Chiral Circulenoid

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A Chiral Dicationic [8]Circulenoid: Photochemical Origin and Facile Thermal Conversion into a Helicene Congener**

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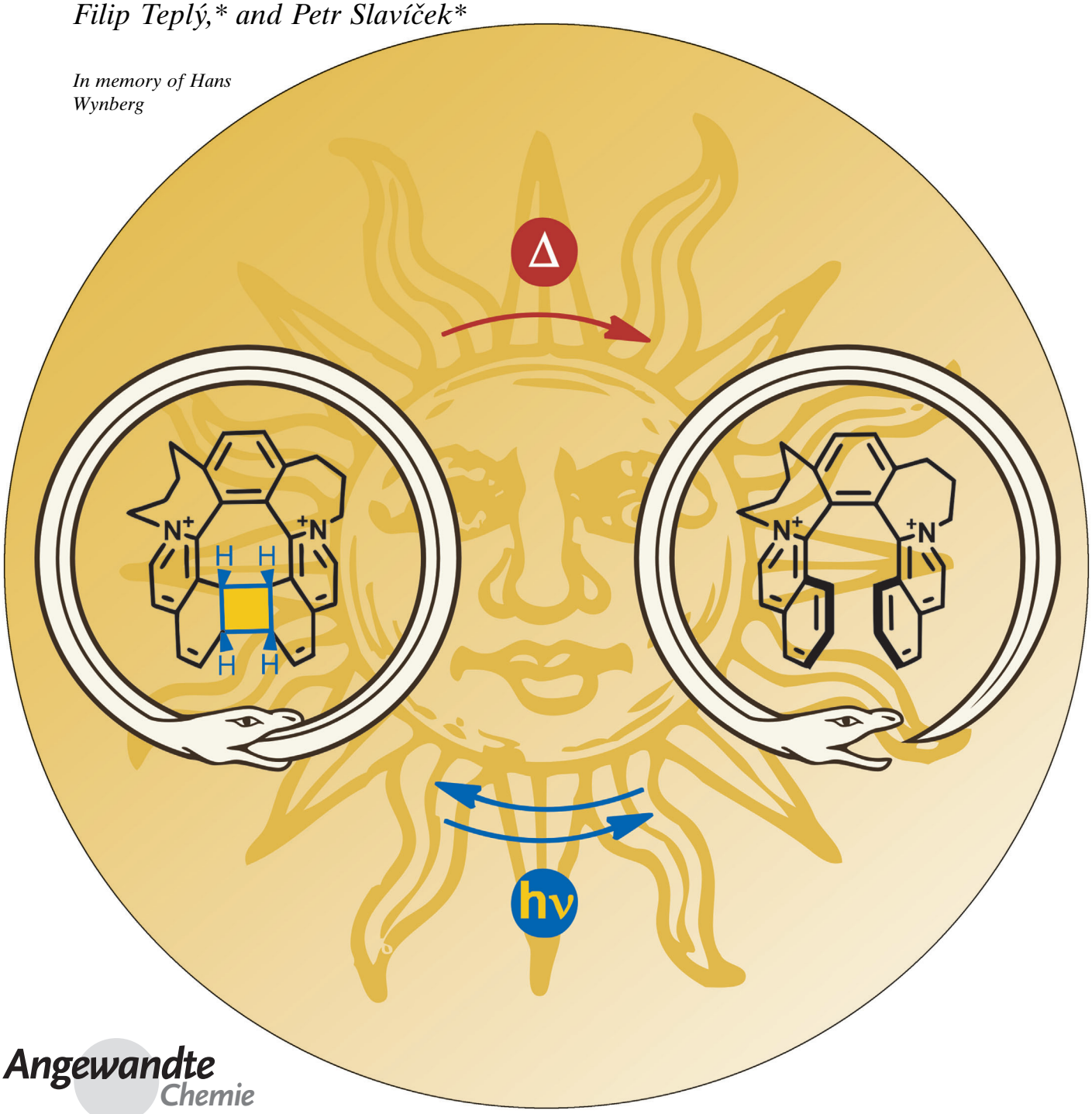
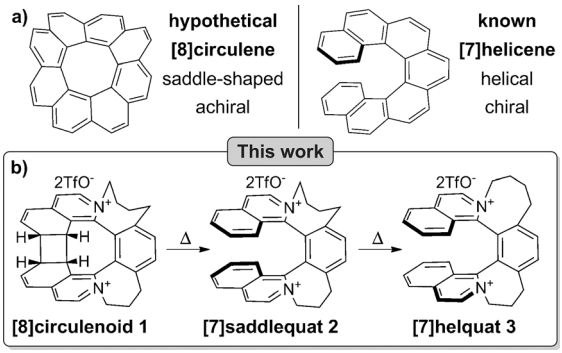
In memory of Hans Wynberg



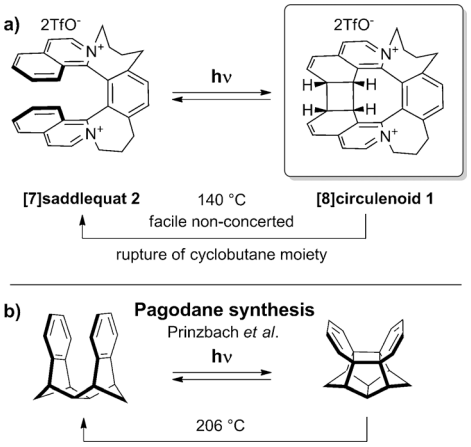
Circulenes were defined by Wynberg[1] as systems comprising aromatic or similar rings fused to each side of a polygon.[2–5] For example, [8]circulene has eight benzene units annelated around a central eight-membered ring (Scheme 1 a). Circulenes have been studied because of their unique 3D structures, their dynamics,[6] and their role as models of larger carbon-rich molecules with curved surfaces, which are important for materials chemistry.[7]



Scheme 1. a) Structural relationship between the hypothetical [8]circulene and the known [7]helicene. b) Thermal transformation of [8]circulenoid **1** into [7]helquat **3** by the [7]saddlequat **2** presented herein.

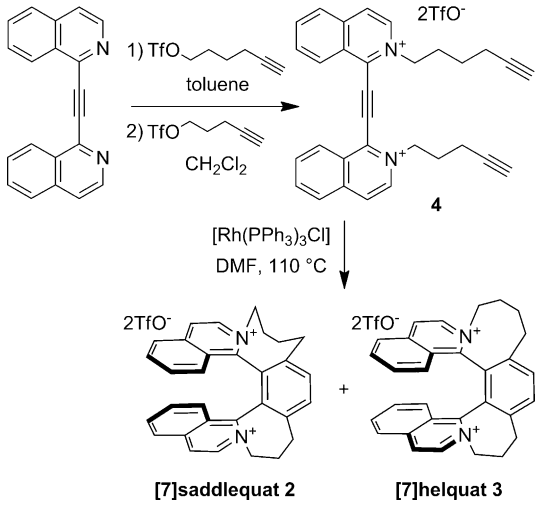
Saddle-shaped [8]circulene is a hypothetical molecule[8] bearing a structural relationship to the known [7]helicene[9] that also has a distorted nonplanar shape (Scheme 1 a). Significant structural similarity between helicenes and circulenes has been explicitly discussed in the seminal report by Wynberg et al. in 1972.[1,10] However, no direct transformation of a circulene into its helical counterpart has been reported to date.

Herein, we describe the synthesis, the structure, and the properties of the chiral dicationic circulene-like species **1** with eight cycles arranged around a central eight-membered ring (Scheme 1 b). The photochemical route to this [8]circulenoid[11] with a highly annelated cyclobutane moiety (Scheme 2 a, **2**→**1**) and its facile thermal transformation into the [7]helicene-like compound **3** is introduced (**1**→**2**→**3**, Scheme 1 b). This is the first time a circulene-like species has been transformed into its helical counterpart by simple heating.



Scheme 2. a) Upon irradiation, [7]saddlequat **2** gives rise to [8]circulenoid **1**. The reverse reaction occurs thermally by a stepwise mechanism. b) Key photochemical reaction in Prinzbach's synthesis of pagodane[26] is a process related to the title reaction **2**→**1**.

Recently, we introduced helquats,[12] which are helical dications that are a structural link between helicenes and viologens. We also reported a [6]saddlequat that can be viewed as a [6]helquat captured on the racemization pathway in a saddle-shaped geometry.[13] By taking advantage of a highly flexible two-step quaternization,[12b,13a] we accessed triyne **4** (Scheme 3). Kinetically controlled, $[Rh(PPh_3)_3Cl]$-



Scheme 3. Synthetic route to [7]saddlequat **2** that is a precursor to [8]circulenoid **1**. For full experimental data, see the Supporting Information.

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catalyzed [2+2+2] cycloaddition[14,15] leads to [7]saddlequat **2** as well as [7]helquat **3**.[16,17] Next, we established that pure [7]saddlequat **2** can be obtained as a solid by repeated trituration of the mixture of **2** and **3** with small amounts of acetone, which selectively dissolves **3**. By employing this simple, non-chromatographic procedure, 150 mg of [7]saddlequat **2** were prepared in just three synthetic operations in overall 20% yield.[17]

During our studies we noted that samples of saddlequat **2** gave rise to a new species **1** upon exposure to sunlight (Scheme 2a).[18] Capillary electrophoretic (CE) analysis with sulfated γ-cyclodextrin as a chiral selector[19] indicated that this new species exhibits chirality and is produced as a racemate starting from racemic saddlequat **2** (Figure 1). Irradiating an acetone solution of *rac*-**2** with a household light bulb[20] led to a photostationary mixture of *rac*-**2** and *rac*-**1** favoring the latter species (ratio of up to 1:2.4).[21] The solubility difference between *rac*-**1** and saddlequat *rac*-**2** in ethanol allowed the isolation of compound *rac*-**1** (top trace in Figure 1). Evidence for **1** having a cyclobutane moiety was deduced from ^{13}C, ^{1}H, HSQC, HMBC, COSY, and ROESY NMR spectra and was unambiguously confirmed by X-ray analysis (Figure 2).[17]

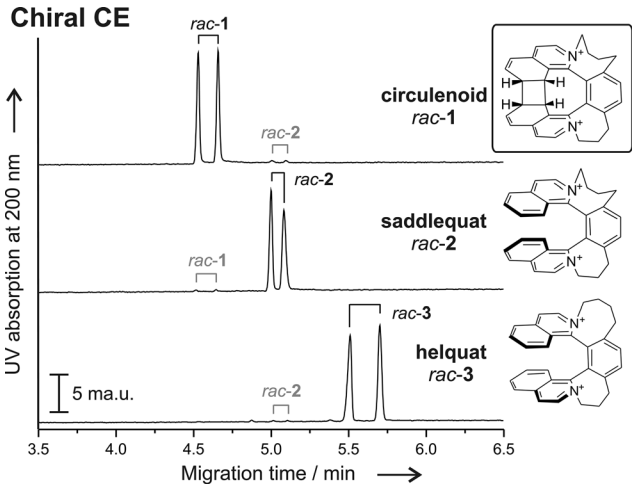


Figure 1. All three species **1**, **2**, and **3** can be isolated as pure compounds. These species are chiral entities generated in racemic form as evidenced by chiral CE analysis with sulfated γ-cyclodextrin selector. For experimental details, see the Supporting Information.

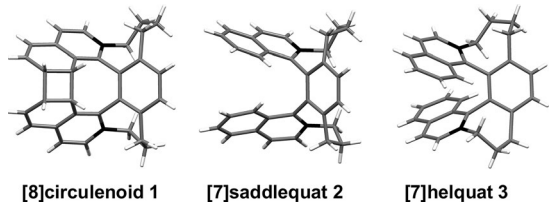


Figure 2. X-ray crystal structures of [8]circulenoid **1**, [7]saddlequat **2**, and [7]helquat **3** obtained after crystallization of the corresponding racemates. Triflate anions are omitted for clarity. For details, see the Supporting Information.

The photochemical[22] transformation **2**→**1** has a relation to several other processes. One of them is the formation of thymine dimer[23] in solar damage of DNA. Other related intramolecular photocycloadditions of two aromatic moieties have been investigated in the context of synthesis of complex hydrocarbon cages, such as prismanes and pagodanes.[24,25] In their landmark work, the Prinzbach,[25] and Misumi[26] groups introduced conformationally restricted species that undergo intramolecular [6+6] photocycloadditions of two benzene moieties (for example, Scheme 2b).[27,28] However, photochemical strategies have never been used for the synthesis of circulene structures.[29]

Theoretical investigations of the photochemistry of the saddlequat/circulenoid (Supporting Information, Scheme S4) predict a nearly barrierless pathway connecting the excited state of saddlequat **2** with the ground state of circulenoid **1**. Likewise, a barrierless pathway connects the excited state of **1** with ground state **2**. The calculations thus suggest a photostationary state upon irradiation with soft UV light. Occurrence of the photochemical reaction in the singlet manifold is consistent with a high quantum yield for the transformation **2**→**1** ($\Phi = 0.19$ in D_2O, $\lambda = 366$ nm).[30]

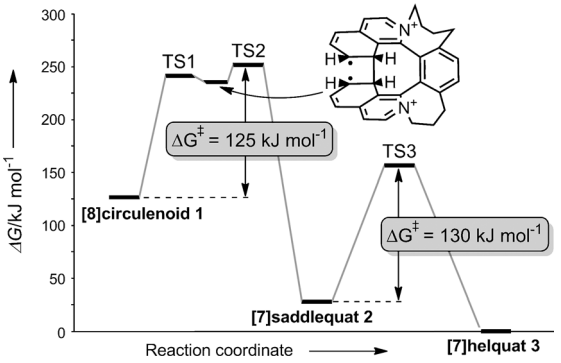
While circulenoid **1** is thermally stable under ambient conditions, we turned our attention to its thermal ring-opening at elevated temperatures. Experimentally, the rupture of the cyclobutane moiety in circulenoid **1** takes place at 140 °C in [D_6]DMSO with a half-life of 9 min ($\Delta G^{\neq} = 125\ kJ\,mol^{-1}$). This process is much more facile than the analogous process in the parent cyclobutane (C_4H_8), which has activation energy of $262\ kJ\,mol^{-1}$, and thus higher temperatures are required.[31]

At 140 °C, the thermal rupture of the cyclobutane moiety in circulenoid **1** leading to saddlequat **2** is followed by saddlequat **2**→helquat **3** isomerization. Kinetic data from the combined thermal process **1**→**2**→**3** obtained by CE (Supporting Information, Scheme S1) were analyzed (Supporting Information, Figure S1). This way, the two-step transformation has been dissected to extract two similar activation free-energy values of $125\ kJ\,mol^{-1}$ for circulenoid opening **1**→**2** (see above) and $130\ kJ\,mol^{-1}$ for saddlequat to helquat isomerization **2**→**3**.

The cyclobutane product should be thermally stable from the perspective of Woodward–Hoffman rules. Indeed, if we consider a concerted mechanism of the cyclobutane ring lesion (represented by the photochemical pathway), the energy needed for the lesion is higher than $200\ kJ\,mol^{-1}$ (calculated at B97D/6-31 g* level[32] with Gaussian 09;[33] Supporting Information, Scheme S4). We have thus examined a two-step mechanism where two cyclobutane C–C bonds are broken consecutively. Such a mechanism is operative for the parent cyclobutane C_4H_8 itself.[34] The intermediate structure (tetramethylene for the parent cyclobutane) probably forms a shallow minimum and we were able to localize the minimum at the DFT/BMK level,[35] while the DFT/B97D method fails to find this structure.[36] The activation energy for the consecutive mechanism was estimated to be $138\ kJ\,mol^{-1}$ at the DFT/B97D level. This is in fair agreement with the experimentally observed activation energy of $125\ kJ\,mol^{-1}$.

The energetic relationships relevant for the combined thermal process **1**→**2**→**3** are summarized in Scheme 4.

In summary, this study introduces the [8]circulenoid **1** and its thermal transformation into [7]helquat **3**. This is the first



Scheme 4. Energy diagram showing the barriers for two thermal processes (125 kJ mol^{-1} for **1**→**2** and 130 kJ mol^{-1} for **2**→**3** at 140 °C) and the calculated structure of biradical intermediate connecting **1** and **2**. $\Delta G^{\ddagger}$ values were determined experimentally and the energies were calculated at B97D/6-31g* level.

time a circulene-like species has been transformed into its helical counterpart exclusively by application of heat. The present results are significant from several further perspectives: 1) no nitrogen-based cationic circulenes have been reported before; 2) a rare saddle-shaped circulene system with order higher than [7] is presented; and 3) the synthetic sequence to the chiral [8]circulenoid **1** by [6+6] photocycloaddition is particularly succinct as it requires only five steps and no chromatographic purification. In this context, it is notable that photochemical strategies towards circulenes have remained overlooked so far, although the photocyclization approach to helicenes introduced by Martin has become widespread.[9,37] The chirality, other properties of species **1** and **2**, and opportunities for molecular recognition are subject of ongoing research.

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[1] a) J. H. Dopper, H. Wynberg, *Tetrahedron Lett.* **1972**, *13*, 763; b) H. Christoph, J. Grunenberg, H. Hopf, I. Dix, P. G. Jones, M. Scholtissek, G. Maier, *Chem. Eur. J.* **2008**, *14*, 5604.

[2] For the pioneering synthesis of bowl-shaped [5]circulene (corannulene), the first non-planar member of the circulene family, see: a) W. E. Barth, R. G. Lawton, *J. Am. Chem. Soc.* **1966**, *88*, 380; for a review, see: b) Y.-T. Wu, J. S. Siegel, *Chem. Rev.* **2006**, *106*, 4843.

[3] For the pioneering syntheses of saddle-shaped hydrocarbon [7]circulene, see: a) K. Yamamoto, T. Harada, M. Nakazaki, T. Nakao, Y. Kai, S. Harada, N. Kasai, *J. Am. Chem. Soc.* **1983**, *105*, 7171; b) K. Yamamoto, *Pure Appl. Chem.* **1993**, *65*, 157; c) K. Yamamoto, H. Sonobe, H. Matsubara, M. Sato, S. Okamoto, K. Kitaura, *Angew. Chem.* **1996**, *108*, 69; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 69.

[4] For overviews including saddle-shaped circulenes, see: a) H. Hopf, *Classics in Hydrocarbon Chemistry*, Wiley-VCH, Weinheim, **2000**, p. 330; b) J. S. Siegel, T. J. Seiders, *Chem. Br.* **1995**, *31*, 313.

[5] For heterocyclic circulenes of interest for materials chemistry, see: K. Y. Chernichenko, V. V. Sumerin, R. V. Shpanchenko, E. S. Balenkova, V. G. Nenajdenko, *Angew. Chem.* **2006**, *118*, 7527; *Angew. Chem. Int. Ed.* **2006**, *45*, 7367; for seminal reports, see: Ref. [1a] and J. H. Dopper, H. Wynberg, *J. Org. Chem.* **1975**, *40*, 1957.

[6] For the dynamics of [5]circulene, see: a) L. T. Scott, M. M. Hashemi, M. S. Bratcher, *J. Am. Chem. Soc.* **1992**, *114*, 1920; b) A. Borchardt, A. Fuchicello, K. V. Kilway, K. K. Baldridge, J. S. Siegel, *J. Am. Chem. Soc.* **1992**, *114*, 1921; c) T. J. Seiders, K. K. Baldridge, G. H. Grube, J. S. Siegel, *J. Am. Chem. Soc.* **2001**, *123*, 517; d) D. Eisenberg, A. S. Filatov, E. A. Jackson, M. Rabinovitz, M. A. Petrukhina, L. T. Scott, R. Shenhar, *J. Org. Chem.* **2008**, *73*, 6073; for the dynamics of [7]circulene, see: e) M. Shen, I. S. Ignatyev, Y. Xie, H. F. Schaefer III, *J. Phys. Chem.* **1993**, *97*, 3212.

[7] a) S. Iijima, T. Ichihashi, Y. Ando, *Nature* **1992**, *356*, 776; b) J.-C. Charlier, *Acc. Chem. Res.* **2002**, *35*, 1063; c) Y.-Z. Tan, et al., *Nat. Commun.* **2011**, *2*, 420; d) Bharat, R. Bhola, T. Bally, A. Valente, M. K. Cyrański, Ł. Dobrzycki, S. M. Spain, P. Rempała, M. R. Chin, B. T. King, *Angew. Chem.* **2010**, *122*, 409; *Angew. Chem. Int. Ed.* **2010**, *49*, 399, and references therein; e) A. Sygula, P. W. Rabideau in *Carbon-Rich Compounds: From Molecules to Materials* (Eds.: M. M. Haley, R. R. Tykwinski), Wiley-VCH, Weinheim, **2006**, p. 529; f) X. Lu, Z. Chen, *Chem. Rev.* **2005**, *105*, 3643; g) V. M. Tsefrikas, L. T. Scott, *Chem. Rev.* **2006**, *106*, 4868; h) B. D. Steinberg, L. T. Scott, *Angew. Chem.* **2009**, *121*, 5504; *Angew. Chem. Int. Ed.* **2009**, *48*, 5400.

[8] R. Salcedo, L. E. Sansores, A. Picazo, L. Sansón, *J. Mol. Struct. (Theochem)* **2004**, *678*, 211; T. N. Gribanova, N. S. Zefirov, V. I. Minkin, *Pure Appl. Chem.* **2010**, *82*, 1011.

[9] For selected reviews on helicenes, see: Y. Shen, C.-F. Chen, *Chem. Rev.* **2012**, *112*, 1463; A. Rajca, M. Miyasaka in *Functional Organic Materials* (Eds.: T. J. J. Müller, U. H. F. Bunz), Wiley-VCH, Weinheim, **2007**, p. 543; A. Urbano, *Angew. Chem.* **2003**, *115*, 4116; *Angew. Chem. Int. Ed.* **2003**, *42*, 3986; T. J. Katz, *Angew. Chem.* **2000**, *112*, 1997; *Angew. Chem. Int. Ed.* **2000**, *39*, 1921; Ref. [4a], p. 323.

[10] The term closed helicene has been also used as an alternative for circulene (see Ref. [3b]); for a discussion of Wynberg's dehydrohelicenes and a definition of quasi-[m]circulenes, see: A. Rajca, M. Miyasaka, S. Xiao, P. J. Boratyn'ski, M. Pink, S. Rajca, *J. Org. Chem.* **2009**, *74*, 9105.

[11] We use the word circulenoid to differentiate **1** from the circulenes that are without a break in conjugation. In this case, a suffix -oid is used according to the convention codified in Merriam–Webster's Collegiate dictionary: -oid noun suffix: something resembling a (specified) object or having a (specified) quality, for example, humanoid.

[12] a) L. Adriaenssens, L. Severa, T. Šálová, I. Císařová, R. Pohl, D. Šaman, S. V. Rocha, N. S. Finney, L. Pospíšil, P. Slavíček, F. Teplý, *Chem. Eur. J.* **2009**, *15*, 1072; b) L. Severa, L. Adriaenssens, J. Vávra, D. Šaman, I. Císařová, P. Fiedler, F. Teplý, *Tetrahedron* **2010**, *66*, 3537; c) L. Severa, D. Koval, P. Novotná, M. Ončák, P. Sázelová, D. Šaman, P. Slavíček, M. Urbanová, V. Kašička, F. Teplý, *New J. Chem.* **2010**, *34*, 1063; d) J. Vávra, L. Severa, P. Švec, I. Císařová, D. Koval, P. Sázelová, V. Kašička, F. Teplý, *Eur. J. Org. Chem.* **2012**, 489; e) L. Pospíšil, F. Teplý, M. Gál, L. Adriaenssens, M. Horáček, L. Severa, *Phys. Chem. Chem. Phys.* **2010**, *12*, 1550.

[13] a) L. Adriaenssens, L. Severa, D. Koval, I. Císařová, M. Martínez Belmonte, E. C. Escudero-Adán, P. Novotná, P. Sázelová, J. Vávra, R. Pohl, D. Šaman, M. Urbanová, V. Kašička, F. Teplý, *Chem. Sci.* **2011**, *2*, 2314; for related study on [5]helquat, see: b) L. Severa, M. Jirásek, P. Švec, F. Teplý, Á. Révész, D. Schröder, D. Koval, V. Kašička, I. Císařová, D. Šaman, *ChemPlusChem* **2012**, *77*, 624.

[14] Intramolecular [2+2+2] cycloaddition as an entry to nonionic helical scaffolds was pioneered in the group of Stará and Starý; for initial report, see: a) I. G. Stará, I. Starý, A. Kollárovič, F. Teplý, D. Šaman, M. Tichý, *J. Org. Chem.* **1998**, *63*, 4046; for further reports, see: b) P. Sehnal, I. G. Stará, D. Šaman, M. Tichý, J. Míšek, J. Cvačka, L. Rulíšek, J. Chocholoušová, J. Vacek, G. Goryl, M. Szymonski, I. Císařová, I. Starý, *Proc. Natl. Acad. Sci. USA* **2009**, *106*, 13169; c) J. Míšek, F. Teplý, I. G. Stará, M. Tichý, D. Šaman, I. Císařová, P. Vojtíšek, I. Starý, *Angew. Chem.* **2008**, *120*, 3232; *Angew. Chem. Int. Ed.* **2008**, *47*, 3188.

[15] a) For the [2+2+2] cycloaddition in the synthesis of circulenes and related species, see Ref. [7d] for King's quadrannulene; b) for Siegel's indenocorrannulenes, see: Y.-T. Wu, T. Hayama, K. K. Baldridge, A. Linden, J. S. Siegel, *J. Am. Chem. Soc.* **2006**, *128*, 6870; c) for Wender's substituted cyclooctatetraenes, see: P. A. Wender, J. P. Christy, A. B. Lesser, M. T. Gieseler, *Angew. Chem.* **2009**, *121*, 7823; *Angew. Chem. Int. Ed.* **2009**, *48*, 7687; d) Shibata's tetraphenylenes: T. Shibata, T. Chiba, H. Hirashima, Y. Ueno, K. Endo, *Angew. Chem.* **2009**, *121*, 8210; *Angew. Chem. Int. Ed.* **2009**, *48*, 8066.

[16] The ratio of saddlequat *rac*-**2** and helquat *rac*-**3** was 4:3, as determined by integration of the peaks in ^{1}H NMR spectra.

[17] CCDC 854998 (*rac*-**1**), 854997 (*rac*-**2**), and 854996 (*rac*-**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[18] Control experiments showed that irradiation of **3** does not lead to **1**.

[19] a) For enantiocomposition analysis of helquats by CE, see Refs. [12c,d,13] and b) D. Koval, L. Severa, L. Adriaenssens, J. Vávra, F. Teplý, V. Kašička, *Electrophoresis* **2011**, *32*, 2683.

[20] Philips MASTER PL-Electronic 27 W/865 E27 230–240 V (1700 Lm, 58.6 Lm W^{-1}).

[21] For NMR spectroscopic data from monitoring the transformation **2**→**1** upon irradiation at room temperature, see the Supporting Information, Scheme S3.

[22] For photochemical key steps in the synthesis of complex organic structures, see: a) T. Bach, J. P. Hehn, *Angew. Chem.* **2011**, *123*, 1032; *Angew. Chem. Int. Ed.* **2011**, *50*, 1000; b) N. Hoffmann, *Chem. Rev.* **2008**, *108*, 1052; c) P. Klán, J. Wirz, *Photochemistry of Organic Compounds: From Concepts to Practice*, Wiley, Chichester, **2009**.

[23] W. J. Schreier, T. E. Schrader, F. O. Koller, P. Gilch, C. E. Crespo-Hernández, V. N. Swaminathan, T. Carell, W. Zinth, B. Kohler, *Science* **2007**, *315*, 625, and references therein.

[24] For reviews on photochemical approaches to various cage compounds and prismanes, see: a) T. Shinmyozu, R. Nogita, M. Akita, C. Lim in *CRC Handbook of Organic Photochemistry and Photobiology*, 2nd ed. (Eds.: W. Horspool, F. Lenci), CRC, Boca Raton, **2004**, pp. 22/1 – 22/21 and 23/1 – 23/11.

[25] For studies towards pagodane, see: a) H. Prinzbach, G. Sedelmeier, C. Krüger, R. Goddard, H.-D. Martin, R. Gleiter, *Angew. Chem.* **1978**, *90*, 297; *Angew. Chem. Int. Ed. Engl.* **1978**, *17*, 271; b) W.-D. Fessner, G. Sedelmeier, P. R. Spurr, G. Rihs, H. Prinzbach, *J. Am. Chem. Soc.* **1987**, *109*, 4626.

[26] For studies towards hexaprismane, see: a) H. Higuchi, K. Takatsu, T. Otsubo, Y. Sakata, S. Misumi, *Tetrahedron Lett.* **1982**, *23*, 671; b) H. Higuchi, E. Kobayashi, Y. Sakata, S. Misumi, *Tetrahedron* **1986**, *42*, 1731; c) S. Misumi, *Pure Appl. Chem.* **1987**, *59*, 1627.

[27] For examples of other than benzo/benzo [6+6] photocycloadditions of aromatic systems, see a) Wasserman's dibenzoequinene: H. H. Wasserman, P. M. Keehn, *J. Am. Chem. Soc.* **1967**, *89*, 2770; H.-D. Becker, *Chem. Rev.* **1993**, *93*, 145; b) Nishimura's naphtalenophane: J. Nishimura, M. Takeuchi, H. Takahashi, M. Sato, *Tetrahedron Lett.* **1990**, *31*, 2911; for Shinmyozu's efforts towards hexaprismane, see: c) C. Lim, M. Yasutake, T. Shinmyozu, *Angew. Chem.* **2000**, *112*, 593; *Angew. Chem. Int. Ed.* **2000**, *39*, 578; d) R. Nogita, K. Matohara, M. Yamaji, T. Oda, Y. Sakamoto, T. Kumagai, C. Lim, M. Yasutake, T. Shimo, C. W. Jefford, T. Shinmyozu, *J. Am. Chem. Soc.* **2004**, *126*, 13732; e) Okamoto's octahedrane: H. Okamoto, K. Satake, H. Ishida, M. Kimura, *J. Am. Chem. Soc.* **2006**, *128*, 16508.

[28] For selected photochemical transformations with cationic nitrogen heterocycles, see: a) H. Ihmels, J. Luo, *J. Photochem. Photobiol. A* **2008**, *200*, 3; b) D. Q. Wu, L. J. Zhi, G. J. Bodwell, G. L. Cui, N. Tsao, K. Müllen, *Angew. Chem.* **2007**, *119*, 5513; *Angew. Chem. Int. Ed.* **2007**, *46*, 5417; c) S. Arai, T. Yafune, M. Ohkubo, M. Hida, *Tetrahedron Lett.* **1989**, *30*, 7217.

[29] For a recent [2+2] photocycloaddition of a helicene to form a dimer, see: K. Yavari, S. Moussa, B. Ben Hassine, P. Retailleau, A. Voituriez, A. Marinetti, *Angew. Chem.* **2012**, *124*, 6852; *Angew. Chem. Int. Ed.* **2012**, *51*, 6748.

[30] $\Phi = 0.185 \pm 0.044$, $\lambda = 366(\pm 5)$ nm. For experimental details, see the Supporting Information.

[31] E. Schaumann, R. Ketcham, *Angew. Chem.* **1982**, *94*, 231; *Angew. Chem. Int. Ed. Engl.* **1982**, *21*, 225.

[32] S. Grimme, *J. Comput. Chem.* **2006**, *27*, 1787.

[33] Gaussian 09, Revision A.1, M. J. Frisch et al., Gaussian, Inc., Wallingford CT, **2009**.

[34] a) C. Doubleday, Jr., R. N. Camp, H. F. King, J. W. McIver, Jr., D. Mullally, M. Page, *J. Am. Chem. Soc.* **1984**, *106*, 447; b) J. Liese, N. Hampp, *J. Phys. Chem. A* **2011**, *115*, 2927; c) R. Hoffmann, S. Swaminathan, B. G. Odell, R. Gleiter, *J. Am. Chem. Soc.* **1970**, *92*, 7091.

[35] A. D. Boese, J. M. L. Martin, *J. Chem. Phys.* **2004**, *121*, 3405.

[36] The biradical intermediate is characterized by a nearly zero singlet/triplet gap. For details, see the Supporting Information.

[37] M. Flammang-Barbieux, J. Nasielski, R. H. Martin, *Tetrahedron Lett.* **1967**, *8*, 743.

