Supporting Information

**London Dispersion in Alkane Solvents**

*Marcel A. Strauss and Hermann A. Wegner*

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General Information

Chemicals:

All reagents and solvents were obtained from Sigma-Aldrich, Acros, TCI or Alfa Aesar and were used as received unless otherwise stated. Technical grade solvents for extraction, recrystallization and column chromatography were bulb-to-bulb distilled prior to usage. Anhydrous solvents were purchased from Acros Organics. Deuterated solvents were purchased from Euriso - Top GmbH. Azobenzene 12 purchased from TCI was recrystallized from n-hexane prior to usage.

NMR:
$^1$H-NMR experiments were performed at 25 °C on a Bruker Avance II 400 MHz or Avance III 400 MHz HD. Chemical shifts are reported in parts per million (ppm) related to the $^1$H (7.26 ppm) or $^{13}$C (77.16 ppm) chemical shift of internal residual CHCl$_3$ from CDCl$_3$. Coupling constants ($J$) are reported in Hertz (Hz). The multiplicities are written as: s=singlet, d=doublet, t=triplet.

For all azobenzenes the shifts of the thermodynamically more stable $E$-isomer are reported.

Column Chromatography:
Standard flash column chromatography was carried out with Silica 60 M (0.04 – 0.063 mm) from Macherey-Nagel GmbH & Co. KG. Thin layer Chromatography (TLC) was carried out on Polygram$^\text{®}$ Sil G/UV254 with a 0.2 mm-coating of silica 60 from Machery-Nagel GmbH & Co. KG and detected with a CAMAG UV Cabinet dual wavelength, 254/366 nm.

Melting Points:
Melting points were determined on a M5000 melting point meter from A.KRÜSS Optronic GmbH Germany. A heating rate of 1 °C min$^{-1}$, a resolution of 0.1 °C and a measurement accuracy of ± 0.3 °C (25–200 °C) or ± 0.5 °C (200–400 °C) apply for this device.

Elemental Analysis:
Elemental Analysis was performed on a FlashEA® 1112 by Thermo Fisher Scientific with 4-(dimethylamino)benzaldehyde as standard. The furnace temperature was set to 900 °C and the oven temperature to 75 °C. Helium carrier gas flow was 130 mL min$^{-1}$, oxygen flow 250 mL min$^{-1}$ and reference flow 100 mL min$^{-1}$. Total run time was 480 seconds. A voltage of 1 mV was applied to the thermal conductivity detector.
Synthesis Procedures

Synthesis of different meta n-alkyl azobenzenes

The alkylated azobenzenes 1-11 were synthesized according to a procedure previously published in Angew. Chem. Int. Ed. The synthesis of symmetrical azobenzenes was carried out according to a procedure published by Zhang and co-worker. Azobenzenes with substituents only on one phenyl ring were synthesized by a Bayer–Mills coupling of nitrosobenzene and the corresponding aniline.

Procedure for the preparation of 3,3',5,5'-tetra(tert-butyl) azobenzene (13)

The 3,5-di(tert-butyl)aniline (744 mg, 3.55 mmol, 1.00 equiv), Cu(I)Br (94.2 mg, 0.657 mmol, 18.5 mol%), and pyridine (110 μL, 1.36 mmol, 38.4 mol%), were mixed in toluene (35 mL) under air (1 atm). The reaction mixture was stirred vigorously at 60 °C for 24 h. After cooling to rt, the reaction mixture was filtered through a short silica plug followed by washing the plug several times with EtOAc, until the washing solution was colourless. The combined solution was concentrated under reduced pressure. The crude product was purified by flash column chromatography (cyclohexane, silica 40 g).

Yield
655 mg (1.77 mmol, 91%), orange solid.

TLC (cyclohexane:EtOAc, 2:1 v/v): Rf = 0.71

$^1$H NMR (400 MHz, CDCl$_3$) δ [ppm]: 7.77 (d, $J = 1.8$ Hz, 4H, H2, H6, H8, H12), 7.56 (t, $J = 1.8$ Hz, 2H, H4, H10), 1.41 (s, 36H, H17-28).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ [ppm]: 153.0 (C1, C7), 151.9 (C3, C5, C9, C11), 125.0 (C4, C10), 117.3 (C2, C6, C8, C12), 35.3 (C13 - C16), 31.6 (C17 – 28).

Melting point: 205.8 °C

Elemental Analysis:
calculated: %N 6.89; %C 82.70; %H 10.41
experimentally: %N 7.14; %C 82.75; %H 10.81

The analytical data corresponded to literature.
Kinetic Measurements

UV-Vis measurements in solution

Kinetic measurements were conducted with a SPECORD® 200 PLUS UV/Vis spectrophotometer equipped with two automatic eightfold cell changers and a Peltier thermostat system for temperature control manufactured by Analytik Jena. The spectrophotometer system was operated by the software ASpect UV from Analytik Jena. The samples were measured in QS High Precision Cells made of Quartz Suprasil® by Hellma Analytics with a light path of 10 mm. The sample volume was 3 mL and the sample concentration $6 \times 10^{-5}$ M. Irradiation at 302 nm was conducted with a 3UV-38 handheld lamp (8 W) by UVP.

For the kinetic measurements of the Z→E isomerization all samples were irradiated at a wavelength of 302 nm for 8 min for compound 1, 5 min for compounds 2-8, 9 min for compounds 9 and 10 and 3 min for compound 11, 30 min for compound 12 and 5 min for compound 13. For each sample one spectrum was recorded after a specific time elapsed, which was 1 h in the case of 1-12 and 6 h for 13. The scan ranged from 230 nm to 600 nm and was performed with a scan speed of 20 nm/s. A total of 48 spectra for samples of 1-12 and 24 for 13 were recorded in this way per experiment. The experiments were conducted at 40 °C internal temperature. Each experiment was conducted three-times. The isobestic point was used to reference the spectra in n-alkanes and 2,2,4-trimethylpentane (iso-octane).

As solvents, n-heptane for spectroscopy was obtained from Uvasol®, n-octane 99+%, extra pure, n-nonane ≥ 99%, anhydrous, n-decane ≥ 99%, anhydrous, n-undecane ≥ 99%, n-dodecane ≥ 99%, anhydrous and cyclooctane ≥ 99% were purchased from Sigma-Aldrich. The 2,2,4-trimethylpentane ≥ 99.0% was obtained from Honeywell.

Half-lives and rate constants calculations

All half-lives and rate constants were determined by a triple determination. Their calculation was conducted with OriginPro® 2017G (64-bit) by the OriginLab Corporation. For this procedure, the absorption at a certain wavelength of the II–II* band was plotted against the time elapsed after irradiation in seconds. The measuring points were fitted with the following ExpDec1 function of the software.

$$y = y_0 + A_1 e^{-x/t_1}$$

Equation S1. Exponential Decay 1 function of Origin.

The exponential time constant $t_1$ obtained by this fitting was further used to calculate the kinetic constant $k$ by Equation S2 and the half-life $t_{1/2}$ by Equation S3.

$$k = 1/t_1$$

Equation S2. Calculation of kinetic constant $k$.

$$t_{1/2} = t_1 \cdot \ln 2$$

Equation S3. Calculation of half-life $t_{1/2}$. 

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Figure S1. Exemplary spectra of compound 4 in n-octane at 40 °C every 4 h (44 h total).

Table S1. Kinetic constants of compounds 1-11, 13 in n-heptane at 40 °C; 6 x 10^{-5} M.

| Cpd | $k$ [s^{-1}] Exp. 1 | $k$ [s^{-1}] Exp. 2 | $k$ [s^{-1}] Exp. 3 | $\bar{k}$ [s^{-1}] | standard deviation [s^{-1}] |
|-----|---------------------|---------------------|---------------------|---------------------|-----------------------------|
| 1   | 2.714 x10^{-5}      | 2.656 x10^{-5}      | 2.702 x10^{-5}      | 2.69 x10^{-5}       | 2 x10^{-7}                 |
| 2   | 9.518 x10^{-6}      | 9.435 x10^{-6}      | 8.853 x10^{-6}      | 9.3 x10^{-6}        | 3 x10^{-7}                 |
| 3   | 6.878 x10^{-6}      | 6.844 x10^{-6}      | 6.951 x10^{-6}      | 6.89 x10^{-6}       | 4 x10^{-8}                 |
| 4   | 5.988 x10^{-6}      | 6.033 x10^{-6}      | 5.998 x10^{-6}      | 6.01 x10^{-6}       | 2 x10^{-8}                 |
| 5   | 6.803 x10^{-6}      | 6.723 x10^{-6}      | 6.967 x10^{-6}      | 6.8 x10^{-6}        | 1 x10^{-7}                 |
| 6   | 7.151 x10^{-6}      | 7.407 x10^{-6}      | 7.279 x10^{-6}      | 7.3 x10^{-6}        | 1 x10^{-7}                 |
| 7   | 7.700 x10^{-6}      | 7.729 x10^{-6}      | 7.686 x10^{-6}      | 7.70 x10^{-6}       | 2 x10^{-8}                 |
| 8   | 6.922 x10^{-6}      | 6.953 x10^{-6}      | 7.002 x10^{-6}      | 6.96 x10^{-6}       | 3 x10^{-8}                 |
| 9   | 1.738 x10^{-6}      | 1.736 x10^{-6}      | 1.757 x10^{-6}      | 1.743 x10^{-6}      | 9 x10^{-8}                 |
| 10  | 1.096 x10^{-5}      | 1.095 x10^{-5}      | 1.118 x10^{-5}      | 1.10 x10^{-5}       | 1 x10^{-7}                 |
| 11  | 1.009 x10^{-5}      | 1.015 x10^{-5}      | 1.029 x10^{-5}      | 1.018 x10^{-5}      | 9 x10^{-8}                 |
| 13  | 1.233 x10^{-6}      | 1.166 x10^{-6}      | 1.154 x10^{-6}      | 1.18 x10^{-6}       | 3 x10^{-8}                 |
Table S2. Kinetic constants of compounds 1-13 in n-octane at 40 °C; 6 x 10⁻⁵ M.

| Cpd | \( k \text{ [s}^{-1}] \) Exp. 1 | \( k \text{ [s}^{-1}] \) Exp. 2 | \( k \text{ [s}^{-1}] \) Exp. 3 | \( \bar{k} \text{ [s}^{-1}] \) | Standard deviation [s⁻¹] |
|-----|---------------------------------|---------------------------------|---------------------------------|----------------|------------------------|
| 1   | 2.855 x 10⁻⁵                    | 2.859 x 10⁻⁵                    | 2.856 x 10⁻⁵                    | 2.857 x 10⁻⁵   | 2 x 10⁻⁸               |
| 2   | 9.969 x 10⁻⁶                    | 1.003 x 10⁻⁵                    | 9.930 x 10⁻⁶                    | 9.98 x 10⁻⁶    | 4 x 10⁻⁸               |
| 3   | 7.191 x 10⁻⁶                    | 7.284 x 10⁻⁶                    | 7.238 x 10⁻⁶                    | 7.24 x 10⁻⁶    | 4 x 10⁻⁸               |
| 4   | 6.323 x 10⁻⁶                    | 6.327 x 10⁻⁶                    | 6.305 x 10⁻⁶                    | 6.32 x 10⁻⁶    | 1 x 10⁻⁸               |
| 5   | 7.269 x 10⁻⁶                    | 7.235 x 10⁻⁶                    | 7.320 x 10⁻⁶                    | 7.27 x 10⁻⁶    | 4 x 10⁻⁸               |
| 6   | 7.571 x 10⁻⁶                    | 7.641 x 10⁻⁶                    | 7.659 x 10⁻⁶                    | 7.62 x 10⁻⁶    | 4 x 10⁻⁸               |
| 7   | 7.527 x 10⁻⁶                    | 7.631 x 10⁻⁶                    | 7.608 x 10⁻⁶                    | 7.59 x 10⁻⁶    | 5 x 10⁻⁸               |
| 8   | 7.303 x 10⁻⁶                    | 7.311 x 10⁻⁶                    | 7.416 x 10⁻⁶                    | 7.34 x 10⁻⁶    | 5 x 10⁻⁸               |
| 9   | 1.820 x 10⁻⁵                    | 1.800 x 10⁻⁵                    | 1.809 x 10⁻⁵                    | 1.810 x 10⁻⁵   | 8 x 10⁻⁸               |
| 10  | 1.150 x 10⁻⁵                    | 1.143 x 10⁻⁵                    | 1.161 x 10⁻⁵                    | 1.152 x 10⁻⁵   | 8 x 10⁻⁸               |
| 11  | 1.048 x 10⁻⁵                    | 1.075 x 10⁻⁵                    | 1.088 x 10⁻⁵                    | 1.07 x 10⁻⁵    | 2 x 10⁻⁷               |
| 12  | 1.395 x 10⁻⁵                    | 1.374 x 10⁻⁵                    | 1.376 x 10⁻⁵                    | 1.382 x 10⁻⁵   | 9 x 10⁻⁸               |
| 13  | 1.216 x 10⁻⁶                    | 1.221 x 10⁻⁶                    | 1.254 x 10⁻⁶                    | 1.23 x 10⁻⁶    | 2 x 10⁻⁸               |

Table S3. Kinetic constants of compounds 1-11, 13 in n-nonane at 40 °C; 6 x 10⁻⁵ M.

| Cpd | \( k \text{ [s}^{-1}] \) Exp. 1 | \( k \text{ [s}^{-1}] \) Exp. 2 | \( k \text{ [s}^{-1}] \) Exp. 3 | \( \bar{k} \text{ [s}^{-1}] \) | Standard deviation [s⁻¹] |
|-----|---------------------------------|---------------------------------|---------------------------------|----------------|------------------------|
| 1   | 2.940 x 10⁻⁵                    | 2.969 x 10⁻⁵                    | 2.976 x 10⁻⁵                    | 2.96 x 10⁻⁵   | 2 x 10⁻⁷               |
| 2   | 9.938 x 10⁻⁶                    | 9.851 x 10⁻⁶                    | 9.961 x 10⁻⁶                    | 9.92 x 10⁻⁶   | 5 x 10⁻⁸               |
| 3   | 7.568 x 10⁻⁶                    | 7.559 x 10⁻⁶                    | 7.560 x 10⁻⁶                    | 7.562 x 10⁻⁶   | 4 x 10⁻⁸               |
| 4   | 6.195 x 10⁻⁶                    | 6.287 x 10⁻⁶                    | 6.136 x 10⁻⁶                    | 6.21 x 10⁻⁶    | 6 x 10⁻⁸               |
| 5   | 7.570 x 10⁻⁶                    | 7.522 x 10⁻⁶                    | 7.591 x 10⁻⁶                    | 7.56 x 10⁻⁶    | 3 x 10⁻⁸               |
| 6   | 8.168 x 10⁻⁶                    | 8.042 x 10⁻⁶                    | 8.089 x 10⁻⁶                    | 8.10 x 10⁻⁶    | 5 x 10⁻⁸               |
| 7   | 8.046 x 10⁻⁶                    | 7.830 x 10⁻⁶                    | 7.921 x 10⁻⁶                    | 7.93 x 10⁻⁶    | 9 x 10⁻⁸               |
| 8   | 7.836 x 10⁻⁶                    | 7.788 x 10⁻⁶                    | 7.776 x 10⁻⁶                    | 7.80 x 10⁻⁶    | 3 x 10⁻⁸               |
| 9   | 1.882 x 10⁻⁵                    | 1.888 x 10⁻⁵                    | 1.879 x 10⁻⁵                    | 1.883 x 10⁻⁵   | 4 x 10⁻⁸               |
| 10  | 1.210 x 10⁻⁵                    | 1.208 x 10⁻⁵                    | 1.200 x 10⁻⁵                    | 1.206 x 10⁻⁵   | 4 x 10⁻⁸               |
| 11  | 1.095 x 10⁻⁵                    | 1.100 x 10⁻⁵                    | 1.112 x 10⁻⁵                    | 1.102 x 10⁻⁵   | 7 x 10⁻⁸               |
| 13  | 1.242 x 10⁻⁶                    | 1.261 x 10⁻⁶                    | 1.297 x 10⁻⁶                    | 1.27 x 10⁻⁶    | 2 x 10⁻⁸               |
Table S4. Kinetic constants of compounds 1-13 in n-decane at 40 °C; 6 x 10⁻⁸ M. Values for compounds 1-12 were previously published and are listed because of completeness.

| Cpd | $k$ [s⁻¹] Exp. 1 | $k$ [s⁻¹] Exp. 2 | $k$ [s⁻¹] Exp. 3 | $\varnothing k$ [s⁻¹] | standard deviation [s⁻¹] |
|-----|-----------------|-----------------|-----------------|-------------------|------------------------|
| 1   | 3.017 x10⁻⁵     | 3.037 x10⁻⁵     | 3.029 x10⁻⁵     | 3.028 x10⁻⁵       | 8 x10⁻⁸               |
| 2   | 1.049 x10⁻⁵     | 1.046 x10⁻⁵     | 1.044 x10⁻⁵     | 1.046 x10⁻⁵       | 2 x10⁻⁸               |
| 3   | 7.405 x10⁻⁶     | 7.442 x10⁻⁶     | 7.480 x10⁻⁶     | 7.44 x10⁻⁶        | 3 x10⁻⁸              |
| 4   | 6.570 x10⁻⁶     | 6.457 x10⁻⁶     | 6.493 x10⁻⁶     | 6.51 x10⁻⁶        | 5 x10⁻⁸              |
| 5   | 7.497 x10⁻⁶     | 7.463 x10⁻⁶     | 7.441 x10⁻⁶     | 7.47 x10⁻⁶        | 2 x10⁻⁸              |
| 6   | 7.962 x10⁻⁶     | 8.101 x10⁻⁶     | 8.010 x10⁻⁶     | 8.02 x10⁻⁶        | 6 x10⁻⁸              |
| 7   | 8.191 x10⁻⁶     | 8.256 x10⁻⁶     | 8.241 x10⁻⁶     | 8.23 x10⁻⁶        | 3 x10⁻⁸              |
| 8   | 7.719 x10⁻⁶     | 7.739 x10⁻⁶     | 7.680 x10⁻⁶     | 7.71 x10⁻⁶        | 2 x10⁻⁸              |
| 9   | 1.958 x10⁻⁵     | 1.949 x10⁻⁵     | 1.955 x10⁻⁵     | 1.954 x10⁻⁵       | 4 x10⁻⁸              |
| 10  | 1.204 x10⁻⁵     | 1.193 x10⁻⁵     | 1.214 x10⁻⁵     | 1.204 x10⁻⁵       | 9 x10⁻⁸              |
| 11  | 1.151 x10⁻⁵     | 1.161 x10⁻⁵     | 1.160 x10⁻⁵     | 1.157 x10⁻⁵       | 5 x10⁻⁸              |
| 12  | 1.418 x10⁻⁵     | 1.449 x10⁻⁵     | 1.428 x10⁻⁵     | 1.43 x10⁻⁵        | 1 x10⁻⁷              |
| 13  | 1.277 x10⁻⁶     | 1.219 x10⁻⁶     | 1.231 x10⁻⁶     | 1.24 x10⁻⁶        | 2 x10⁻⁸              |

Table S5. Kinetic constants of compounds 1-11, 13 in n-undecane at 40 °C; 6 x 10⁻⁸ M.

| Cpd | $k$ [s⁻¹] Exp. 1 | $k$ [s⁻¹] Exp. 2 | $k$ [s⁻¹] Exp. 3 | $\varnothing k$ [s⁻¹] | standard deviation [s⁻¹] |
|-----|-----------------|-----------------|-----------------|-------------------|------------------------|
| 1   | 3.062 x10⁻⁵     | 3.084 x10⁻⁵     | 3.070 x10⁻⁵     | 3.072 x10⁻⁵       | 9 x10⁻⁸               |
| 2   | 1.027 x10⁻⁵     | 1.023 x10⁻⁵     | 1.036 x10⁻⁵     | 1.029 x10⁻⁵       | 5 x10⁻⁸               |
| 3   | 7.320 x10⁻⁶     | 7.351 x10⁻⁶     | 7.408 x10⁻⁶     | 7.36 x10⁻⁶        | 4 x10⁻⁸              |
| 4   | 6.387 x10⁻⁶     | 6.333 x10⁻⁶     | 6.311 x10⁻⁶     | 6.34 x10⁻⁶        | 3 x10⁻⁸              |
| 5   | 7.490 x10⁻⁶     | 7.921 x10⁻⁶     | 7.422 x10⁻⁶     | 7.6 x10⁻⁶         | 2 x10⁻⁷              |
| 6   | 7.889 x10⁻⁶     | 7.938 x10⁻⁶     | 7.992 x10⁻⁶     | 7.94 x10⁻⁶        | 4 x10⁻⁸              |
| 7   | 8.381 x10⁻⁶     | 8.222 x10⁻⁶     | 8.209 x10⁻⁶     | 8.27 x10⁻⁶        | 8 x10⁻⁸              |
| 8   | 8.028 x10⁻⁶     | 8.174 x10⁻⁶     | 8.276 x10⁻⁶     | 8.2 x10⁻⁶         | 1 x10⁻⁷              |
| 9   | 1.986 x10⁻⁵     | 1.952 x10⁻⁵     | 1.953 x10⁻⁵     | 1.96 x10⁻⁵        | 2 x10⁻⁷              |
| 10  | 1.209 x10⁻⁵     | 1.190 x10⁻⁵     | 1.210 x10⁻⁵     | 1.203 x10⁻⁵       | 9 x10⁻⁸              |
| 11  | 1.141 x10⁻⁵     | 1.161 x10⁻⁵     | 1.168 x10⁻⁵     | 1.16 x10⁻⁵        | 1 x10⁻⁷              |
| 13  | 1.303 x10⁻⁶     | 1.397 x10⁻⁶     | 1.232 x10⁻⁶     | 1.31 x10⁻⁶        | 7 x10⁻⁸              |
### Table S6. Kinetic constants of compounds 1-11, 13 in n-dodecane at 40 °C; 6 x 10^{-6} M.

| Cpd | $k$ [s^{-1}] Exp. 1 | $k$ [s^{-1}] Exp. 2 | $k$ [s^{-1}] Exp. 3 | $\Theta k$ [s^{-1}] | standard deviation [s^{-1}] |
|-----|---------------------|---------------------|---------------------|---------------------|-----------------------------|
| 1   | 3.170 x 10^{-5}     | 3.172 x 10^{-5}     | 3.136 x 10^{-5}     | 3.16 x 10^{-5}      | 2 x 10^{-7}                |
| 2   | 1.030 x 10^{-5}     | 1.015 x 10^{-5}     | 1.014 x 10^{-5}     | 1.020 x 10^{-5}     | 7 x 10^{-8}                |
| 3   | 7.128 x 10^{-6}     | 7.091 x 10^{-6}     | 6.998 x 10^{-6}     | 7.07 x 10^{-6}      | 5 x 10^{-8}                |
| 4   | 6.238 x 10^{-6}     | 6.183 x 10^{-6}     | 6.176 x 10^{-6}     | 6.20 x 10^{-6}      | 3 x 10^{-8}                |
| 5   | 7.654 x 10^{-6}     | 7.884 x 10^{-6}     | 7.824 x 10^{-6}     | 7.8 x 10^{-6}       | 1 x 10^{-7}                |
| 6   | 8.201 x 10^{-6}     | 8.069 x 10^{-6}     | 8.130 x 10^{-6}     | 8.13 x 10^{-6}      | 5 x 10^{-8}                |
| 7   | 8.035 x 10^{-6}     | 7.953 x 10^{-6}     | 8.071 x 10^{-6}     | 8.02 x 10^{-6}      | 5 x 10^{-8}                |
| 8   | 7.993 x 10^{-6}     | 7.882 x 10^{-6}     | 7.909 x 10^{-6}     | 7.93 x 10^{-6}      | 5 x 10^{-8}                |
| 9   | 2.013 x 10^{-5}     | 1.994 x 10^{-5}     | 1.983 x 10^{-5}     | 2.00 x 10^{-5}      | 1 x 10^{-7}                |
| 10  | 1.226 x 10^{-5}     | 1.221 x 10^{-5}     | 1.218 x 10^{-5}     | 1.221 x 10^{-5}     | 3 x 10^{-8}                |
| 11  | 1.137 x 10^{-5}     | 1.155 x 10^{-5}     | 1.152 x 10^{-5}     | 1.148 x 10^{-5}     | 8 x 10^{-8}                |
| 13  | 1.159 x 10^{-6}     | 1.229 x 10^{-6}     | 1.149 x 10^{-5}     | 1.18 x 10^{-5}      | 4 x 10^{-8}                |

### Table S7. Kinetic constants of compounds 1-13 in iso-octane at 40 °C; 6 x 10^{-6} M.

| Cpd | $k$ [s^{-1}] Exp. 1 | $k$ [s^{-1}] Exp. 2 | $k$ [s^{-1}] Exp. 3 | $\Theta k$ [s^{-1}] | standard deviation [s^{-1}] |
|-----|---------------------|---------------------|---------------------|---------------------|-----------------------------|
| 1   | 2.786 x 10^{-5}     | 2.779 x 10^{-5}     | 2.747 x 10^{-5}     | 2.77 x 10^{-5}      | 2 x 10^{-7}                |
| 2   | 8.265 x 10^{-6}     | 8.220 x 10^{-6}     | 8.445 x 10^{-6}     | 8.3 x 10^{-6}       | 1 x 10^{-7}                |
| 3   | 6.098 x 10^{-6}     | 6.106 x 10^{-6}     | 6.196 x 10^{-6}     | 6.13 x 10^{-6}      | 5 x 10^{-8}                |
| 4   | 5.451 x 10^{-6}     | 5.311 x 10^{-6}     | 5.280 x 10^{-6}     | 5.35 x 10^{-6}      | 7 x 10^{-8}                |
| 5   | 6.007 x 10^{-6}     | 5.970 x 10^{-6}     | 5.962 x 10^{-6}     | 5.98 x 10^{-6}      | 2 x 10^{-8}                |
| 6   | 6.329 x 10^{-6}     | 6.439 x 10^{-6}     | 6.332 x 10^{-6}     | 6.37 x 10^{-6}      | 5 x 10^{-8}                |
| 7   | 6.208 x 10^{-6}     | 6.310 x 10^{-6}     | 6.337 x 10^{-6}     | 6.28 x 10^{-6}      | 6 x 10^{-8}                |
| 8   | 6.118 x 10^{-6}     | 6.036 x 10^{-6}     | 6.054 x 10^{-6}     | 6.07 x 10^{-6}      | 4 x 10^{-8}                |
| 9   | 1.722 x 10^{-5}     | 1.726 x 10^{-5}     | 1.712 x 10^{-5}     | 1.720 x 10^{-5}     | 6 x 10^{-8}                |
| 10  | 1.073 x 10^{-5}     | 1.074 x 10^{-5}     | 1.066 x 10^{-5}     | 1.070 x 10^{-5}     | 3 x 10^{-8}                |
| 11  | 9.837 x 10^{-6}     | 9.796 x 10^{-6}     | 9.869 x 10^{-6}     | 9.83 x 10^{-6}      | 3 x 10^{-8}                |
| 12  | 1.323 x 10^{-5}     | 1.328 x 10^{-5}     | 1.326 x 10^{-5}     | 1.326 x 10^{-5}     | 2 x 10^{-8}                |
| 13  | 1.043 x 10^{-6}     | 1.031 x 10^{-6}     | 1.022 x 10^{-6}     | 1.032 x 10^{-6}     | 9 x 10^{-9}                |
Table S8. Kinetic constants of compounds 1-13 in cyclooctane at 40 °C; 6 x 10⁻⁴ M.

| Cpd | $k$ [s⁻¹] Exp. 1 | $k$ [s⁻¹] Exp. 2 | $k$ [s⁻¹] Exp. 3 | $\phi k$ [s⁻¹] | standard deviation [s⁻¹] |
|-----|------------------|------------------|------------------|----------------|--------------------------|
| 1   | 3.574 x 10⁻⁵     | 3.667 x 10⁻⁵     | 3.554 x 10⁻⁵     | 3.60 x 10⁻⁵    | 5 x 10⁻⁷                 |
| 2   | 1.197 x 10⁻⁵     | 1.234 x 10⁻⁵     | 1.216 x 10⁻⁵     | 1.22 x 10⁻⁵    | 2 x 10⁻⁷                 |
| 3   | 8.344 x 10⁻⁶     | 8.391 x 10⁻⁶     | 8.264 x 10⁻⁶     | 8.33 x 10⁻⁶    | 5 x 10⁻⁸                 |
| 4   | 7.027 x 10⁻⁶     | 7.310 x 10⁻⁶     | 7.311 x 10⁻⁶     | 7.2 x 10⁻⁶     | 1 x 10⁻⁷                 |
| 5   | 8.814 x 10⁻⁶     | 9.282 x 10⁻⁶     | 8.544 x 10⁻⁶     | 8.9 x 10⁻⁶     | 3 x 10⁻⁷                 |
| 6   | 8.831 x 10⁻⁶     | 9.268 x 10⁻⁶     | 9.302 x 10⁻⁶     | 9.1 x 10⁻⁶     | 2 x 10⁻⁷                 |
| 7   | 8.827 x 10⁻⁶     | 8.825 x 10⁻⁶     | 9.193 x 10⁻⁶     | 8.9 x 10⁻⁶     | 2 x 10⁻⁷                 |
| 8   | 8.866 x 10⁻⁶     | 9.242 x 10⁻⁶     | 9.053 x 10⁻⁶     | 9.1 x 10⁻⁶     | 2 x 10⁻⁷                 |
| 9   | 2.261 x 10⁻⁵     | 2.270 x 10⁻⁵     | 2.282 x 10⁻⁵     | 2.271 x 10⁻⁵   | 9 x 10⁻⁸                 |
| 10  | 1.345 x 10⁻⁵     | 1.406 x 10⁻⁵     | 1.442 x 10⁻⁵     | 1.40 x 10⁻⁵    | 4 x 10⁻⁷                 |
| 11  | 1.305 x 10⁻⁵     | 1.277 x 10⁻⁵     | 1.231 x 10⁻⁵     | 1.27 x 10⁻⁵    | 3 x 10⁻⁷                 |
| 12  | 1.657 x 10⁻⁶     | 1.678 x 10⁻⁶     | 1.673 x 10⁻⁶     | 1.669 x 10⁻⁶   | 9 x 10⁻⁸                 |
| 13  | 9.888 x 10⁻⁷     | 9.830 x 10⁻⁷     | 9.667 x 10⁻⁷     | 9.795 x 10⁻⁷   | 9 x 10⁻⁸                 |

Table S9. Half-lives of compounds 1-11, 13 in n-heptane at 40 °C; 6 x 10⁻⁴ M.

| Cpd | $t_{1/2}$ [s] Exp. 1 | $t_{1/2}$ [s] Exp. 2 | $t_{1/2}$ [s] Exp. 3 | $t_{1/2}$ [h] Exp. 1 | $t_{1/2}$ [h] Exp. 2 | $t_{1/2}$ [h] Exp. 3 | $\phi t_{1/2}$ [h] | standard deviation [h⁻¹] |
|-----|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|----------------------|--------------------------|
| 1   | 25,537              | 26,095              | 25,651              | 7.09                | 7.25                | 7.13                | 7.16                 | 0.07                     |
| 2   | 72,824              | 73,468              | 78,298              | 20.23               | 20.41               | 21.75               | 20.8                 | 0.7                      |
| 3   | 100,771             | 101,274             | 99,715              | 27.99               | 28.13               | 27.70               | 27.9                 | 0.2                      |
| 4   | 115,764             | 114,896             | 115,568             | 32.16               | 31.92               | 32.10               | 32.1                 | 0.1                      |
| 5   | 101,889             | 103,108             | 99,491              | 28.30               | 28.64               | 27.64               | 28.2                 | 0.4                      |
| 6   | 96,932              | 93,580              | 95,220              | 26.93               | 25.99               | 26.45               | 26.5                 | 0.4                      |
| 7   | 90,017              | 89,683              | 90,186              | 25.00               | 24.91               | 25.05               | 24.99                | 0.06                     |
| 8   | 100,132             | 99,687              | 98,988              | 27.81               | 27.69               | 27.50               | 27.7                 | 0.1                      |
| 9   | 39,890              | 39,922              | 39,461              | 11.08               | 11.09               | 10.96               | 11.04                | 0.06                     |
| 10  | 63,221              | 63,300              | 62,024              | 17.56               | 17.58               | 17.23               | 17.5                 | 0.2                      |
| 11  | 68,716              | 68,323              | 67,332              | 19.09               | 18.98               | 18.70               | 18.9                 | 0.2                      |
| 13  | 562,247             | 594,662             | 600,495             | 156.18              | 165.18              | 166.80              | 162                  | 5                        |
Table S10. Half-lives of compounds 1-13 in n-octane at 40 °C; 6 x 10^{-5} M.

| Cpd | \( t_{1/2} \) [s] Exp. 1 | \( t_{1/2} \) [s] Exp. 2 | \( t_{1/2} \) [s] Exp. 3 | \( t_{1/2} \) [h] Exp. 1 | \( t_{1/2} \) [h] Exp. 2 | \( t_{1/2} \) [h] Exp. 3 | \( \phi t_{1/2} \) [h] | standard deviation [h⁻¹] |
|-----|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|
| 1   | 24,282         | 24,242         | 24,269         | 6.74           | 6.73           | 6.74           | 6.74           | 0.005          |
| 2   | 69,534         | 69,130         | 69,802         | 19.31          | 19.20          | 19.39          | 19.30          | 0.08           |
| 3   | 96,387         | 95,157         | 95,763         | 26.77          | 26.43          | 26.60          | 26.6           | 0.1            |
| 4   | 109,615        | 109,553        | 109,943        | 30.45          | 30.43          | 30.54          | 30.47          | 0.05           |
| 5   | 95,357         | 95,811         | 94,694         | 26.49          | 26.61          | 26.30          | 26.5           | 0.1            |
| 6   | 91,552         | 90,711         | 90,504         | 25.43          | 25.20          | 25.14          | 25.3           | 0.1            |
| 7   | 92,093         | 90,828         | 91,105         | 25.58          | 25.23          | 25.31          | 25.4           | 0.2            |
| 8   | 94,908         | 94,815         | 93,463         | 26.36          | 26.34          | 25.96          | 26.2           | 0.2            |
| 9   | 38,079         | 38,512         | 38,318         | 10.58          | 10.70          | 10.64          | 10.6           | 0.05           |
| 10  | 60,264         | 60,637         | 59,685         | 16.74          | 16.84          | 16.58          | 16.7           | 0.1            |
| 11  | 66,168         | 64,502         | 63,695         | 18.38          | 17.92          | 17.69          | 18.0           | 0.3            |
| 12  | 49,699         | 50,432         | 50,367         | 13.81          | 14.01          | 13.99          | 13.93          | 0.09           |
| 13  | 570,181        | 567,739        | 552,935        | 158.38         | 157.71         | 153.59         | 156            | 2              |

Table S11. Half-lives of compounds 1-11, 13 in n-nonane at 40 °C; 6 x 10^{-5} M.

| Cpd | \( t_{1/2} \) [s] Exp. 1 | \( t_{1/2} \) [s] Exp. 2 | \( t_{1/2} \) [s] Exp. 3 | \( t_{1/2} \) [h] Exp. 1 | \( t_{1/2} \) [h] Exp. 2 | \( t_{1/2} \) [h] Exp. 3 | \( \phi t_{1/2} \) [h] | standard deviation [h⁻¹] |
|-----|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|
| 1   | 23,575         | 23,344         | 23,290         | 6.55           | 6.48           | 6.47           | 6.50           | 0.03           |
| 2   | 69,747         | 70,365         | 69,584         | 19.37          | 19.55          | 19.33          | 19.42          | 0.09           |
| 3   | 91,588         | 91,696         | 91,684         | 25.44          | 25.47          | 25.47          | 25.46          | 0.01           |
| 4   | 111,891        | 110,252        | 112,963        | 31.08          | 30.63          | 31.38          | 31.0           | 0.3            |
| 5   | 91,563         | 92,148         | 91,315         | 25.43          | 25.60          | 25.37          | 25.5           | 0.1            |
| 6   | 84,858         | 86,196         | 85,685         | 23.57          | 23.94          | 23.80          | 23.8           | 0.2            |
| 7   | 86,147         | 88,522         | 87,505         | 23.93          | 24.59          | 24.31          | 24.3           | 0.3            |
| 8   | 88,456         | 89,007         | 89,141         | 24.57          | 24.72          | 24.76          | 24.69          | 0.08           |
| 9   | 36,821         | 36,707         | 36,891         | 10.23          | 10.20          | 10.25          | 10.22          | 0.02           |
| 10  | 57,292         | 57,360         | 57,740         | 15.91          | 15.93          | 16.04          | 15.96          | 0.05           |
| 11  | 63,275         | 63,024         | 62,361         | 17.58          | 17.51          | 17.32          | 17.5           | 0.1            |
| 13  | 557,893        | 549,742        | 534,327        | 154.97         | 152.71         | 148.42         | 152            | 3              |
Table S12. Half-lives of compounds 1-13 in n-decane at 40 °C; 6 x 10⁻⁶ M. Values for compounds 1-12 were previously published and are listed because of completeness.

| Cpd | $t_{1/2}$ [s] Exp. 1 | $t_{1/2}$ [s] Exp. 2 | $t_{1/2}$ [s] Exp. 3 | $t_{1/2}$ [h] Exp. 1 | $t_{1/2}$ [h] Exp. 2 | $t_{1/2}$ [h] Exp. 3 | $\overline{\theta t_{1/2}}$ [h] | standard deviation [h⁻¹] |
|-----|----------------------|----------------------|----------------------|----------------------|----------------------|----------------------|----------------------|----------------------|
| 1   | 22,974               | 22,825               | 22,885               | 6.38                 | 6.34                 | 6.36                 | 6.36                 | 0.02                 |
| 2   | 66,081               | 66,259               | 66,392               | 18.36                | 18.41                | 18.44                | 18.40                | 0.04                 |
| 3   | 93,600               | 93,134               | 92,665               | 26.00                | 25.87                | 25.74                | 25.9                 | 0.1                  |
| 4   | 105,510              | 107,346              | 106,761              | 29.31                | 29.82                | 29.66                | 29.6                 | 0.2                  |
| 5   | 92,458               | 92,874               | 93,150               | 25.68                | 25.80                | 25.88                | 25.79                | 0.08                 |
| 6   | 87,054               | 85,558               | 86,540               | 24.18                | 23.77                | 24.04                | 24.0                 | 0.2                  |
| 7   | 84,618               | 83,959               | 84,114               | 23.51                | 23.32                | 23.36                | 23.40                | 0.08                 |
| 8   | 89,797               | 89,562               | 90,257               | 24.94                | 24.88                | 25.07                | 24.96                | 0.08                 |
| 9   | 35,395               | 35,563               | 35,448               | 9.83                 | 9.88                 | 9.85                 | 9.85                 | 0.02                 |
| 10  | 57,568               | 58,094               | 57,091               | 15.99                | 16.14                | 15.86                | 16.0                 | 0.1                  |
| 11  | 60,216               | 59,693               | 59,745               | 16.73                | 16.58                | 16.60                | 16.63                | 0.07                 |
| 12  | 48,898               | 47,825               | 48,550               | 13.58                | 13.28                | 13.49                | 13.5                 | 0.1                  |
| 13  | 542,813              | 568,625              | 562,932              | 150.78               | 157.95               | 156.37               | 155                  | 3                    |

Table S13. Half-lives of compounds 1-11, 13 in n-undecane at 40 °C; 6 x 10⁻⁶ M.

| Cpd | $t_{1/2}$ [s] Exp. 1 | $t_{1/2}$ [s] Exp. 2 | $t_{1/2}$ [s] Exp. 3 | $t_{1/2}$ [h] Exp. 1 | $t_{1/2}$ [h] Exp. 2 | $t_{1/2}$ [h] Exp. 3 | $\overline{\theta t_{1/2}}$ [h] | standard deviation [h⁻¹] |
|-----|----------------------|----------------------|----------------------|----------------------|----------------------|----------------------|----------------------|----------------------|
| 1   | 22,634               | 22,477               | 22,578               | 6.29                 | 6.24                 | 6.27                 | 6.27                 | 0.02                 |
| 2   | 67,508               | 67,751               | 66,921               | 18.75                | 18.82                | 18.59                | 18.7                 | 0.1                  |
| 3   | 94,694               | 94,298               | 93,569               | 26.30                | 26.19                | 25.99                | 26.2                 | 0.1                  |
| 4   | 108,525              | 109,450              | 109,828              | 30.15                | 30.40                | 30.51                | 30.4                 | 0.2                  |
| 5   | 92,540               | 87,506               | 93,393               | 25.71                | 24.31                | 25.94                | 25.3                 | 0.7                  |
| 6   | 87,868               | 87,321               | 86,728               | 24.41                | 24.26                | 24.09                | 24.3                 | 0.1                  |
| 7   | 82,709               | 84,305               | 84,442               | 22.97                | 23.42                | 23.46                | 23.3                 | 0.2                  |
| 8   | 86,343               | 84,796               | 83,752               | 23.98                | 23.55                | 23.26                | 23.6                 | 0.3                  |
| 9   | 34,902               | 35,515               | 35,482               | 9.69                 | 9.87                 | 9.86                 | 9.81                 | 0.08                 |
| 10  | 57,334               | 58,232               | 57,298               | 15.93                | 16.18                | 15.92                | 16.0                 | 0.1                  |
| 11  | 60,746               | 59,725               | 59,325               | 16.87                | 16.59                | 16.48                | 16.7                 | 0.2                  |
| 13  | 532,081              | 495,997              | 562,510              | 147.80               | 137.78               | 156.25               | 147                  | 8                    |
Table S14. Half-lives of compounds 1-11, 13 in n-dodecane at 40 °C; 6 x 10^{-5} M.

| Cpd | $t_{1/2}$ [s] Exp. 1 | $t_{1/2}$ [s] Exp. 2 | $t_{1/2}$ [s] Exp. 3 | $t_{1/2}$ [h] Exp. 1 | $t_{1/2}$ [h] Exp. 2 | $t_{1/2}$ [h] Exp. 3 | $ar{t}_{1/2}$ [h] | standard deviation [h^{-1}] |
|-----|----------------------|----------------------|----------------------|----------------------|----------------------|----------------------|----------------|-----------------------------|
| 1   | 21,869               | 21,851               | 22,103               | 6.07                 | 6.07                 | 6.14                 | 6.09           | 0.03                        |
| 2   | 67,278               | 68,306               | 68,328               | 18.69                | 18.97                | 18.98                | 18.9           | 0.1                         |
| 3   | 97,238               | 97,756               | 99,045               | 27.01                | 27.15                | 27.51                | 27.2           | 0.2                         |
| 4   | 111,125              | 112,099              | 112,240              | 30.87                | 31.14                | 31.18                | 31.1           | 0.1                         |
| 5   | 90,563               | 87,917               | 88,588               | 25.16                | 24.42                | 24.61                | 24.7           | 0.3                         |
| 6   | 84,520               | 85,906               | 85,257               | 23.48                | 23.86                | 23.68                | 23.7           | 0.2                         |
| 7   | 86,267               | 87,157               | 85,879               | 24.09                | 24.43                | 24.34                | 24.3           | 0.1                         |
| 8   | 86,721               | 87,936               | 87,640               | 23.96                | 24.24                | 24.36                | 24.0           | 0.2                         |
| 9   | 34,432               | 34,767               | 34,958               | 9.56                 | 9.66                 | 9.71                 | 9.64           | 0.06                        |
| 10  | 56,559               | 56,756               | 56,927               | 15.71                | 15.77                | 15.81                | 15.76          | 0.04                        |
| 11  | 60,980               | 60,035               | 60,159               | 16.94                | 16.68                | 16.71                | 16.8           | 0.1                         |
| 13  | 598,303              | 563,828              | 603,359              | 166.20               | 156.62               | 167.60               | 163            | 5                           |

Table S15. Half-lives of compounds 1-13 in iso-octane at 40 °C; 6 x 10^{-5} M.

| Cpd | $t_{1/2}$ [s] Exp. 1 | $t_{1/2}$ [s] Exp. 2 | $t_{1/2}$ [s] Exp. 3 | $t_{1/2}$ [h] Exp. 1 | $t_{1/2}$ [h] Exp. 2 | $t_{1/2}$ [h] Exp. 3 | $ar{t}_{1/2}$ [h] | standard deviation [h^{-1}] |
|-----|----------------------|----------------------|----------------------|----------------------|----------------------|----------------------|----------------|-----------------------------|
| 1   | 24,877               | 24,940               | 25,229               | 6.91                 | 6.93                 | 7.01                 | 6.95           | 0.04                        |
| 2   | 83,863               | 84,322               | 82,075               | 23.30                | 23.42                | 22.80                | 23.2           | 0.3                         |
| 3   | 113,670              | 113,517              | 111,864              | 31.58                | 31.53                | 31.07                | 31.4           | 0.2                         |
| 4   | 127,150              | 130,515              | 131,282              | 35.32                | 36.25                | 36.47                | 36.0           | 0.5                         |
| 5   | 115,385              | 116,108              | 116,252              | 32.05                | 32.25                | 32.29                | 32.2           | 0.1                         |
| 6   | 109,534              | 107,649              | 109,475              | 30.43                | 29.90                | 30.41                | 30.3           | 0.2                         |
| 7   | 111,655              | 109,852              | 109,379              | 31.02                | 30.51                | 30.38                | 30.6           | 0.3                         |
| 8   | 113,300              | 114,839              | 114,487              | 31.47                | 31.90                | 31.80                | 31.7           | 0.2                         |
| 9   | 40,261               | 40,150               | 40,479               | 11.18                | 11.15                | 11.24                | 11.19          | 0.04                        |
| 10  | 64,595               | 64,698               | 65,043               | 17.94                | 17.97                | 18.07                | 17.99          | 0.05                        |
| 11  | 70,463               | 70,761               | 70,238               | 19.57                | 19.66                | 19.51                | 19.58          | 0.06                        |
| 12  | 52,378               | 52,176               | 52,263               | 14.55                | 14.49                | 14.52                | 14.52          | 0.02                        |
| 13  | 664,563              | 672,368              | 678,279              | 184.60               | 186.77               | 188.41               | 187            | 2                           |
Table S16. Half-lives of compounds 1-13 in cyclooctane at 40 °C; 6 x 10⁻⁵ M.

| Cpd | \(t_{1/2}\) [s] Exp. 1 | \(t_{1/2}\) [s] Exp. 2 | \(t_{1/2}\) [s] Exp. 3 | \(t_{1/2}\) [h] Exp. 1 | \(t_{1/2}\) [h] Exp. 2 | \(t_{1/2}\) [h] Exp. 3 | \(\bar{t}_{1/2}\) [h] | \(\text{standard deviation} [\text{h}^{-1}]\) |
|-----|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|
| 1   | 19,393         | 18,904         | 19,504         | 5.39           | 5.25           | 5.42           | 5.35           | 0.07           |
| 2   | 57,927         | 56,171         | 56,990         | 16.09          | 15.60          | 15.83          | 15.8           | 0.2            |
| 3   | 83,067         | 82,610         | 83,874         | 23.07          | 22.95          | 23.30          | 23.1           | 0.2            |
| 4   | 98,645         | 94,827         | 94,810         | 27.40          | 26.34          | 26.34          | 26.7           | 0.5            |
| 5   | 78,644         | 74,676         | 81,130         | 21.85          | 20.74          | 22.54          | 21.7           | 0.7            |
| 6   | 78,489         | 74,791         | 74,517         | 21.80          | 20.78          | 20.70          | 21.1           | 0.5            |
| 7   | 78,529         | 78,542         | 75,397         | 21.81          | 21.82          | 20.94          | 21.5           | 0.4            |
| 8   | 78,181         | 74,999         | 76,569         | 21.72          | 20.83          | 21.27          | 21.3           | 0.4            |
| 9   | 30,660         | 30,534         | 30,370         | 8.52           | 8.48           | 8.44           | 8.48           | 0.03           |
| 10  | 51,551         | 49,300         | 48,082         | 14.32          | 13.69          | 13.36          | 13.8           | 0.4            |
| 11  | 53,109         | 54,296         | 56,288         | 14.75          | 15.08          | 15.64          | 15.2           | 0.4            |
| 12  | 41,836         | 41,311         | 41,432         | 11.62          | 11.48          | 11.51          | 11.54          | 0.06           |
| 13  | 700,994        | 705,122        | 717,047        | 194.72         | 195.87         | 199.18         | 197            | 2              |
Substituent Dependency of Half-lives in all Investigated Solvents

The following figures show the dependency of the Z-isomer half-lives on the substituents. As can be seen, influence of the substituents stays dominant for all investigated solvents leading to a similar trend in all alkane solutions.

Figure S2. Half-lives of azobenzenes 1-8, 13 with different chain lengths at 40 °C in n-heptane.

Figure S3. Half-lives of azobenzenes 1-8, 13 with different chain lengths at 40 °C in n-nonane.
Figure S4. Half-lives of azobenzenes 1-8, 12, 13 with different chain lengths at 40 °C in n-decane

Figure S5. Half-lives of azobenzenes 1-8, 13 with different chain lengths at 40 °C in n-undecane
Figure S6. Half-lives of azobenzenes 1-8, 13 with different chain lengths at 40 °C in n-dodecane.

Figure S7. Half-lives of azobenzenes 1-8, 12, 13 with different chain lengths at 40 °C in iso-octane.
Figure S8. Half-lives of azobenzenes 1-8, 12, 13 with different chain lengths at 40 °C in cyclooctane
Computational Analysis

The all-Me 1, all-Et 2, all-n-Bu 4 and all-n-Hept 7 azobenzene structures were chosen for further evaluation of the intramolecular interactions with computational methods. Therefore, the E-state, the transition state and the Z-state of azobenzene 1 were computed on the PBE0[4] level of theory with a def2-TZVP[5] basis set and the D3-BJ[6] dispersion correction using Gaussian16[7]. Afterwards conformer ensembles for all three states of azobenzenes 2, 4 and 7 were computed with the Conformer–Rotamer Ensemble Sampling Tool (CREST)[8] from Grimme and co-workers. Therefore, the azobenzene core structure obtained from the previous optimization of 1 was constrained for all three states, allowing conformational and rotational flexibility only for the elongated alkyl substituents. The conformational energies of the computed conformer/rotamer ensemble at a semiempirical level with CREST ranges up to 6 kcal mol$^{-1}$. For narrowing this range, single point energies at the B97-3c[9] level from all these conformers/rotamers were computed using the Orca 4.2.1[10] software package. Afterwards structures with single point energies more than 3 kcal mol$^{-1}$ higher than the lowest energy conformer were sorted out because they would only play a minor role at the investigated temperature.

With the remaining conformer ensemble, distances between the carbon atoms of opposing alkyl chains were determined in order to find close contacts, which can lead to attractive dispersive interactions. Since the distances in all-Me azobenzene 1 are too large for attractive interactions between the methyl substituents, the first methylene carbon at the aryl ring was not included for this analysis. For azobenzene 2, distances between the last carbon atoms of the alkyl chain, for 4, distances between the last three carbon atoms and for 7 distances between the last six carbon atoms were determined. A maximum threshold of 5 Å between the carbon atoms was set, which is a distance where attractive dispersive interactions for mid-size groups start to become significant.[11] In this way, a certain number of contacts were found for each conformer structure. To evaluate the importance of the contacts over the conformer ensemble, the probability for each conformer was calculated with a Boltzmann distribution using the computed single point energies. The so generated average contact numbers for each state were used for further analysis. Structures as xyz-files of all obtained conformers, the out-files from the single point energy calculations as well as further geometry optimizations of the lowest energy conformers for the NCI analysis can be provided on request.
Non-covalent Interaction Analysis (NCI)

The NCIPlot 4.0 software[12] allows to identify non-covalent interactions from the reduced density gradient (s). It is based on the electron density $\rho$ and its derivatives. This non-covalent interaction analysis indicates the regions in the molecules as isosurfaces, where these interactions occur. They are differentiated by taking into account the sign of the second density Hessian eigenvalue ($\lambda_2$). The colour code further allows to distinguish between attractive (blue), repulsive (red) and weak interactions (green). The following parameters on $\text{sign}(\lambda_2)\rho$ were set: -2.0 (blue) < 0.0 (green) < 2.0 (red). The final visualization of the depicted molecules and isosurfaces was created with the VMD[13] software package.

Figure S9. Isosurface of the reduced density gradient s of the transition state for azobenzene 7.
Figure S10. Isosurface of the reduced density gradient $s$ of the Z-state for azobenzene 7.

Figure S11. Reduced density gradient $s$ versus $\text{sign}(\lambda_2)\rho$ plot of the transition state for azobenzene 4.
Figure S12. Reduced density gradient $s$ versus $\text{sign}(\lambda_2)\rho$ plot of the Z-state for azobenzene 4.

Figure S13. Reduced density gradient $s$ versus $\text{sign}(\lambda_3)\rho$ plot of the transition state for azobenzene 7.
Figure S14. Reduced density gradient $s$ versus $\text{sign}(\lambda_2)\rho$ plot of the Z-state for azobenzene 7.
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