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

Supporting Information

Solvent Viscosity-Dependent Isomerization Equilibrium of Tetramethoxy-Substituted Bianthrone

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Contents

General procedures.
All experiments with moisture- or air-sensitive compounds were conducted in anhydrous solvents under nitrogen atmosphere in well-dried glassware. Anhydrous dichloromethane (DCM), tetrahydrofuran (THF) and *N*, *N*-dimethylformamide (DMF) were purchased from Kanto Chemical Co., Inc. and used without further purification. Other anhydrous solvents were prepared by distillation over calcium hydride. Column chromatography was performed on a silica gel (Silica gel 60N, Kanto Chemical Co., Inc.). UV-vis absorption spectra were measured on a JASCO V-570 spectrometer. ^{1}H and ^{13}C NMR spectra were obtained JEOL RESONANCE ECS-400 (400 MHz) and JEOL RESONANCE ECAMX-500SP (500 MHz) spectrometers. Variable-temperature ^{1}H NMR spectra were obtained on the same spectrometers. The chemical shift was recorded by using tetramethylsilane (0.00 ppm) as an internal standard for ^{1}H NMR and $CHCl_3$ (77.00 ppm) for ^{13}C NMR spectra. For quantitative analysis of ^{1}H NMR spectra, dimethyl sulfone (TraceCERT®, 41867-1G, lot #BCBQ8884V) was used as an internal standard. Positive ESI mass spectra were taken by Thermo Fisher Scientific Orbitrap XL. Data collection for X-ray crystal analysis for bianthrone **1** and bianthrone **2** was performed on Rigaku MicroMax-007HF VariMax-Mo and RAPID II diffractometer (Mo-Kα, λ = 0.71075 Å). CCDC 1539754 (**1**), CCDC 1872162 (**2**) and CCDC 1877284 (**5**) contain the supplementary crystallographic data. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. The structure was conducted by direct methods (SHELXL-2016/6 and SIR2004/2014) using Yadokari-XG.[S1] ESR spectra were measured using a JEOL RESONANCE JES-FA200 spectrometer, in which temperature was controlled by a JEOL ES-13060DVT5 variable temperature unit. *g*-value and hyperfine coupling constants were determined by the use of a Mn^{2+}/MgO solid as a standard.

Materials.

Methyl 4-methoxybenzoate (7). *p*-Anisic acid (5670 mg, 37.2 mmol) and potassium carbonate (20556 mg, 149 mmol) were suspended in acetone. Then, dimethyl sulfate (7.00 mL, 73.8 mmol) was added dropwise into the suspension under a nitrogen atmosphere. The mixture was stirred for 12 h at reflux. After cooling, water was added to the mixture and the aqueous layer was extracted, with DCM three times. The combined organic layer was washed with saturated $NaHCO_3$ aq. and brine, dried over anhydrous sodium sulfate. After filtration and concentration, the residue was washed with methanol to afford the title compound as a white solid (5809 mg, 94%):^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.99 (d, J = 8.8 Hz, 2H), 6.91 (d, J = 8.8 Hz, 2H), 3.89 (s, 3H), 3.86 (s, 3H).

2-Bromo-5-methoxybenzonic acid (6). *m*-Anisic acid (9129 mg, 60.0 mmol) was dissolved in DMF (30 mL) and the solution was stirred at 0 °C. Then, a solution of *N*-bromosuccinimide (12992 mg, 72.9 mmol) in DMF (30 mL) was added dropwise. After stirring overnight, water was added at 0 °C and the appeared yellow precipitate was washed 50% ethanol/water to afford the title compound as a white solid (10252 mg, 74%):^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.58 (d, J = 8.8 Hz, 1H), 7.52 (d, J = 3.2 Hz, 1H), 6.95 (dd, J = 9.2, 3.2 Hz, 1H), 3.84 (s, 3H).

5-Methoxy-2-(4-methoxybenzonyl)benzonic acid (8). Brominated benzoic acid **6** (2890 mg, 12.5 mmol) was placed in a flame-dried three-necked flask with a septum and dropping funnel under a nitrogen atmosphere and dissolved in THF (75 mL). The solution was cooled at –105 °C with a liquid N_2/ethanol bath. To the solution, a solution of *n*-butyllithium in hexane (1.6 M, 16.0 mL, 25.6 mmol) was added dropwise at -105 °C with stirring. After 30 min, **7** (1870 mg, 11.3 mmol) was added dropwise to the reaction mixture at -105 °C. The reaction mixture was then warmed to room temperature and stirred overnight. After evaporating the solvent, the residue was poured into 2 M aqueous solution of sodium hydroxide and the aqueous phase was washed with ether three times. Then, the aqueous phase was acidified with 2 M hydrochloric acid and extracted with DCM three times. The combined organic phase was washed with water and brine and dried over anhydrous sodium sulfate. After filtration and concentration, recrystallization from toluene was conducted to afford the title compound as white solid (2100 mg, 65%):^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.73 (d, J = 8.4 Hz, 2H), 7.58 (d, J = 2.4 Hz, 1H), 7.35 (d, J = 8.4 Hz, 1H), 7.13(dd, J = 7.8, 2.8 Hz, 1H), 6.91 (d, J = 7.6 Hz, 2H), 3.91 (s, 3H), 3.86 (s, 3H).

5-Methoxy-2-(4-methoxybenzyl)benzonic acid (3). Diarylketone **8** (410 mg, 1.43 mmol) and 10% Pd/C (174 mg) were suspended in dry ethanol (10 mL). The mixture was stirred under hydrogen atmosphere at

room temperature overnight. The reaction mixture was filtered through celite and the solvent was evaporated to afford the title compound as gray solid (391 mg, quant):^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.54 (d, J = 2.8 Hz, 2H), 7.13 (d, J = 8.4 Hz, 1H), 7.06 (d, J = 8.8 Hz, 2H), 7.02 (dd, J = 8.4, 2.8 Hz, 1H), 6.80 (d, J = 8.8 Hz, 2H), 4.30 (s, 2H), 3.83 (s, 3H), 3.77 (s, 3H).

2,7-Dimethoxyanthracen-9(10*H*)-one (4) and 3,3',6,6'-tetramethoxy-[9,9'-bianthracene]-10,10'(9*H*,9'*H*)-dione (5). Benzoic acid **3** (334 mg, 1.35 mmol) was dissolved in concentrated sulfuric acid (4.5 mL) and cooled at 0 °C with an ice bath. The solution was stirred for 1.5 h at 0 °C. After quenching with water at 0 °C, the reaction mixture was extracted with DCM three times. The combined organic phase was washed with brine and dried over anhydrous sodium sulfate. After filtration and concentration, the crude product obtained as yellowish green solid was purified by column chromatography on silica gel using DCM as an eluent. After elution of **4** and the oxidized byproduct (anthraquinone), the eluent was changed to a mixed solvent of DCM and ethyl acetate (1/15, *v/v*). Evaporation of the solvent gave **4** as white solids (144 mg, 46%) and **5** as white solids (91 mg, 29%).

2,7-Dimethoxyanthracen-9(10*H*)-one (4). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.84 (d, J = 3.2 Hz, 2H), 7.40 (d, J = 8.8 Hz, 2H), 7.20 (dd, J = 8.4, 2.8 Hz, 2H), 4.24 (s, 2H), 3.93 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) 183.99, 158.61, 133.46, 132.67, 129.74, 121.73, 108.84, 55.56, 31.12; HRMS (ESI, positive): *m/z* Calcd for $C_{16}H_{14}O_3Na$: 277.0835 $[M+Na]^+$; found: 277.0834

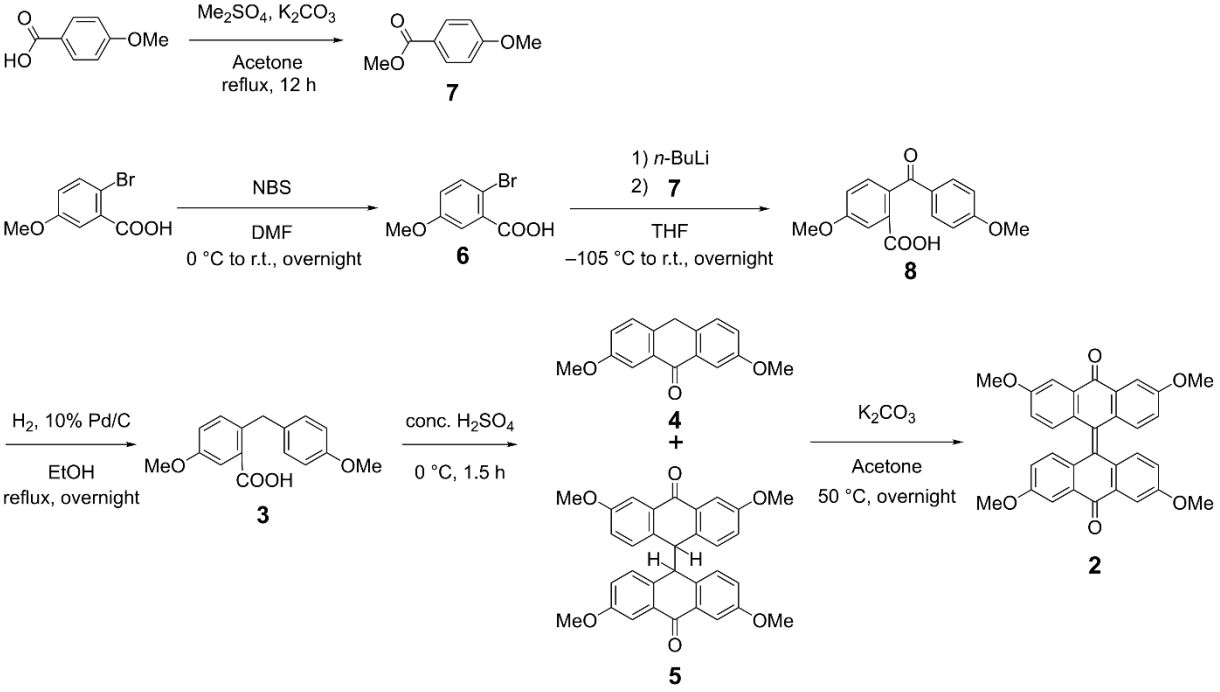
3,3',6,6'-tetramethoxy-[9,9'-bianthracene]-10,10'(9*H*,9'*H*)-dione (5). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.43 (d, J = 2.8 Hz, 4H), 6.98 (dd, J = 8.4, 2.8 Hz, 4H), 6.76 (d, J = 8.4, 4H), 4.66 (s, 2H), 3.86 (s, 12H); ^{13}C NMR (125 MHz, $CDCl_3$) δ **(**ppm) 182.98, 159.15, 134.58, 133.15, 129.68, 120.22, 108.96, 55.60, 52.92; HRMS (ESI, positive): *m/z* Calcd for $C_{32}H_{26}O_6Na$: 529.1622 $[M+Na]^+$; found: 529.1621

3,3',6,6'-Tetramethoxy-10*H*,10'*H*-[9,9'-bianthracene]-10,10'-dione (2). Potassium carbonate (609 mg, 4.41 mmol) was added into a solution of a mixture of anthrone **4** and the dimer **5** (240 mg) dissolved in acetone (15 mL) and stirred at 50 °C under aerated condition overnight. After evaporating the acetone, water was added into the residue and the mixture was extracted with DCM three times. The combined organic phase was washed with water and brine, dried over anhydrous sodium sulfate. After filtration and concentration, the residue was fractionated by column chromatography on silica gel using DCM as an eluent. After elution of the undesired anthraquinone, the eluent was changed to a mixed solvent of DCM and ethyl acetate (1/15, *v/v*). The elute was evapotrated to give the title compound as a black solid (131 mg, 40% in 2steps):^{1}H NMR (400 MHz, $CDCl_3$) of **f-2** δ (ppm) 7.55 (d, J = 2.8 Hz, 4H), 7.02 (d, J = 8.8 Hz, 4H), 6.73 (dd, J = 8.8, 2.8 Hz, 4H), 3.90 (s, 12H); ^{13}C NMR of **f-2** (125 MHz, $CDCl_3$) δ **(**ppm) 186.72, 159.40, 135.56, 132.83, 131.26, 129.66, 117.70, 109.28, 55.60; HRMS (ESI, positive): *m/z* Calcd for $C_{32}H_{25}O_6$: 505.1646 $[M+H]^+$; found: 505.1642.

Computational Details.

Geometrical optimizations and Potential energy calculations of all of the possible conformers were performed with the Gaussian 09 program[S2] at the CAM-B3LYP functional with GD3 empirical dispersion and 6-31G(d,p) basis set. Unrestricted broken symmetry (BS) approach was adopted for the twisted conformation. The molecular geometries of the folded and twisted conformers of bianthrone were optimized with a C_{2h} symmetry and D_2 symmetry constraint, respectively. Ground state optimizations had no imaginary frequencies. Spin densities of the orthogonal triplet species were estimated by the UBLYP/6-31G(d,p) level of theory. Electronic transition energies and oscillator strengths were calculated using time-dependent density functional theory (TD-DFT).

Scheme S1 Synthetic route to **2**.



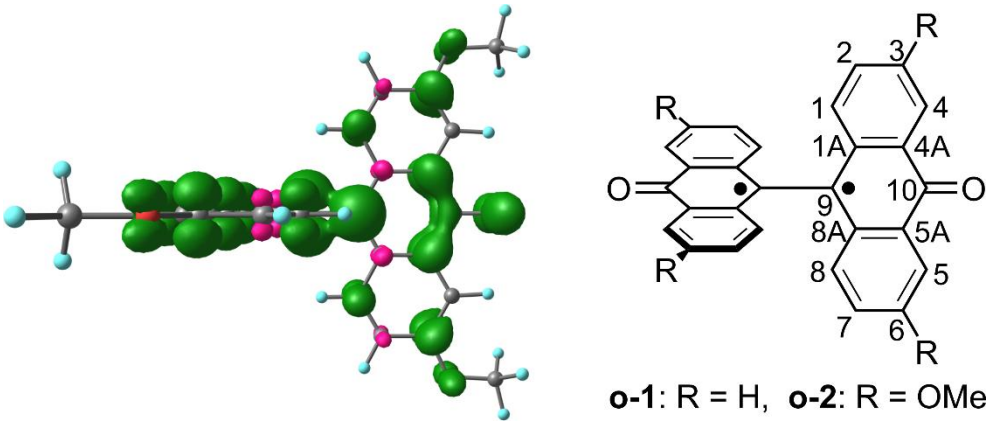


Fig. S1 Spin distribution of ^{3}**o-2** calculated at the UBLYP-GD3/6-31G(d,p)//CAM-B3LYP-GD3/6-31G(d,p) level of theory.

Table S1 Spin densities of the triplet species of **1** (^{3}**o-1**) and **2** (^{3}**o-2**) at the orthogonal orientation calculated at the UBLYP/6-31G(d,p)//CAM-B3LYP-GD3/6-31G(d,p) level of theory.

	C1/C8	C2/C7	C3/C6	C4/C5	C1A/C8A	C4A/C5A	C9	C10	O	O(OMe)
^{3}**o-1**	0.124	−0.046	0.130	−0.033	−0.082	0.124	0.448	−0.010	0.147	na
^{3}**o-2**	0.085	−0.040	0.089	0.009	−0.072	0.120	0.377	0.014	0.166	0.030

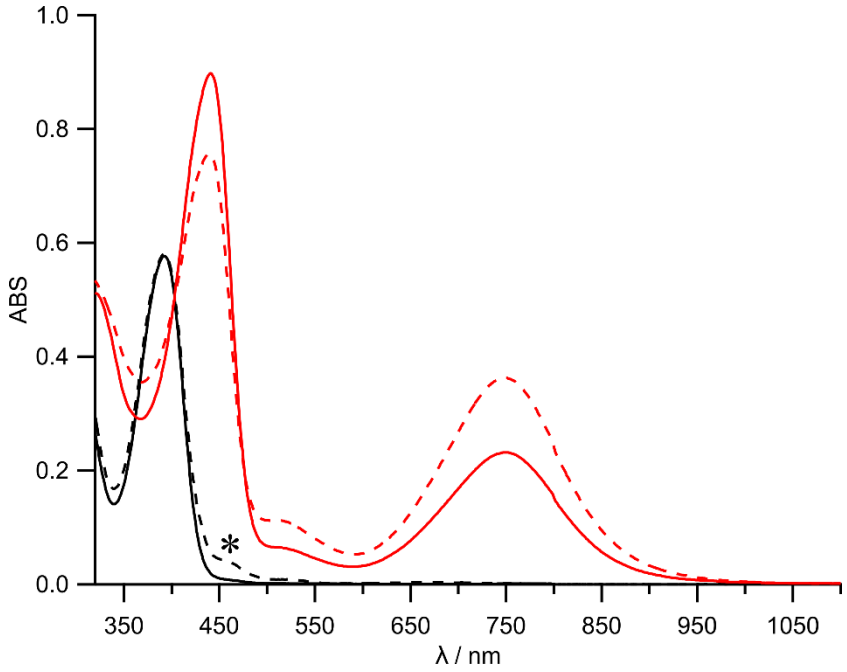


Fig. S2 UV-vis-NIR spectra of (black solid line) **1** in dichloromethane, (black dashed lone) **1** in DMF, (red solid line) **2** in dichloromethane, and (red dashed lone) **2** in DMF. All spectra were normalized to 0.06 mM concentration. The asterisk mark (*) is the absorption band derived from a very small amount of helianthrone produced by a photo-cyclization reaction (see reference 6).

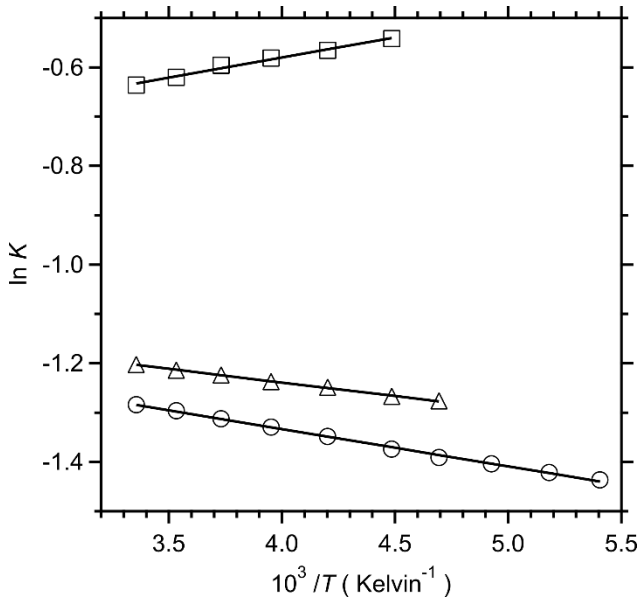


Fig. S3 Van't Hoff plots for the isomerization reaction of **2** in (open circle) dichloromethane, (open triangle) chloroform and (open square) DMF.

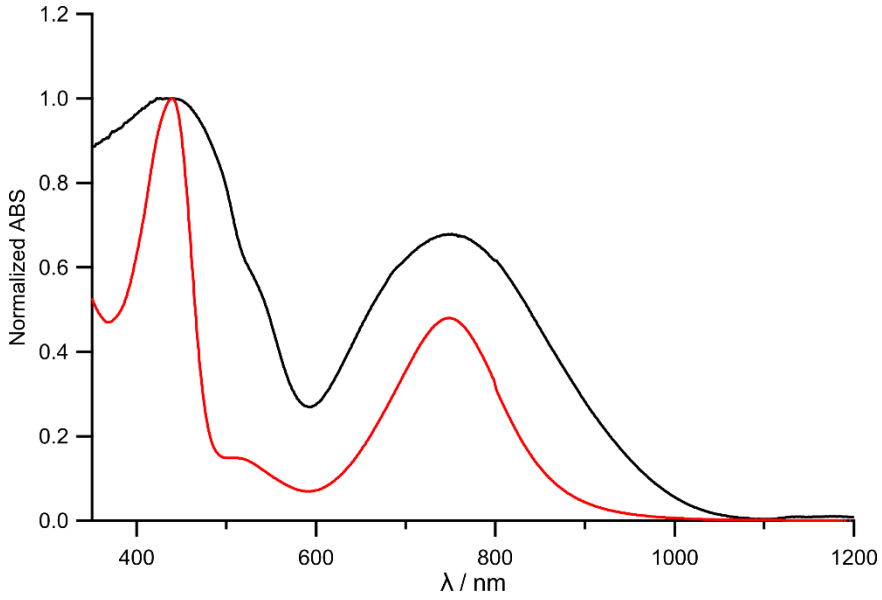


Fig. S4 (black solid line) Diffuse reflection spectrum of the dark yellow powder sample of **2** and (red solid line) absorption spectrum of **2** in DMF.

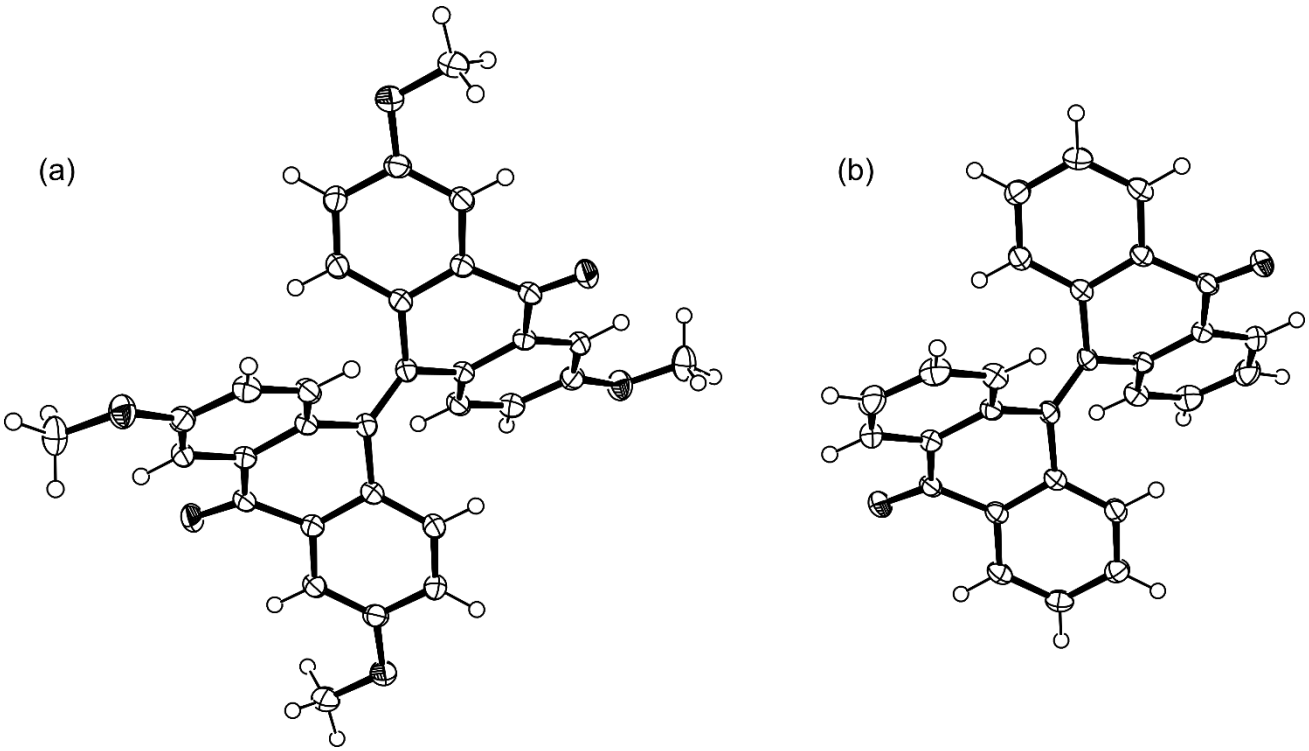


Fig. S5 X-ray structures of the folded conformation (a) **f-2** and (b) **f-1**.

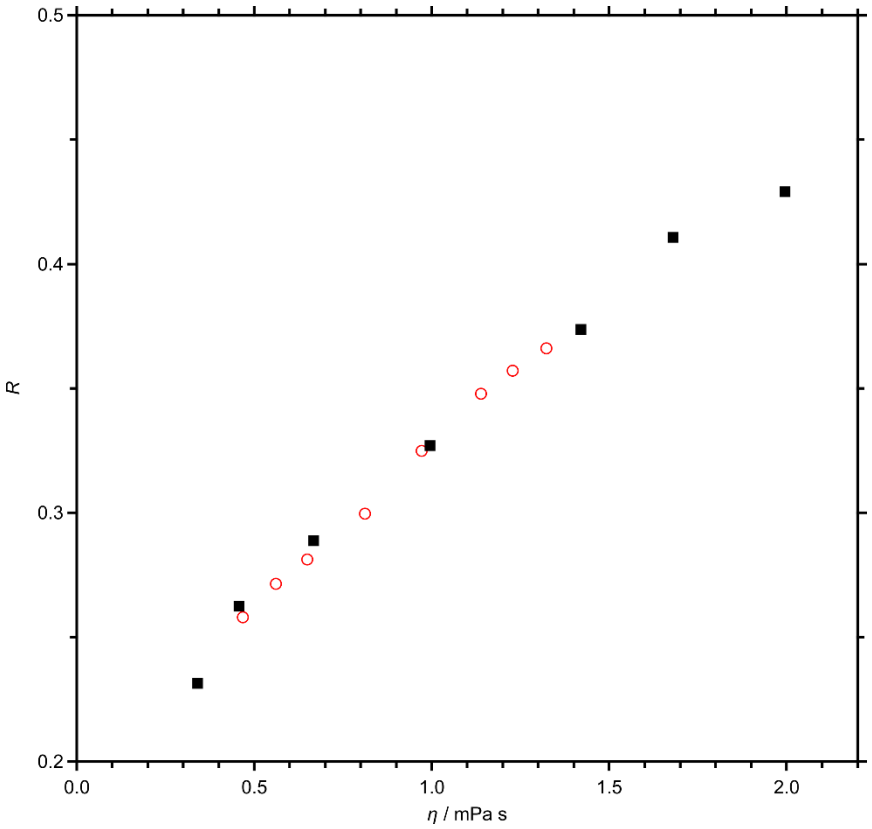


Fig. S6 Relationship between the *R* value and the viscosity of the binary liquid mixtures consisitng of (black filled square) acetonitrile/DMSO or (red open circle) THF/1,2-dicchlorobenzene. The viscosity of each mixing ratio is cited from ref. S3.

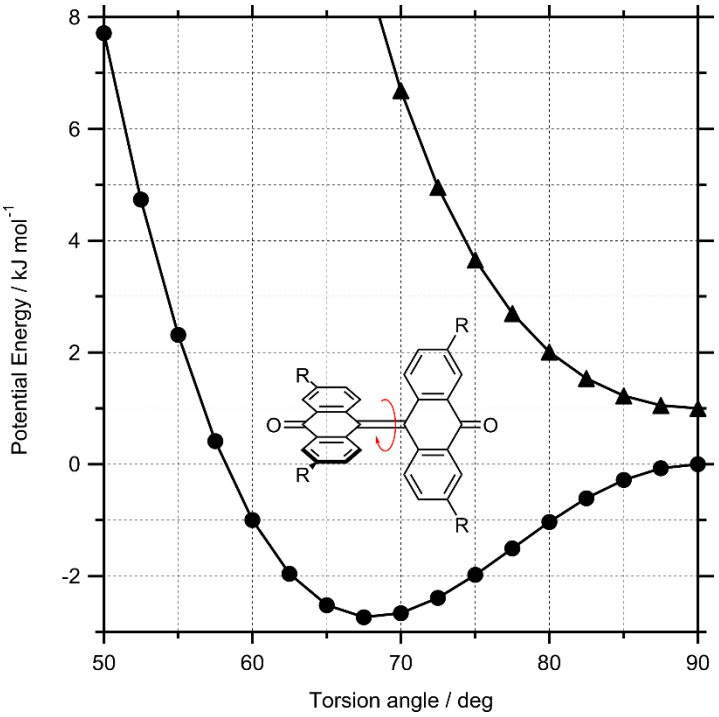


Fig. S7 Potential energy surfaces of the ground state (filled circle) and the triplet state (filled triangle) of **t-2** along the torsional coordinate between anthrone moieties.

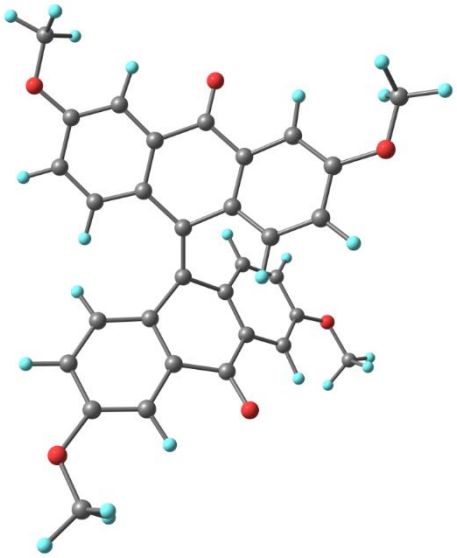


Fig. S8 The predicted structure of the transition state for the isomerization of **2** by using the CAM-B3LYP-GD3/6-31G(d,p) functional. This transition state is calculated to lie 92.5 kJ mol^{-1} higher than **f-2**.

Table S2. Optimized geometries and Hartree-Fock energies of **2** and **1** at the CAM-B3LYP/6-31G(d,p) level of theory with the D3 version of Grimme's dispersion (gd3).

f-2 (Folded) "Singlet"

E(RCAM-B3LYP) = -1684.4090433 a.u. *E*+*ZPE*(RCAM-B3LYP) = -1683.916843 a.u.

	x	y	z		x	y	z
C	0.238227	2.754001	1.252965	O	0.554106	-3.779989	4.695478
C	-0.325335	1.474181	1.233112	H	-0.679331	-4.524013	2.343928
C	-0.167717	0.658321	0.000000	H	0.679331	4.524013	2.343928
C	-0.325335	1.474181	-1.233112	O	-0.554106	3.779989	4.695478
C	0.238227	2.754001	-1.252965	H	-1.522744	0.092653	2.368743
C	0.773412	3.353772	0.000000	H	-1.522744	0.092653	-2.368743
C	0.167717	-0.658321	0.000000	O	-0.554106	3.779989	-4.695478
C	0.325335	-1.474181	1.233112	H	0.679331	4.524013	-2.343928
C	-0.238227	-2.754001	1.252965	H	-0.679331	-4.524013	-2.343928
C	-0.773412	-3.353772	0.000000	O	0.554106	-3.779989	-4.695478
C	-0.238227	-2.754001	-1.252965	H	1.522744	-0.092653	-2.368743
C	0.325335	-1.474181	-1.233112	C	0.063842	5.049029	-4.771647
C	1.026426	-1.055070	2.370362	H	-0.122515	5.417483	-5.780045
C	1.094743	-1.850755	3.495773	H	-0.364755	5.749830	-4.045719
C	0.451808	-3.094536	3.529953	H	1.145195	4.980796	-4.605037
C	-0.205740	-3.552498	2.397261	C	0.063842	5.049029	4.771647
C	0.205740	3.552498	2.397261	H	-0.364755	5.749830	4.045719
C	-0.451808	3.094536	3.529953	H	-0.122515	5.417483	5.780045
C	-1.094743	1.850755	3.495773	H	1.145195	4.980796	4.605037
C	-1.026426	1.055070	2.370362	C	-0.063842	-5.049029	-4.771647
C	-1.026426	1.055070	-2.370362	H	0.364755	-5.749830	-4.045719
C	-1.094743	1.850755	-3.495773	H	-1.145195	-4.980796	-4.605037
C	-0.451808	3.094536	-3.529953	H	0.122515	-5.417483	-5.780045
C	0.205740	3.552498	-2.397261	C	-0.063842	-5.049029	4.771647
C	-0.205740	-3.552498	-2.397261	H	0.122515	-5.417483	5.780045
C	0.451808	-3.094536	-3.529953	H	-1.145195	-4.980796	4.605037
C	1.094743	-1.850755	-3.495773	H	0.364755	-5.749830	4.045719
C	1.026426	-1.055070	-2.370362	H	-1.644596	1.532724	4.374220
O	1.470720	4.354367	0.000000	H	1.644596	-1.532724	4.374220
O	-1.470720	-4.354367	0.000000	H	1.644596	-1.532724	-4.374220
H	1.522744	-0.092653	2.368743	H	-1.644596	1.532724	-4.374220

t-2 (Twisted) "Closed-shell singlet"
E(RCAM-B3LYP) = -1684.401495 a.u. *E*+*ZPE*(RCAM-B3LYP) = -1683.909397 a.u.

	x	y	z		x	y	z
C	-0.533274	1.140310	2.868747	C	2.285054	4.333543	-4.979483
C	-0.542925	1.131550	1.463805	O	-2.324776	-4.281750	-3.566260
C	0.000000	0.000000	0.702671	O	2.324776	-4.281750	3.566260
C	0.542925	-1.131550	1.463805	C	-2.285054	-4.333543	-4.979483
C	0.533274	-1.140310	2.868747	C	2.285054	-4.333543	4.979483
C	0.000000	0.000000	3.641701	O	-2.324776	4.281750	3.566260
C	0.000000	0.000000	-0.702671	C	-2.285054	4.333543	4.979483
C	0.542925	1.131550	-1.463805	H	1.401107	2.161707	0.234684
C	0.533274	1.140310	-2.868747	H	1.065148	2.099578	-4.684201
C	0.000000	0.000000	-3.641701	H	-1.065148	-2.099578	-4.684201
C	-0.533274	-1.140310	-2.868747	H	-1.401107	-2.161707	0.234684
C	-0.542925	-1.131550	-1.463805	H	1.401107	-2.161707	-0.234684
C	1.273201	2.170444	-0.839170	H	1.065148	-2.099578	4.684201
C	1.834976	3.196762	-1.555513	H	-1.065148	2.099578	4.684201
C	1.742523	3.223323	-2.956722	H	-1.401107	2.161707	-0.234684
C	1.114477	2.177489	-3.606411	H	1.254144	4.354894	-5.350789
C	-1.114477	-2.177489	-3.606411	H	2.790878	5.255825	-5.263491
C	-1.742523	-3.223323	-2.956722	H	2.807440	3.480213	-5.426733
C	-1.834976	-3.196762	-1.555513	H	-2.790878	-5.255825	-5.263491
C	-1.273201	-2.170444	-0.839170	H	-2.807440	-3.480213	-5.426733
C	1.273201	-2.170444	0.839170	H	-1.254144	-4.354894	-5.350789
C	1.834976	-3.196762	1.555513	H	1.254144	-4.354894	5.350789
C	1.742523	-3.223323	2.956722	H	2.790878	-5.255825	5.263491
C	1.114477	-2.177489	3.606411	H	2.807440	-3.480213	5.426733
C	-1.114477	2.177489	3.606411	H	-2.790878	5.255825	5.263491
C	-1.742523	3.223323	2.956722	H	-2.807440	3.480213	5.426733
C	-1.834976	3.196762	1.555513	H	-1.254144	4.354894	5.350789
C	-1.273201	2.170444	0.839170	H	2.380879	-3.991573	1.059992
O	0.000000	0.000000	4.867132	H	-2.380879	3.991573	1.059992
O	0.000000	0.000000	-4.867132	H	-2.380879	-3.991573	-1.059992
O	2.324776	4.281750	-3.566260	H	2.380879	3.991573	-1.059992

t-2 (Twisted) "Open-shell singlet"
E(RCAM-B3LYP) = -1684.4079843 a.u. *E*+*ZPE*(RCAM-B3LYP) = -1683.917992 a.u.

	x	y	z		x	y	z
C	-0.699168	1.042235	2.870707	C	2.800732	4.061406	-4.912802
C	-0.693983	1.027452	1.456741	O	-2.784837	-4.008577	-3.498903
C	0.000000	0.000000	0.736458	O	2.784837	-4.008577	3.498903
C	0.693983	-1.027452	1.456741	C	-2.800732	-4.061406	-4.912802
C	0.699168	-1.042235	2.870707	C	2.800732	-4.061406	4.912802
C	0.000000	0.000000	3.641330	O	-2.784837	4.008577	3.498903
C	0.000000	0.000000	-0.736458	C	-2.800732	4.061406	4.912802
C	0.693983	1.027452	-1.456741	H	1.496289	2.037371	0.283582
C	0.699168	1.042235	-2.870707	H	1.347376	1.968862	-4.665107
C	0.000000	0.000000	-3.641330	H	-1.347376	-1.968862	-4.665107
C	-0.699168	-1.042235	-2.870707	H	-1.496289	-2.037371	0.283582
C	-0.693983	-1.027452	-1.456741	H	1.496289	-2.037371	-0.283582
C	1.447832	2.033903	-0.798184	H	1.347376	-1.968862	4.665107
C	2.117538	2.999611	-1.501233	H	-1.347376	1.968862	4.665107
C	2.089085	3.009091	-2.910310	H	-1.496289	2.037371	-0.283582
C	1.388306	2.025663	-3.585483	H	1.790733	4.183028	-5.320245
C	-1.388306	-2.025663	-3.585483	H	3.404201	4.929276	-5.176759
C	-2.089085	-3.009091	-2.910310	H	3.252589	3.160077	-5.342121
C	-2.117538	-2.999611	-1.501233	H	-3.404201	-4.929276	-5.176759
C	-1.447832	-2.033903	-0.798184	H	-3.252589	-3.160077	-5.342121
C	1.447832	-2.033903	0.798184	H	-1.790733	-4.183028	-5.320245
C	2.117538	-2.999611	1.501233	H	1.790733	-4.183028	5.320245
C	2.089085	-3.009091	2.910310	H	3.404201	-4.929276	5.176759
C	1.388306	-2.025663	3.585483	H	3.252589	-3.160077	5.342121
C	-1.388306	2.025663	3.585483	H	-3.404201	4.929276	5.176759
C	-2.089085	3.009091	2.910310	H	-3.252589	3.160077	5.342121
C	-2.117538	2.999611	1.501233	H	-1.790733	4.183028	5.320245
C	-1.447832	2.033903	0.798184	H	2.689878	-3.769179	0.995879
O	0.000000	0.000000	4.872561	H	-2.689878	3.769179	0.995879
O	0.000000	0.000000	-4.872561	H	-2.689878	-3.769179	-0.995879
O	2.784837	4.008577	-3.498903	H	2.689878	3.769179	-0.995879

o-2 (Orthogonal) "Triplet"

E(RCAM-B3LYP) = -1684.4065601 a.u. *E*+*ZPE*(RCAM-B3LYP) = -1683.916963 a.u.

	x	y	z		x	y	z
C	-0.887244	-0.887262	2.866386	C	-3.500029	3.500106	-4.876554
C	-0.873493	-0.873509	1.450548	O	3.454340	-3.454414	-3.463036
C	0.000000	0.000000	0.742887	O	3.454340	3.454414	3.463036
C	0.873493	0.873509	1.450548	C	3.500029	-3.500106	-4.876554
C	0.887244	0.887262	2.866386	C	3.500029	3.500106	4.876554
C	0.000000	0.000000	3.636948	O	-3.454340	-3.454414	3.463036
C	0.000000	0.000000	-0.742887	C	-3.500029	-3.500106	4.876554
C	-0.873493	0.873509	-1.450548	H	-1.767907	1.767937	0.306236
C	-0.887244	0.887262	-2.866386	H	-1.698045	1.698082	-4.651137
C	0.000000	0.000000	-3.636948	H	1.698045	-1.698082	-4.651137
C	0.887244	-0.887262	-2.866386	H	1.767907	-1.767937	0.306236
C	0.873493	-0.873509	-1.450548	H	1.767907	1.767937	-0.306236
C	-1.757207	1.757239	-0.777592	H	1.698045	1.698082	4.651137
C	-2.591013	2.591064	-1.473135	H	-1.698045	-1.698082	4.651137
C	-2.590065	2.590119	-2.883903	H	-1.767907	-1.767937	-0.306236
C	-1.740129	1.740165	-3.570809	H	-3.794569	2.532859	-5.299092
C	1.740129	-1.740165	-3.570809	H	-4.249080	4.249173	-5.131225
C	2.590065	-2.590119	-2.883903	H	-2.532775	3.794626	-5.299090
C	2.591013	-2.591064	-1.473135	H	4.249080	-4.249173	-5.131225
C	1.757207	-1.757239	-0.777592	H	2.532775	-3.794626	-5.299090
C	1.757207	1.757239	0.777592	H	3.794569	-2.532859	-5.299092
C	2.591013	2.591064	1.473135	H	3.794569	2.532859	5.299092
C	2.590065	2.590119	2.883903	H	4.249080	4.249173	5.131225
C	1.740129	1.740165	3.570809	H	2.532775	3.794626	5.299090
C	-1.740129	-1.740165	3.570809	H	-4.249080	-4.249173	5.131225
C	-2.590065	-2.590119	2.883903	H	-2.532775	-3.794626	5.299090
C	-2.591013	-2.591064	1.473135	H	-3.794569	-2.532859	5.299092
C	-1.757207	-1.757239	0.777592	H	3.267614	3.267678	0.963660
O	0.000000	0.000000	4.869559	H	-3.267614	-3.267678	0.963660
O	0.000000	0.000000	-4.869559	H	3.267614	-3.267678	-0.963660
O	-3.454340	3.454414	-3.463036	H	-3.267614	3.267678	-0.963660

2 (Transition state)
E(RCAM-B3LYP) = -1684.372855 a.u. *E*+*ZPE*(RCAM-B3LYP) = -1683.881596 a.u.

	x	y	z		x	y	z
C	-0.587002	2.478775	1.200791	H	-1.119725	3.931867	2.652471
C	-0.569265	1.145454	0.781492	H	-1.454652	-0.772572	1.237292
C	0.058332	0.699695	-0.498331	H	0.847402	0.599164	-3.173413
C	0.229337	1.779587	-1.500261	H	0.314343	5.188230	-1.573795
C	0.148216	3.133584	-1.100225	H	-1.131376	-4.863657	-1.370525
C	-0.113438	3.539792	0.301472	H	0.759316	-0.861801	-3.471047
C	0.436211	-0.648090	-0.542232	H	1.173257	2.418728	-4.732580
C	0.964548	-1.181284	0.741540	H	-2.475172	-0.082791	3.345761
C	0.649201	-2.452783	1.217496	H	3.024549	-0.279569	3.310213
C	-0.220137	-3.310300	0.398586	H	-0.052409	-2.622436	-4.858724
C	-0.282143	-2.954902	-1.047002	O	-0.006806	4.703419	0.665457
C	0.199690	-1.723027	-1.561502	O	2.489434	-2.487448	4.398486
C	1.847969	-0.409586	1.516223	C	2.139669	-3.751321	4.927143
C	2.339151	-0.873895	2.716775	H	1.058642	-3.834130	5.088227
C	1.964651	-2.135004	3.200521	H	2.466048	-4.566059	4.270375
C	1.118054	-2.929263	2.441060	H	2.653799	-3.832734	5.884358
C	-1.166896	2.878853	2.408801	O	-1.166184	-4.779259	-4.126641
C	-1.802406	1.946777	3.209146	C	-1.729384	-5.967802	-3.605540
C	-1.907027	0.625298	2.753369	H	-1.000114	-6.532224	-3.013118
C	-1.318913	0.246415	1.569978	H	-2.607399	-5.757478	-2.984231
C	0.654356	1.588284	-2.823936	H	-2.031286	-6.563027	-4.466770
C	0.865921	2.618816	-3.712268	O	-2.388669	2.212858	4.400353
C	0.713229	3.945237	-3.304388	C	-2.331114	3.541747	4.880362
C	0.383385	4.189317	-1.983163	H	-1.295649	3.876155	5.012207
C	-0.761619	-3.976321	-1.867170	H	-2.846115	4.235260	4.205611
C	-0.726139	-3.850731	-3.245223	H	-2.835261	3.537957	5.846350
C	-0.154342	-2.699534	-3.782121	O	0.936713	4.894979	-4.242417
C	0.284210	-1.677416	-2.963128	C	0.816221	6.249278	-3.851233
O	-0.766538	-4.306597	0.849026	H	-0.193538	6.473819	-3.489148
H	2.146447	0.569421	1.160627	H	1.540652	6.508045	-3.070616
H	0.797731	-3.915293	2.750813	H	1.020035	6.841526	-4.742807

f-1 (Folded) "Singlet"
E(RCAM-B3LYP) = -1226.4719249 a.u. *E*+*ZPE*(RCAM-B3LYP) = -1226.111831 a.u.

	x	y	z		x	y	z
C	0.162526	2.751889	1.252403	C	0.097600	3.535866	-2.402297
C	-0.384144	1.460014	1.234133	C	-0.097600	-3.535866	-2.402297
C	-0.194881	0.649386	0.000000	C	0.564677	-3.065587	-3.524931
C	-0.384144	1.460014	-1.234133	C	1.179344	-1.815653	-3.486322
C	0.162526	2.751889	-1.252403	C	1.086741	-1.017202	-2.355168
C	0.697070	3.354542	0.000000	O	1.392435	4.354868	0.000000
C	0.194881	-0.649386	0.000000	O	-1.392435	-4.354868	0.000000
C	0.384144	-1.460014	1.234133	H	1.556569	-0.041378	2.341663
C	-0.162526	-2.751889	1.252403	H	-0.551718	-4.520271	2.375899
C	-0.697070	-3.354542	0.000000	H	0.551718	4.520271	2.375899
C	-0.162526	-2.751889	-1.252403	H	-1.556569	0.041378	2.341663
C	0.384144	-1.460014	-1.234133	H	-1.556569	0.041378	-2.341663
C	1.086741	-1.017202	2.355168	H	0.551718	4.520271	-2.375899
C	1.179344	-1.815653	3.486322	H	-0.551718	-4.520271	-2.375899
C	0.564677	-3.065587	3.524931	H	1.556569	-0.041378	-2.341663
C	-0.097600	-3.535866	2.402297	H	-0.628508	3.677713	-4.418187
C	0.097600	3.535866	2.402297	H	-1.735908	1.458156	-4.346478
C	-0.564677	3.065587	3.524931	H	-1.735908	1.458156	4.346478
C	-1.179344	1.815653	3.486322	H	-0.628508	3.677713	4.418187
C	-1.086741	1.017202	2.355168	H	1.735908	-1.458156	-4.346478
C	-1.086741	1.017202	-2.355168	H	0.628508	-3.677713	-4.418187
C	-1.179344	1.815653	-3.486322	H	0.628508	-3.677713	4.418187
C	-0.564677	3.065587	-3.524931	H	1.735908	-1.458156	4.346478

t-1 (Twisted) "Closed-shell singlet"
E(RCAM-B3LYP) = -1226.4585447 a.u. *E*+*ZPE*(RCAM-B3LYP) = -1226.098606 a.u.

	x	y	z		x	y	z
C	-1.758943	3.220672	2.944340	C	-1.758943	-3.220672	-2.944340
C	-1.852015	3.190815	1.550902	C	-1.124516	-2.181877	-3.593806
C	-1.283705	2.159968	0.831257	C	1.124516	2.181877	-3.593806
C	-0.550309	1.134748	1.463362	C	1.758943	3.220672	-2.944340
C	-0.535953	1.140187	2.871075	C	1.852015	3.190815	-1.550902
C	-1.124516	2.181877	3.593806	C	1.283705	2.159968	-0.831257
C	0.000000	0.000000	0.700571	O	0.000000	0.000000	-4.867187
C	0.550309	-1.134748	1.463362	H	-2.211114	4.029165	3.508513
C	0.535953	-1.140187	2.871075	H	-2.393561	3.970073	1.024675
C	0.000000	0.000000	3.643832	H	-1.410907	2.142315	-0.242546
C	1.283705	-2.159968	0.831257	H	-1.078768	2.126132	4.675260
C	1.852015	-3.190815	1.550902	H	1.410907	-2.142315	-0.242546
C	1.758943	-3.220672	2.944340	H	2.393561	-3.970073	1.024675
C	1.124516	-2.181877	3.593806	H	2.211114	-4.029165	3.508513
O	0.000000	0.000000	4.867187	H	1.078768	-2.126132	4.675260
C	0.000000	0.000000	-0.700571	H	-1.410907	-2.142315	0.242546
C	-0.550309	-1.134748	-1.463362	H	-2.393561	-3.970073	-1.024675
C	-0.535953	-1.140187	-2.871075	H	-2.211114	-4.029165	-3.508513
C	0.000000	0.000000	-3.643832	H	-1.078768	-2.126132	-4.675260
C	0.535953	1.140187	-2.871075	H	1.078768	2.126132	-4.675260
C	0.550309	1.134748	-1.463362	H	2.211114	4.029165	-3.508513
C	-1.283705	-2.159968	-0.831257	H	2.393561	3.970073	-1.024675
C	-1.852015	-3.190815	-1.550902	H	1.410907	2.142315	0.242546

t-1 (Twisted) "Open-shell singlet"
E(RCAM-B3LYP) = -1226.4642149 a.u. *E*+*ZPE*(RCAM-B3LYP) = -1226.106576 a.u.

	x	y	z		x	y	z
C	-2.101048	3.009928	2.896723	C	-2.101048	-3.009928	-2.896723
C	-2.129260	2.997339	1.497297	C	-1.397019	-2.030521	-3.572369
C	-1.452492	2.025999	0.790733	C	1.397019	2.030521	-3.572369
C	-0.699261	1.031870	1.456761	C	2.101048	3.009928	-2.896723
C	-0.701650	1.044125	2.872468	C	2.129260	2.997339	-1.497297
C	-1.397019	2.030521	3.572369	C	1.452492	2.025999	-0.790733
C	0.000000	0.000000	0.735025	O	0.000000	0.000000	-4.871213
C	0.699261	-1.031870	1.456761	H	-2.638593	3.775154	3.446256
C	0.701650	-1.044125	2.872468	H	-2.695168	3.751433	0.960250
C	0.000000	0.000000	3.643984	H	-1.499837	2.021214	-0.291040
C	1.452492	-2.025999	0.790733	H	-1.367030	1.993023	4.655355
C	2.129260	-2.997339	1.497297	H	1.499837	-2.021214	-0.291040
C	2.101048	-3.009928	2.896723	H	2.695168	-3.751433	0.960250
C	1.397019	-2.030521	3.572369	H	2.638593	-3.775154	3.446256
O	0.000000	0.000000	4.871213	H	1.367030	-1.993023	4.655355
C	0.000000	0.000000	-0.735025	H	-1.499837	-2.021214	0.291040
C	-0.699261	-1.031870	-1.456761	H	-2.695168	-3.751433	-0.960250
C	-0.701650	-1.044125	-2.872468	H	-2.638593	-3.775154	-3.446256
C	0.000000	0.000000	-3.643984	H	-1.367030	-1.993023	-4.655355
C	0.701650	1.044125	-2.872468	H	1.367030	1.993023	-4.655355
C	0.699261	1.031870	-1.456761	H	2.638593	3.775154	-3.446256
C	-1.452492	-2.025999	-0.790733	H	2.695168	3.751433	-0.960250
C	-2.129260	-2.997339	-1.497297	H	1.499837	2.021214	0.291040

o-1 (Orthogonal) "Triplet"
E(RCAM-B3LYP) = -1226.462762 a.u. *E*+*ZPE*(RCAM-B3LYP) = -1226.105535 a.u.

	x	y	z		x	y	z
C	-2.595604	2.595622	2.868960	C	-2.595604	-2.595622	-2.868960
C	-2.594487	2.594522	1.468325	C	-1.746616	-1.746617	-3.557067
C	-1.754171	1.754199	0.769475	C	1.746616	1.746617	-3.557067
C	-0.877959	0.877967	1.450512	C	2.595604	2.595622	-2.868960
C	-0.889637	0.889635	2.868074	C	2.594487	2.594522	-1.468325
C	-1.746616	1.746617	3.557067	C	1.754171	1.754199	-0.769475
C	0.000000	0.000000	0.742284	O	0.000000	0.000000	-4.868006
C	0.877959	-0.877967	1.450512	H	-3.259872	3.259881	3.411256
C	0.889637	-0.889635	2.868074	H	-3.259298	3.259354	0.926730
C	0.000000	0.000000	3.639853	H	-1.759382	1.759430	-0.314433
C	1.754171	-1.754199	0.769475	H	-1.720736	1.720733	4.640597
C	2.594487	-2.594522	1.468325	H	1.759382	-1.759430	-0.314433
C	2.595604	-2.595622	2.868960	H	3.259298	-3.259354	0.926730
C	1.746616	-1.746617	3.557067	H	3.259872	-3.259881	3.411256
O	0.000000	0.000000	4.868006	H	1.720736	-1.720733	4.640597
C	0.000000	0.000000	-0.742284	H	-1.759382	-1.759430	0.314433
C	-0.877959	-0.877967	-1.450512	H	-3.259298	-3.259354	-0.926730
C	-0.889637	-0.889635	-2.868074	H	-3.259872	-3.259881	-3.411256
C	0.000000	0.000000	-3.639853	H	-1.720736	-1.720733	-4.640597
C	0.889637	0.889635	-2.868074	H	1.720736	1.720733	-4.640597
C	0.877959	0.877967	-1.450512	H	3.259872	3.259881	-3.411256
C	-1.754171	-1.754199	-0.769475	H	3.259298	3.259354	-0.926730
C	-2.594487	-2.594522	-1.468325	H	1.759382	1.759430	0.314433

1 (Transition state)
E(RCAM-B3LYP) = -1226.4329854 a.u. *E*+*ZPE*(RCAM-B3LYP) = -1226.073730 a.u.

	x	y	z		x	y	z
C	-2.177529	-1.240540	1.325445	C	-4.006812	-0.198001	-1.737224
C	-0.864531	-1.209483	0.847507	C	4.031603	1.109941	-1.918378
C	-0.495429	-0.510939	-0.415896	C	3.878124	0.714515	-3.233267
C	-1.593281	-0.570673	-1.443682	C	2.685042	0.104583	-3.601050
C	-2.903405	-0.402563	-0.912732	C	1.664160	-0.051008	-2.679233
C	-3.219445	-0.564936	0.535223	O	4.470466	1.593444	0.744762
C	0.674323	0.248076	-0.351269	H	-1.168190	1.184829	1.432948
C	0.921453	0.958897	0.944177	H	3.415729	2.331333	2.806050
C	2.195285	1.391889	1.340135	H	-3.526499	-1.833525	2.863235
C	3.328027	1.321676	0.405562	H	1.136348	-1.904158	1.207455
C	2.994521	0.973265	-0.995858	H	-0.621700	-0.945573	-3.342608
C	1.737753	0.438089	-1.370736	H	-4.964667	-0.047770	-1.252230
C	-0.153383	1.367242	1.753794	H	4.966414	1.519114	-1.553249
C	0.046725	2.020437	2.956032	H	0.801726	-0.602351	-2.979448
C	1.335297	2.329348	3.389060	H	-2.519268	-0.609896	-4.727294
C	2.401025	2.039708	2.560011	H	0.571826	-3.064670	3.306313
C	-2.497263	-1.870293	2.523796	H	-0.813583	2.304945	3.552834
C	-1.509696	-2.522826	3.245033	H	2.549990	-0.275754	-4.608515
C	-0.204003	-2.540167	2.758280	O	-4.304017	-0.261437	1.005257
C	0.117022	-1.891065	1.575496	H	-1.752574	-3.024599	4.175459
C	-1.528501	-0.674468	-2.838148	H	-4.749736	-0.072192	-3.752021
C	-2.641209	-0.508535	-3.653757	H	4.684474	0.838351	-3.947824
C	-3.885983	-0.225282	-3.114624	H	1.493373	2.833020	4.336564

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