0.2761481867
31	H	-4.6024145865	2.2203181358	0.1716078383
32	H	-2.7563612894	1.1447414821	-1.1405316465
33	H	-3.6551697274	-0.3659343157	-1.1743591130
34	H	-1.3874904716	-1.1732880062	1.4841400564
35	H	-3.6170158788	-2.5636239385	0.8111465433
36	H	-2.3129191909	-4.2272684086	-0.7707939546
37	H	-1.3835076391	-0.7013878795	-1.5060280948
38	H	1.7841950954	3.8094745641	-0.6166573264
39	H	0.8031327388	3.2484570110	-1.9976035175
40	H	4.4609948334	0.3070971494	1.2624534947
41	H	4.1104417069	-1.3605066651	0.7417538462
42	H	3.3951044386	-0.7251936366	2.2433336541
43	H	2.5816199484	3.1386006430	-2.0563141622
Absolute energy = 1049.41860847750 Eh				

Supplementary Table 7 Optimised geometry of the DASA isomer C' using DFT theory, the range-separated hybrid exchange-correlation (xc)-functional ωB97X-D3 and the 6-311G(d,p) basis-set.

No.	Atom	x	y	z
1	C	2.7082412240	1.2621411024	-0.1627573814
2	N	1.7001675983	1.7185244874	-0.9822376537
3	C	0.4773214000	1.0407032646	-1.1977349075
4	C	0.3225074407	-0.1780709714	-0.5146577179
5	C	1.3042084467	-0.6838264405	0.3560316165
6	N	2.4850575817	0.0692155372	0.4909622511
7	C	-0.9371966954	-0.9541212654	-0.6792423181
8	C	-0.7494814556	-2.4004170652	-1.1505483835
9	O	0.0777186594	-2.7778936216	-1.9465744256
10	O	-0.3715239965	1.5586652454	-1.9436057200
11	O	1.1923897205	-1.7323276683	1.0127363728
12	C	1.9415682226	2.9859851652	-1.6598270544
13	C	3.5155691141	-0.4529702276	1.3793147139
14	O	3.7465594097	1.8996134219	-0.0284523592
15	C	-1.7890517486	-3.2279989582	-0.4987070117
16	C	-2.4267085217	-2.5039145245	0.4174898028
17	C	-1.8487799045	-1.1194585484	0.5549105285
18	N	-2.9540208237	-0.0911102993	0.7597680481
19	C	-3.4937992577	0.4906886636	-0.5186928196
20	C	-4.7489038221	1.3121126384	-0.2970714300
21	C	-2.6256412504	0.9375800296	1.8160851350
22	C	-1.5718801113	1.9435758234	1.4090760443
23	H	-1.4371477215	2.6388063795	2.2397258244
24	H	-1.8663394097	2.5229985218	0.5321129650
25	H	-0.6135550049	1.4632074721	1.2062326911
26	H	-3.5687655581	1.4246048135	2.0633761584
27	H	-2.3121662550	0.3630962311	2.6887689855
28	H	-5.1607952390	1.5705314548	-1.2740023072
29	H	-5.5077104190	0.7461046507	0.2502021489
30	H	-4.5474549477	2.2432267708	0.2352975187
31	H	-2.6965449325	1.0799566627	-0.9725497861
32	H	-3.7042595819	-0.3621991796	-1.1671762835
33	H	-1.2410804549	-1.0813312328	1.4621384195
34	H	-3.2309128036	-2.8521350938	1.0587928342
35	H	-1.9619430942	-4.2690404119	-0.7401855129
36	H	-1.5006140810	-0.4921005402	-1.4945318213
37	H	2.1094873894	3.7807040056	-0.9313544356
38	H	1.0600811928	3.2075665295	-2.2539922961
39	H	4.3785056176	0.2031752530	1.3216681628
40	H	3.7943948439	-1.4616082148	1.0725919597
41	H	3.1470297705	-0.4895052688	2.4059184293
42	H	2.8171598313	2.9117807305	-2.3070020806
43	H	-3.7300803727	-0.6179653223	1.1667630952
Absolute energy = 1049.43353746842 Eh				

Supplementary Table 8 Optimised geometry of *E*-Azo using DFT theory, the range-separated hybrid exchange-correlation (xc)-functional ωB97X-D3 and the 6-311G(d,p) basis-set.

No.	Atom	x	y	z
1	C	-4.3192821955	2.9117833359	-0.0942194766
2	C	-4.1970227182	1.5302219794	0.0475945910
3	C	-3.1841620639	3.7084130376	-0.0805655452
4	C	-1.9230809553	3.1330525107	0.0628765195
5	C	-1.7988045241	1.7489747295	0.2116494965
6	C	-2.9324688313	0.9568862491	0.2031641742
7	H	-5.2981287633	3.3604048024	-0.2105380152
8	H	-3.2579008001	4.7852898481	-0.1846272935
9	H	-0.8160683794	1.3113119683	0.3332341931
10	H	-2.8510877583	-0.1178682910	0.3198493478
11	C	1.3287996934	5.7549215992	0.1154691384
12	C	1.3981911769	4.3587944192	0.0075207765
13	C	2.4733882922	6.5184869846	0.1170627181
14	C	3.7562903807	5.9174113418	0.0118346462
15	C	3.8123469921	4.5079156312	-0.1007372545
16	C	2.6539163360	3.7574795760	-0.0991858108
17	N	-0.8281771295	4.0407637916	0.0647741881
18	N	0.2915746822	3.4962121823	-0.0054378843
19	N	4.8879224822	6.6724760831	0.0207858066
20	C	4.8019833288	8.1214670436	0.0695896089
21	H	4.2697629386	8.5268843723	-0.7988047192
22	H	5.8087386096	8.5342348993	0.0745293977
23	H	4.2923643885	8.4627280040	0.9766774001
24	C	6.1861064522	6.0416288129	-0.1381878887
25	H	6.9594831428	6.8042513268	-0.0730358266
26	H	6.2773183506	5.5383003322	-1.1080953729
27	H	6.3702057702	5.3044504744	0.6502075697
28	H	0.3595271574	6.2327451118	0.1963409563
29	H	2.3816236889	7.5935005130	0.2010945461
30	H	4.7640888011	4.0012654324	-0.1884539177
31	H	2.7047107564	2.6765215836	-0.1846643599
32	C	-5.3832162001	0.6270191562	0.0454235891
33	O	-6.5302297675	1.2853417383	-0.1133095592
34	C	-7.7228829279	0.4872409428	-0.1270522040
35	H	-7.6899724612	-0.2263583166	-0.9514018038
36	H	-8.5409225919	1.1898276696	-0.2644392015
37	H	-7.8306804138	-0.0462143635	0.8182182506
38	O	-5.3193149398	-0.5745265122	0.1727292190
Absolute energy = 934.574900111347 Eh				

Supplementary Table 9 Optimised geometry of the transition state between *E*-Azo and *Z*-Azo using DFT theory, the range-separated hybrid exchange-correlation (xc)-functional ωB97X-D3 and the 6-311G(d,p) basis-set.

No.	Atom	x	y	z
1	C	3.8008497112	-1.2718930839	0.1603814213
2	C	3.8291071264	0.0965548691	-0.1159168511
3	C	2.6118409806	-1.9734776931	0.0409743868
4	C	1.4413869260	-1.3144225813	-0.3271331303
5	C	1.4694180190	0.0487688349	-0.6153233205
6	C	2.6599292833	0.7489305703	-0.5120442555
7	H	4.7070253875	-1.7814767713	0.4639800771
8	H	2.5669345877	-3.0399246528	0.2367524998
9	H	0.5623061812	0.5467465497	-0.9380792349
10	H	2.6979992524	1.8080824010	-0.7408532845
11	C	-2.1455497391	0.4239978117	0.0749451278
12	C	-2.0189676511	-0.9366125955	-0.3029943179
13	C	-3.3710060450	1.0315510252	0.2009831870
14	C	-4.5692229354	0.3198048515	-0.0797887038
15	C	-4.4529104772	-1.0436501858	-0.4661038826
16	C	-3.2216353917	-1.6430076695	-0.5572593201
17	N	0.2605484137	-2.1453852233	-0.4430918535
18	N	-0.8315962782	-1.5559694394	-0.4001820797
19	N	-5.7792142207	0.9168622327	0.0175365039
20	C	-5.8837092453	2.3069069973	0.4340294436
21	H	-5.4939878433	2.4528026614	1.4471744133
22	H	-6.9314523955	2.5993735125	0.4257958355
23	H	-5.3384190116	2.9679917908	-0.2467289746
24	C	-6.9954633817	0.1654369065	-0.2524758778
25	H	-7.8500581206	0.8299939393	-0.1470102144
26	H	-7.1186164341	-0.6663760057	0.4493021526
27	H	-6.9985663170	-0.2355491677	-1.2708852128
28	H	-1.2471844169	0.9925169925	0.2893390438
29	H	-3.4131197503	2.0676598247	0.5100196462
30	H	-5.3389604268	-1.6261771739	-0.6816611353
31	H	-3.1494381320	-2.6882085392	-0.8403084905
32	C	5.0805387176	0.8961386089	-0.0137402833
33	O	6.1294644874	0.1617211391	0.3566617806
34	C	7.3770492928	0.8567786897	0.4875612397
35	H	7.6702152795	1.2932815478	-0.4682024965
36	H	8.0980217605	0.1045190990	0.7975751533
37	H	7.2948593229	1.6411657188	1.2410980749
38	O	5.1493870536	2.0834033097	-0.2387388671
Absolute energy = 934.502985475218 Eh				

Supplementary Table 10 Optimised geometry of *Z*-Azo using DFT theory, the range-separated hybrid exchange-correlation (xc)-functional ωB97X-D3 and the 6-311G(d,p) basis-set.

No.	Atom	x	y	z
1	C	2.8438996586	-0.8469799348	0.7501133643
2	C	2.8292069145	-0.1944344929	-0.4830362175
3	C	1.9055556430	-1.8291145735	1.0270765321
4	C	0.9268740533	-2.1354390953	0.0845130001
5	C	0.9182600381	-1.5029289454	-1.1593450233
6	C	1.8687126636	-0.5361907663	-1.4356404899
7	H	3.5954603185	-0.5936247199	1.4875420435
8	H	1.9159842271	-2.3564909391	1.9745297581
9	H	0.1703281819	-1.7689447600	-1.8980995062
10	H	1.8741059534	-0.0338413565	-2.3960650561
11	C	-1.5360563805	-0.6875408955	0.7553919476
12	C	-1.9038113074	-1.9224720550	0.2094630584
13	C	-2.3663123847	0.4094688830	0.6415527361
14	C	-3.5987675028	0.3304655118	-0.0506913155
15	C	-3.9756674662	-0.9328531605	-0.5620253264
16	C	-3.1521546855	-2.0295812740	-0.4069830743
17	N	0.0504475961	-3.2358915355	0.3499214868
18	N	-1.1876081548	-3.1455607194	0.3338782426
19	N	-4.4012799980	1.4248729649	-0.2008525063
20	C	-4.0608066938	2.6707127518	0.4624884657
21	H	-4.0511476003	2.5689361147	1.5553188709
22	H	-4.7989746629	3.4244226198	0.1948483808
23	H	-3.0798558923	3.0329865029	0.1409125726
24	C	-5.7315206674	1.2738539177	-0.7634585900
25	H	-6.1982222904	2.2546891862	-0.8329785220
26	H	-6.3705421267	0.6297673373	-0.1457256436
27	H	-5.6888397397	0.8500934651	-1.7712526774
28	H	-0.6111829427	-0.5811562427	1.3082782834
29	H	-2.0553292561	1.3385292448	1.1005644032
30	H	-4.9257800103	-1.0609400827	-1.0635474056
31	H	-3.4670582678	-2.9998598883	-0.7776883170
32	C	3.8231919759	0.8554074922	-0.8372889250
33	O	4.7124800592	1.0680751196	0.1316302516
34	C	5.7084875298	2.0669016922	-0.1294695807
35	H	6.3052090755	1.7883546531	-0.9991064279
36	H	6.3284215027	2.0981340015	0.7629535002
37	H	5.2368897866	3.0354418883	-0.3006865138
38	O	3.8311528521	1.4541620902	-1.8889957794
Absolute energy = 934.556531647269 Eh				

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