

tural feature of these (TMPDO)₂TCNE arrays is rectangular four-site O–C binding at the TCNE olefinic carbon atoms, which appear to interact through their π^* lobes. The topological requirement for DA complexation at the N-oxide center is more flexible, allowing the formation of both ladder and web (cross-linked ladder) DA arrays in the (TMPDO)₂TCNE crystals as the N–O–C angle flexes.

Experimental Section

TMPDO (2.58 g, 69%, m.p. 498 K (493 K [22])) was prepared by treatment of 2,3,5,6-tetramethylpyrazine (2.95 g, Aldrich) in CH₂Cl₂ (50 mL) with potassium peroxomonosulfate (66.6 g, 5 equiv; OXONE, Aldrich) in H₂O (400 mL) with vigorous stirring at 298 K for 24 h. TCNE (Aldrich) was purified by multiple sublimation (373 K, 0.05 mmHg) through activated charcoal. Conditions for the Benesi–Hildebrand analysis: [TMPDO] = 1.90 mM; [TCNE] = 18.7, 34.0, 51.1, 66.4, 75.7, and 90.6 mM. Purple crystals of (TMPDO)₂TCNE were prepared by cooling a mixture of TMPDO (40 mM) and TCNE (20 mM) in CH₃CN to 253 K for 2–5 h. Red prismatic crystals of (TMPDO)₂TCNE were prepared analogously, after 2–3 d crystallization.

Crystal X-ray diffraction was performed on a Siemens SMART diffractometer with CCD area detection at 293 (purple [11]) and 173 K (red [13]) with monochromatic Mo_{K α} radiation ($\lambda = 0.71073 \text{ \AA}$). Solution and refinement (against $|F^2|$) were performed with SHELXTL. No absorption correction was employed. Hydrogen atoms were placed in calculated positions (0.95 \AA from the methyl carbon atom with tetrahedral angles). They were given torsional freedom and their thermal parameters were set to $1.2 \times U_{\text{eq}}$ of the bonded carbon atom. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-100438. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: int. code + (1223) 336-033; e-mail: deposit@chemcrs.cam.ac.uk). Powder Cu_{K α} X-ray spectra were obtained on a Rigaku powder diffractometer.

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[1] J.-M. Lehn, *Supramolecular Chemistry*, VCH, Weinheim, 1995.
[2] Reviews: a) G. R. Desiraju, *Crystal Engineering: The Design of Organic Solids*, Elsevier, Amsterdam, 1989; b) A. Gavezzotti, *Acc. Chem. Res.* 1994, 27, 309; c) *The Crystal as a Supramolecular Entity. Perspectives in Supramolecular Chemistry* (Ed.: G. R. Desiraju), Wiley, New York, 1996.
[3] D. S. Reddy, Y. E. Ovchinnikov, O. V. Shishkin, Y. T. Struchkov, G. R. Desiraju, *J. Am. Chem. Soc.* 1996, 118, 4085, and references therein.
[4] Reviews: a) H. A. Bent, *Chem. Rev.* 1968, 68, 587; b) R. S. Mulliken, W. B. Person, *Molecular Complexes: A Lecture and Reprint Volume*, Wiley-Interscience, New York, 1969; c) R. Foster, *Organic Charge-Transfer Complexes*, Academic Press, New York, 1969, chap. 8; d) F. H. Herstein, *Perspect. Struct. Chem.* 1971, 4, 166.
[5] S. C. Blackstock, K. Poehling, M. L. Greer, *J. Am. Chem. Soc.* 1995, 117, 6617.
[6] M. L. Greer, S. C. Blackstock, *J. Org. Chem.* 1996, 61, 7895.
[7] a) P. Bruni, C. Conti, E. Giorgini, G. Tosi, G. Marrosu, *Spectrochim. Acta Part A* 1991, 47, 665; b) A. V. Ryzhakov, L. L. Rodina, *Russ. J. Heterocycl. Chem.* 1991, 4, 386; c) P. Bruni, G. Tosi, L. Cardellini, E. Giorgini, P. Stipa, *Spectrochim. Acta Part A* 1989, 45, 519; d) A. V. Ryzhakov, V. V. Vapirov, L. L. Rodina, *Zh. Org. Khim.* 1991, 27, 955.
[8] The standard potential of TMPDO was determined by cyclic voltammetry to be 1.61 V versus SCE (0.1 M nBu₄NBF₄ in CH₂Cl₂).
[9] H. A. Benesi, J. H. Hildebrand, *J. Am. Chem. Soc.* 1949, 71, 2703.
[10] This value derives from a single Benesi–Hildebrand analysis with [TCNE] \gg [TMPDO], in which absorbances at 484, 504, 524, and 544 nm (with ϵ values of 1928, 2771, 2701, and 2371 M⁻¹ cm⁻¹, respectively) were monitored to calculate K_f on the assumption of 1:1 complexation.
[11] Crystal structure data for the purple crystal: dimensions: 0.30 × 0.55 × 0.70 mm; monoclinic, space group C2/c, $a = 15.7184(5)$, $b = 10.3443(3)$, $c = 14.2302(2) \text{ \AA}$, $\beta = 91.824(2)^\circ$, $V = 2312.6(1)$, $\rho_{\text{calcd}} = 1.334 \text{ g mL}^{-1}$; $2.36 \leq \theta \leq 27.86^\circ$; of 2738 unique data 1632 with $I > 2\sigma(I)$, 159 parameters; $R_1 = 0.054$, $wR_2 = 0.134$, GOF = 0.981. Several different purple crystals were analyzed at 293 and at 173 K. All gave the same unit cell.
[12] For van der Waals radii in crystals, see a) A. Bondi, *J. Phys. Chem.* 1964, 68, 441; b) R. S. Rowland, R. Taylor, *ibid.* 1996, 100, 7384.
[13] Crystal structure data for the red crystal: dimensions: 0.40 × 0.30 × 0.25 mm; monoclinic, space group P2₁/n, $a = 9.2619(4)$, $b = 9.8160(4)$, $c = 12.7949(5) \text{ \AA}$, $\beta = 99.590(1)^\circ$, $V = 1146.99(8)$, $\rho_{\text{calcd}} = 1.345 \text{ g mL}^{-1}$;

$2.53 \leq \theta \leq 27.91^\circ$; of 2634 unique data 1967 with $I > 2\sigma(I)$, 159 parameters; $R = 0.054$, $wR_2 = 0.123$, GOF = 1.133. Several different red crystals were analyzed, and all gave the same unit-cell parameters.
[14] Both the red and purple solids melt at 177–180 °C with decomposition.
[15] A 40 nm shift in the visible absorption of the red crystal is observed after heating the red solid to 90 °C for 20 min.
[16] Reviews of thermal solid-state transformations: a) I. C. Paul, D. Y. Curtin, *Acc. Chem. Res.* 1973, 6, 217; b) J. D. Dunitz, *Pure Appl. Chem.* 1991, 63, 177.
[17] A differential scanning calorimetric (DSC) scan of the red polymorph shows an endotherm (13.16 J g⁻¹) at 376 K corresponding to the lattice transition. This transition is not observed for the purple polymorph.
[18] Average intraweb (red) and intraladder (purple) TCNE–TCNE distances (olefin C-to-C) are 9.9 and 10.5 \AA , respectively.
[19] Distances between TMPDO oxygen atoms at a single TCNE are 3.97 (1,2) and 4.97 \AA (1,1) in the red crystal, and 3.67 and 5.19 \AA in the purple crystal.
[20] Precedence for this type of NO...C interaction is found in azooxide–TCNE complexes of ref. [5,6]. Such interactions appear to be general as indicated by their occurrence in the crystal structures of phenazine-*N,N'*-dioxide/TCNE and 2,3-dimethylquinoxaline-*N,N'*-dioxide/TCNE (to be reported elsewhere).
[21] A Cambridge Structure Database (edition December 1996) search of crystal structures with NO...C interactions, O–C distances of 2.0–3.0 \AA and O–C–C angles of 80–140° yielded 25 structures (excluding the azooxide complexes mentioned above), all of which involve nitrate or nitro oxygen donors and (in all but one case) arene acceptors with O–C contacts of 2.89–3.00 \AA . Of the 25 structures found, 14 contain metal-coordinated donor and/or acceptor groups.
[22] G. A. Tolstikov, U. M. Jemilev, V. P. Jurjev, F. B. Gershanov, S. R. Rafikov, *Tetrahedron Lett.* 1971, 30, 2807.

In Search of Molecular Ratchets**

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The creation and the control of movement are fundamental aspects of dynamics on both macroscopic and microscopic levels. Much current interest is focused on constructing molecular scale analogues of macroscopic devices, in part because of the intellectual challenge, but also because of their potential applications in nanotechnology.^[1] We now report the results of an effort to synthesize the first molecular ratchets. The work was undertaken partly as a result of a continuing^[1a] interest in molecular devices, but it also serves to demonstrate that macro-mechanical principles do not always transfer to the molecular scale.

In their simplest form, ratchets consist of three components (Figure 1): a) a toothed ratchet wheel, b) a pawl that prevents unintended rotation of the ratchet wheel, and c) a spring that holds the pawl in place. Both the tension of the spring and the contours of the ratchet wheel and pawl determine the ease (and direction) of rotation.

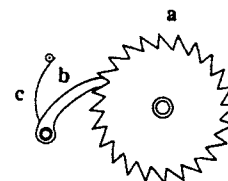
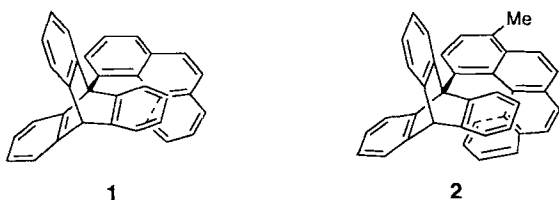


Figure 1. A simple ratchet: a) toothed wheel, b) pawl, c) spring.

In the present instance a triptycene^[2] was chosen as the ratchet wheel and helixenes^[3] as the pawls and springs. The two molecular “ratchets” are 1^[4] and 2. Molecular modeling calcu-

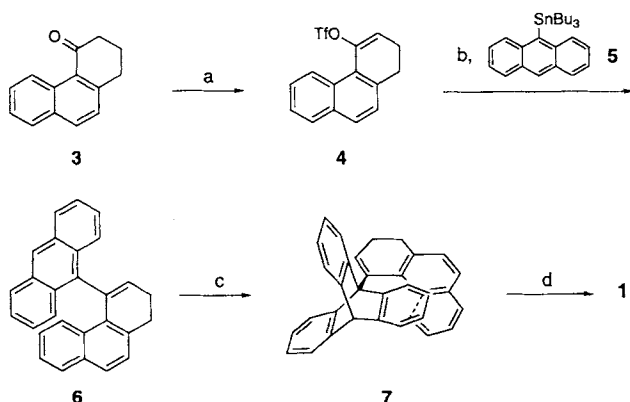
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lations^[5] indicated unexpectedly—at least to us—that the [3]helicene spring and pawl in **1** present a greater barrier to rotation (ΔH calculated to be 27 kcal mol⁻¹) than the [4]helicene in **2** ($\Delta H = 22$ kcal mol⁻¹).

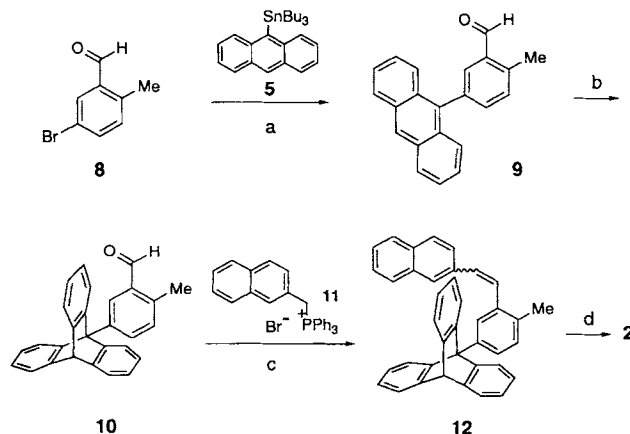
Compound **1** was prepared from the known ketone **3** (Scheme 1).^[6] Conversion of **3** to the enol triflate **4** and palladium-catalyzed coupling with anthracenyl stannane **5**^[1a] gave **6**.^[7]



Scheme 1. a) $(F_3CSO_2)_2O$, 2,6-lutidine, CH_2Cl_2 , 0 °C, 77%; b) $[Pd(PPh_3)_4]$, LiCl, dioxane, 120 °C, sealed tube, 3 d, 55%; c) benzyne, dioxane, reflux; d) 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), C_6H_6 , reflux, 53% (overall yield for steps c and d).

Addition of benzyne^[8] across the 9,10 positions of the anthracene in **6** generated the triptycene unit **7**; dehydrogenation^[9] of **7** completed the synthesis.^[10]

Compound **2** was synthesized by the route in Scheme 2. Palladium-catalyzed coupling of bromoaldehyde **8**^[11] with stannane **5** gave **9**, which was converted into triptycene **10** by addition of benzyne.^[8] Wittig reaction of the aldehyde group in **10** with the ylide from **11**^[12] delivered an *E/Z* mixture of stilbenes **12**. Irradiation^[3, 13, 14] through Pyrex of a benzene solution of **12** with a medium pressure (100 W) mercury lamp under argon in the presence of I_2 (1 equiv) and excess propylene oxide generated



Scheme 2. a) $[Pd(PPh_3)_2]Cl_2$, dioxane, 130 °C, sealed tube, 60 h, 60%; b) benzyne, dioxane, reflux, 68%; c) *n*-BuLi, THF, -78 °C, 84%; d) *hν*, 54%.

2^[15] in 54% yield. The methyl group blocks photocyclization in the undesired, but otherwise less hindered direction.

The ¹H NMR spectra of **1** and **2** indicate that at room temperature rotation around the triptycene/helicene bond is frozen in both compounds, but that the topology of the two is distinctly different. In particular, the ¹H NMR spectrum of **1** reveals a plane of symmetry; two (but not all three) of the rings of the triptycene unit are equivalent. The phenanthrene component of **1** is therefore either planar or exists as a rapidly racemizing mixture of two helical enantiomers.^[4] Even at 160 °C, ¹H NMR spin polarization transfer experiments^[16] reveal no detectable rotation within two seconds of polarization, which indicates a barrier (ΔG^\ddagger) to rotation in excess of 27 kcal mol⁻¹.

The ¹H NMR spectrum of **2** recorded at room temperature reflects an absence of symmetry; all three rings of the triptycene are nonequivalent. At 160 °C, however, peak-broadening of triptycene (but not helicene) resonances indicates slow rotation. Extrapolation, based on analogy to our earlier work,^[1a] suggests a coalescence temperature of about 220 °C, which corresponds to $\Delta G^\ddagger \approx 25$ kcal mol⁻¹, a value that is corroborated by the studies described below, and which is reassuringly close to the calculated barrier (ΔH^\ddagger not ΔG^\ddagger) of 22 kcal mol⁻¹. We suggest that the barrier to rotation in **2** is smaller than in **1** because in **2** the interaction between the one-ring-longer helicene and the blade of the triptycene prevents the molecule from relaxing to as stable a ground state conformation (relative to the energy maximum) as is accessible to **1**.

The remaining question is whether **2** functions as a ratchet; that is, whether rotation of the triptycene is uni- or bidirectional. Given the helicity of the [4]helicene in **2**, it is not surprising that the calculated^[5] energy diagram (Figure 2) for rotation around the triptycene/[4]helicene bond in **2** is decidedly asymmetric. Clockwise rotation ($\alpha = 0 \rightarrow 120^\circ$) has a more gradual energetic slope than counterclockwise rotation ($\alpha = 120 \rightarrow 0^\circ$).

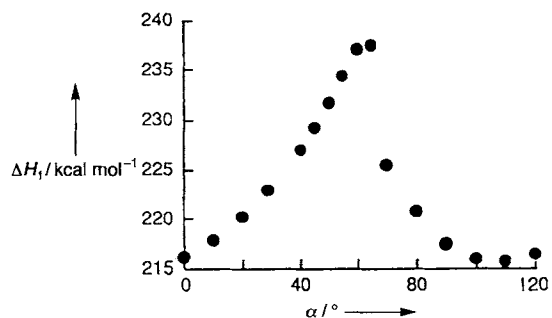


Figure 2. Calculated energy diagram (AM1 [5]) for rotation around the triptycene/[4]helicene bond. Clockwise rotation of the triptycene in **2** corresponds to a rotation from $\alpha = 0$ to $\alpha = 120^\circ$.

One should be able to establish the direction of rotation of the triptycene in **2** by using isotopically labeled rotamers of **2**, but their synthesis, rotamer separation, and structure determination would be very laborious. Fortunately, the spin polarization transfer NMR technique^[16] affords the same information at a small fraction of the effort. In short, if a system is conformationally mobile, but that mobility is slow on the NMR time scale, the spin of a slowly conformationally mobile atom can be polarized, and after an appropriate time an assay will show where (if anywhere) that polarization has moved to.

In the present case in which a single rotamer has an experimentally determined half-life of about 0.17 sec at 160 °C, the barrier (ΔG^\ddagger) to rotation is approximately 24.5 kcal mol⁻¹. Thus, if one selectively polarizes one of the three H_a , H_b , and H_c protons (see **13** in Figure 3) and—after appropriate time de-

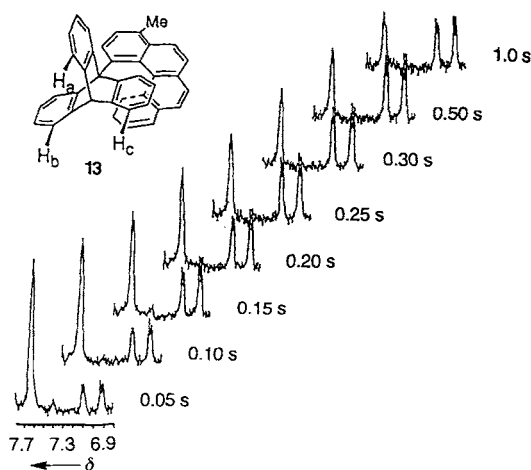


Figure 3. Results of spin polarization transfer experiment in $[D_6]DMSO$ at $160^\circ C$ (calibrated temperature). The resonances for H_a , H_b , and H_c (see **13**) appear at $\delta = 7.6, 7.1,$ and 6.9 (not necessarily respectively). The spin of the proton resonating at $\delta = 7.6$ was polarized, and transfer of that polarization was monitored over time.

lays—assays for the location of that polarization, a clearcut distinction between predominantly unidirectional rotation and bidirectional rotation is available. In the first case, a disproportionate share of the polarization that has moved should be transferred to a resonance for only one of the two other protons. In the second case, the polarization that moves should be transferred equally to the remaining two resonances.

Spin polarization of one (see **13**) of the three H_x protons in **2** was achieved with a selective 180° -pulse–delay–observe sequence. As is evident from Figure 3, the triptycene rotates clockwise and counterclockwise to the same extent. Control experiments polarizing the spin of each of the other two H_x protons gave equivalent results.^[17] The asymmetry of the rotational energy curve in Figure 2 is thus deceptive: In contrast to mountain climbing, it is only the height of the summit, not the steepness of the terrain that matters. The chemical principle of microscopic reversibility prevails.

The current study also provides experimental corroboration of a theoretical, thermodynamic analysis of a ratchet and pawl by the physicist Richard Feynman.^[18]

In conclusion, the synthesis of triptycene[4]helicene **2** successfully incorporates into a single molecule the essential components of a simple ratchet: the asymmetric combination of a ratchet wheel, a pawl, and a spring. Tantalizing as models of **2** are, the experimental demonstration that **2** rotates equally in both directions illustrates the perils of extrapolating from macroscopic to molecular scales. It follows that molecular units such as **2** cannot by themselves be used to induce unidirectional rotation in an isothermal environment. Nonetheless, their ability to modulate the barrier to free rotation should make them useful components of more complex systems such as molecular motors and machines.

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[1] a) For the report of a molecular brake from this laboratory see T. R. Kelly, M. C. Bowyer, K. V. Bhaskar, D. Bebbington, A. Garcia, F. Lang, M. H. Kim, M. P. Jette, *J. Am. Chem. Soc.* **1994**, *116*, 3657–3658. For leading references to other studies see b) T. C. Bedard, J. S. Moore, *ibid.* **1995**, *117*, 10662–10671; c) J. Rebek, Jr., *Acc. Chem. Res.* **1984**, *17*, 258–264; d) K. Mislow, *Chemtracts: Org. Chem.* **1989**, *2*, 151–174; e) H. Iwamura, K. Mislow, *Acc. Chem. Res.*

1988, *21*, 175–182; f) D. H. Evans, A. Fitch, *J. Am. Chem. Soc.* **1984**, *106*, 3039–3041; g) R. Ballardini, V. Balzini, A. Credi, M. T. Ganfoli, S. J. Langford, S. Menzer, L. Prodi, J. F. Stoddart, M. Venturi, D. J. Williams, *Angew. Chem.* **1996**, *108*, 1056–1059; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 978–981; h) K. V. Kilway, J. S. Siegel, *J. Am. Chem. Soc.* **1991**, *113*, 2332–2333; i) N. P. M. Huck, W. F. Jager, B. de Lange, B. L. Feringa, *Science* **1996**, *273*, 1686–1688; j) M. Jorgenson, K. Lerstrup, P. Frederiksen, T. Bjornholm, P. Sommer-Larsen, K. Schaumburg, K. Brunfeldt, K. Bechgaard, *J. Org. Chem.* **1993**, *58*, 2785–2790; k) R. M. Metzger, C. A. Panetta, *New. J. Chem.* **1991**, *15*, 209–221; l) A. C. Benniston, A. Harriman, *Angew. Chem.* **1993**, *105*, 1553–1555; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1459–1461.

[2] Review: V. R. Skvarchenko, V. K. Shalaev, E. I. Klabunovskii, *Russ. Chem. Rev.* **1974**, *43*, 951–966.

[3] Reviews of helicene chemistry: a) R. H. Martin, *Angew. Chem.* **1974**, *86*, 627–638; *Angew. Chem. Int. Ed. Engl.* **1974**, *13*, 649–660; b) W. H. Laarhoven, W. J. C. Prinsen, *Top. Curr. Chem.* **1984**, *125*, 63–130; c) K. P. Meurer, F. Vögtle, *ibid.* **1985**, *127*, 1–76. Some more recent references: d) N. D. Willmore, L. Liu, T. J. Katz, *Angew. Chem.* **1992**, *104*, 1082–1083; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 1093–1094; e) R. H. Janke, G. Haufe, E. Würthwein, J. H. Borkent, *J. Am. Chem. Soc.* **1996**, *118*, 6031–6035.

[4] Although the parent phenanthrene itself is planar, calculations [5] indicate that the phenanthrene ring system in **1** is helical. For the discussion of another helical phenanthrene, see E. L. Eliel, S. H. Wilen, *Stereochemistry of Organic Compounds*, Wiley, New York, **1994**, p. 1163.

[5] Calculations (AM1) were carried out with the coordinate drive feature of the Spartan molecular modeling program (Wavefunction, Inc., Irvine, CA), Version 4.0, on a Silicon Graphics workstation.

[6] S. Huggenberg, M. Hesse, *Helv. Chem. Acta* **1980**, *63*, 2295–2301.

[7] J. K. Stille, *Angew. Chem.* **1986**, *98*, 504–520; *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 508–524.

[8] F. M. Logullo, A. H. Seitz, L. Friedman, *Org. Synth. Coll. Vol. 5* **1973**, 54–59.

[9] M. Tashiro, T. Yamato, K. Kobayashi, T. Arimura, *J. Org. Chem.* **1987**, *52*, 3196–3199.

[10] **1**: M.p. 316–317°C; 1H NMR ($CDCl_3$, 400 MHz): $\delta = 8.38$ (d, $J = 8.0$ Hz, 1H), 8.06 (d, $J = 8.0$ Hz, 1H), 7.87–7.80 (m, 2H), 7.75 (d, $J = 8.4$ Hz, 1H), 7.72 (d, $J = 8.0$ Hz, 1H), 7.56–7.54 (m, 1H), 7.50 (d, $J = 7.6$ Hz, 2H), 7.35–7.33 (m, 1H), 7.21 (d, $J = 8.8$ Hz, 1H), 7.17 (t, $J = 7.3$ Hz, 1H), 7.00–6.96 (m, 2H), 6.89–6.86 (m, 2H), 6.79 (d, $J = 7.6$ Hz, 2H), 6.59–6.55 (m, 2H), 6.38–6.34 (m, 1H), 5.46 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = 150.2, 148.7, 145.3, 144.1, 134.6, 134.0, 133.7, 132.2, 131.7, 131.6, 131.5, 130.6, 128.9, 127.5, 127.1, 126.9, 125.9, 125.3, 124.9, 124.7, 124.6, 124.1, 123.5, 123.3, 122.0, 63.5, 55.2$ (two peaks are coincident); LR-MS (EI, 70 eV): m/z (%): 431 (45, $[M+H]^+$), 430 (100, M^+), 253 (21), 252 (30); HR-MS (EI): calcd: for $C_{34}H_{22}$: 430.1721, found: 430.1721.

[11] I. Stoilov, D. S. Watt, J. P. Goodman, J. S. Pyrek, *J. Heterocycl. Chem.* **1993**, *30*, 1645–1651.

[12] J. P. Geerts, R. H. Martin, *Bull. Soc. Chim. Belg.* **1960**, *60*, 563–569.

[13] F. B. Mallory, C. W. Mallory, *Org. React.* **1984**, *30*, 1–456.

[14] L. Lui, B. Yang, T. J. Katz, M. K. Poindexter, *J. Org. Chem.* **1991**, *56*, 3769–3775.

[15] **2**: M.p. 310°C; 1H NMR ($CDCl_3$, 300 MHz): $\delta = 8.43$ (m, 1H), 8.33 (d, $J = 8.4$ Hz, 1H), 8.23 (d, $J = 7.2$ Hz, 1H), 7.96 (d, $J = 7.5$ Hz, 1H), 7.87 (t, $J = 8.4$ Hz, 2H), 7.76 (d, $J = 8.1$ Hz, 1H), 7.75 (d, $J = 8.4$ Hz, 1H), 7.57 (m, 1H), 7.35 (m, 3H), 7.05 (dd, $J = 7.2, 1.5$ Hz, 1H), 6.88 (dd, $J = 7.6, 1.2$ Hz, 1H), 6.82 (t, $J = 7.8$ Hz, 1H), 6.61 (dq, $J = 7.5, 1.8$ Hz, 2H), 6.48 (d, $J = 8.0$ Hz, 1H), 6.38 (dt, $J = 7.2, 1.2$ Hz, 1H), 5.92 (dt, $J = 7.8, 1.2$ Hz, 1H), 5.87 (d, $J = 7.8$ Hz, 1H), 5.79 (dt, $J = 7.8, 1.2$ Hz, 1H), 5.10 (s, 1H), 3.00 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = 151.9, 150.4, 147.0, 145.2, 143.8, 143.6, 137.3, 134.9, 134.4, 133.2, 131.5, 130.9, 130.8, 130.4, 129.9, 129.7, 127.9, 127.6, 126.4, 126.2, 126.1, 126.0, 125.9, 125.6, 125.5, 124.6, 124.2, 124.0, 124.0, 123.9, 123.9, 123.5, 123.1, 122.7, 122.2, 65.8, 55.8, 20.6$; LR-MS (EI, 70 eV): m/z (%): 496 (M^+ , 87), 252 ($[M - triptyceny]^+$, 100); HR-MS (EI): calcd for $C_{39}H_{26}$: 494.2030, found: 494.2034; elemental analysis calcd. for $C_{39}H_{26}$: C 94.70, H 5.30; found: 94.80, 5.13.

[16] Leading references to the spin polarization transfer method: F. W. Dahlquist, K. J. Longmur, R. B. Du Vernet, *J. Magn. Reson.* **1975**, *17*, 406–410; R. Frim, G. Zilber, M. Rabinovitz, *J. Chem. Soc. Chem. Commun.* **1991**, 1202–1203; A. H. Abdourazak, A. Sygula, P. W. Rabideau, *J. Am. Chem. Soc.* **1993**, *115*, 3010–3011. For a more general review of the application of 2D NMR spectroscopy to the kinetics of exchange processes, see: C. L. Perrin, T. J. Dwyer, *Chem. Rev.* **1990**, *90*, 935–967.

[17] The experiment distinguishes between rotation of the triptycene and racemization of the helicene. Racemization would not transfer polarization to both other resonances. Note that it is not necessary to resolve **2** to carry out the NMR experiments because the NMR spectra of enantiomers are identical in an achiral environment.

[18] R. P. Feynman, R. B. Leighton, M. Sands, *The Feynman Lectures on Physics, Vol. 1*, Addison-Wesley, Reading, MA, USA, **1963**, chap. 46.