From 1,4-phenylenebis(phenylmaleate) to a room temperature liquid crystalline benzo[*ghi*]perylene-diimide

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Abstract: The photocyclization of tetraethyl 1,4-phenylene-bis(phenylmaleate) in the presence of iodine and oxygen predominantly yields tetraethyl [5]helicene-5,6,9,10-tetracarboxylate, together with traces of tetraethyl dibenz[*a,h*]anthracene-5,6,12,13-tetracarboxylate and tetraethyl benzo[*ghi*]perylene-3,4,11,12-tetracarboxylate. The helicene-tetraester is planarized to the benzoperylene-tetraester by Scholl reaction with AlCl₃ followed by reesterification of the partially hydrolyzed crude product. Treatment with a branched alkylamine yields a columnar liquid crystalline benzoperylene-diimide whose mesophase is stable at room temperature despite its limited and non-centrosymmetric alkyl periphery. Its absorption spectrum is markedly red-shifted compared to a similar PDI-derived benzoperylene-triimide.

Tetraesters of polycyclic arenetetracarboxylic acids tend to form columnar liquid crystals [1] that are of interest as anisotropic charge transport materials.[2] The corresponding diimides with secondary alkyl residues have recently been found to also tend to form such mesophases, in spite of the presence of only two flexible substituents [3],[4] (Scheme 1). Imides are of particular interest due to their improved stability towards hydrolysis compared to esters, and the electron-withdrawing effect of imide groups is considerably stronger in six-membered-ring diimides (like perylene-diimide (PDI) **1** [4]) than in five-membered-ring diimides (like **2** [5]), such that the latter may be considered as electron donors with respect to the former; all-imide donor-acceptor junction devices may thus be envisaged.[5]

Scheme 1. Perylene- and pyrene-derived di- and triimides with secondary alkyl substituents. Hex = *n*-hexyl, Hept = *n*-heptyl, Non = *n*-nonyl.

As benzo[*ghi*]perylene with two hexagonal imide substituents and a further pentagonal imide group (such as **3**) are easily accessible from perylene-tetracarboxdiimides by Diels-Alder reaction with maleic anhydride,[6][7] we wondered whether benzo[*ghi*]perylene with two pentagonal imide groups could be obtained with similar ease, to provide complementary columnar donor materials. The oxidative photocyclization of 1,4-phenylene-bis(phenylmaleic anhydride) is known to yield preferentially the cisoid [5]helicene-dianhydride at the expense of the transoid dibenz[*a,h*]anthracene-dianhydride.[8] Although, contrary to unsubstituted [5]helicene,[9] the helicene-dianhydride resists further photooxidation to the corresponding benzoperylene-dianhydride,[8] we hoped that the corresponding tetraester **4** could undergo further photooxidation to the benzo[*ghi*]perylene-tetraester **5** due to the less electron-withdrawing effect of ester substituents compared to anhydride groups (Scheme 2). Our recent finding that even polycyclic aromatic diimides with both substituents on the same side of the arene moiety (such as **6**) can exhibit liquid crystalline behavior over broad temperature ranges[10] made us confident that benzo[*ghi*]perylene-3,4:11,12-tetracarboxdiimides with secondary alkyl residues (such as **7**) would exhibit mesogenic behavior despite their non-transoid substitution pattern.

Scheme 2. Synthesis of benzoperylene-tetraester **5** and -diimide **7** from 1,4-phenylenediacetic acid **11**. **5**'s isomer **15**,[7] previously obtained from 1-bromonaphthalene via 4,4'-dicyano-1,1'-binaphthyl **14**, is shown for comparison. a: Ac₂O, NEt₃, THF, reflux, 20h, then add EtOH, EtBr, DBU, reflux, 20h, 81%; b: hv, I₂, O₂, EtOAc, 11d, 77% (**4**) + 8% (**13**); c: 1. AlCl₃, DCM, 3d, 2. EtOH, EtBr, DBU, THF, 48%; d: NonHexCHNH₂, imidazole, o-C₆H₄Cl₂, reflux, 5h, 88%. Hex = *n*-hexyl, Non = *n*-nonyl.

Following our previously established procedure [5] for glyoxylic Perkin reactions [11] with in situ esterification in refluxing THF, we obtained tetraethyl 1,4-phenylene-bis(phenylmaleate) **10** in 81% isolated yield on a 30 mmol (18 g) scale from phenylene-1,4-diacetic acid **11** and phenylglyoxylic acid **12**. Photoreaction at room temperature in 0.9 L of ethyl acetate under air in the presence of catalytic amounts of iodine in a Peschl photoreactor with

pyrex-filtered irradiation by a medium-pressure 150W mercury immersion lamp yielded after 11 days the [5]helicene-tetraester **4** in 77% isolated yield, accompanied by ca. 8% of dibenz[*a,h*]anthracene-tetraester **13** (as quantified by $^1\text{H-NMR}$ prior to recrystallization). Irrespectively of the amount of starting material (300 mg, 1 g or 17.5 g of **10**), about 100 mg of benzoperylene-tetraester **5** are formed as side product, suggesting that the latter quenches its own formation.

We thus could obtain up to 13 g of helicene-tetraester **4** in one go, but only 100 mg of benzoperylene-tetraester **5**. Therefore we looked for a more efficient approach to the latter from the former. Scholl dehydrogenations of arenes with electron-withdrawing substrates have been reported: e.g. the reaction of 4,4'-dicyano-1,1'-binaphthyl **14** with AlCl_3 at 140°C gives 3,10-dicyanoperylene,[12] from which we previously obtained benzoperylene-tetraester **15**, an isomer of **5**, via addition of maleic anhydride.[7] Albeit the conceivable AlCl_3 -induced Scholl cyclodehydrogenation of the [5]helicene-tetraester **4** is no doubt accompanied by attack by the Lewis acid on the ester groups, we were hopeful that this side reaction could lead to reesterifiable intermediates, because we previously observed that the slow double AlCl_3 -mediated Friedel-Crafts acylation of pyrene or perylene with ClCOCO_2Et gives useful yields of pyrenylene- or perylenylene-diglyoxylic esters despite concomitant ester hydrolysis, if the crude product is reesterified prior to purification.[5][10] Indeed we found that if the [5]helicene-tetraester **4** is reacted for 3 days with excess AlCl_3 in DCM and the crude product obtained after acidic work-up is subjected to esterification with EtOH, EtBr and DBU in THF, the benzoperylene-tetraester **5** is obtained in 48% yield on a 10 mmol (5 g) scale. Contrary to its isomer **15**, **5** bears its ester substituents in vicinal positions allowing its transformation into a five-membered-ring diimide. Although **15** is hexagonal columnar liquid crystalline between its melting point at 200°C and its clearing point at 302°C ,[7] **5** shows no mesophase and melts directly to the isotropic liquid at 242°C .

We previously found that racemic 1-hexyldecyl imide substituents are particularly efficient in inducing broad range columnar mesophases and in suppressing crystallization to stabilize the liquid crystalline state (e.g. of **2** and **3**) at room temperature. We therefore treated the tetraester **5** with excess 7-aminohexadecane and found that the resulting diimide **7** shows a hexagonal columnar liquid crystalline mesophase at room temperature and above, up to a clearing transition to the isotropic liquid at 266°C . Upon cooling through the clearing transition, the mesophase grows between glass plates in homeotropic domains (i.e. column axes perpendicular to the substrates) of six-fold symmetry (inset in Figure 1). No crystalline state is induced by precipitation from solution, and **7** separates from hot butanol upon cooling as a liquid crystalline wax. Accordingly, differential scanning calorimetry (DSC) shows no other phase transition than the clearing point (Figure 1, left), and the powder X-ray diffractogram of a pristine sample at room temperature shows the typical reflections of a hexagonal column lattice with a column-to-column distance of $20.8\text{\AA}$, together with a broad peak corresponding to the liquid-like packing of alkyl chains and a particularly strong peak corresponding to an intracolumnar disk-to-disk stacking distance of $3.45\text{\AA}$ (yielding a density of 1.1g/cm^3) (Figure 1, right). This strong disk-to-disk peak hints to a rather extended contact area between the π electron systems of adjacent molecules within the column.

Figure 1. Left: DSC traces for **7** (top trace: heating of a pristine sample obtained by precipitation from solution, bottom trace: subsequent cooling; 10°C/min); measured transition enthalpies in gray (J/g); Col_{hex} = hexagonal columnar mesophase, Iso = isotropic liquid. Right: Powder X-ray diffractogram at room temperature of a pristine sample of **7** obtained by precipitation from solution (logarithmic intensity scaling; Miller indices corresponding to a hexagonal columnar lattice are given in brackets). Inset: Growth of a homeotropic domain of the hexagonal columnar mesophase of **7** from the isotropic liquid at 265°C between glass plates (polarizing optical microscopy with slightly uncrossed polarizers, 0.30mm × 0.24mm).

The liquid crystalline state of diimide **7** is thus markedly more stable against crystallization than the ones of perylene-diimide **1** [4] and dinaphthoperylene-diimide **2** [5] (whose columnar mesophases can be maintained at room temperature upon fast cooling down from high temperature, but which crystallize upon slower cooling or from solution), as well as of the dinaphthopyrene-diimide **6** [10] (which shows hexagonal and rectangular mesophases only at elevated temperatures and cannot be obtained in a liquid crystalline state at room temperature). **7** is thus the first arene-bis(alkylimide) with an apparently thermodynamically stable columnar mesophase at room temperature. Its large mesophase range is all the more surprising in view of its non-centrosymmetric (i.e. non-transoid) substitution pattern and in view of the lack of any mesophase in its ethylester homologue **5**.

Whereas the visible light absorption of tetraester **5** in solution is slightly less intense and slightly blue-shifted compared to its isomer **15**, the absorption of diimide **7** is not only markedly less intense than the one of triimide **3**, but also considerably red-shifted (absorption edges in 20μM chloroform solution: ca. 535nm for **7**, ca. 490nm for **3**), despite the larger number of conjugated imide substituents in **3** (Figure 2). The absorption edge of **7** at 535nm corresponds to an optical band gap of 2.32eV.

Figure 2. Absorption spectra of diimide **7** (black) and tetraester **5** (gray) compared to isomeric tetraester **15** (dashed gray) and triimide **3** (dashed black), [7] 20μM in CHCl₃.

Using cyclic voltammetry, and scanning cathodically between −0.5 and −1.8 V with a scan rate of 500mV/s, two reversible reduction processes can be observed with diimide **7**. The first reduction is at $E_{1/2} = -1.42\text{V}$ vs. Fc^+/Fc , the second is at $E_{1/2} = -1.69\text{V}$ vs. Fc^+/Fc . Scanning anodically, a very broad irreversible curve is observed. As it was too featureless to be characterized by cyclic voltammetry, we obtained $E_{1/2} = +1.27\text{V}$ vs. Fc^+/Fc from differential pulse voltammetry (Figure 3). With $E_{1/2}(\text{Fc}^+/\text{Fc})$ at 4.80 eV below vacuum, the first oxidation and reduction potentials of **7** correspond to E_{HOMO} and E_{LUMO} levels of −6.07 eV and −3.38 eV, yielding an electrochemical band gap of 2.69 eV, and an exciton binding energy of 0.37 eV when comparing with the optical

band gap. Compared to triimide **3** with two six-membered- and one five-membered-ring imide substituents, whose E_{HOMO} and E_{LUMO} levels have been determined as -6.67 eV and -3.79 eV,[7] five-membered-ring diimide **7** may be considered as a less strong electron acceptor by about 0.4eV and a stronger electron donor by about 0.6eV.

Figure 3. Left: Cyclic voltammogram diimide **7** in DCM, scanning cathodically at 500 mV/s. Right: Differential pulse voltammogram of **7** in DCM .

In summary, whilst the oxidative photocyclization of 1,4-phenylene-bis(phenylmaleate) **10** predominantly stalls at the [5]helicene **4** accompanied only by traces of benzoperylene-teraester **5**, the latter surprisingly is accessible in fair yield from **4** via AlCl_3 -induced Scholl dehydrogenation despite the presence of four carboxy substituents. This offers a straightforward access to the related orange swallow-tail diimide **7**, which is a moderately strong electron acceptor and forms an enantiotropic hexagonal columnar liquid crystalline phase over an astonishingly broad temperature range, notably including room temperature, despite the presence of only two imide substituents and their location in non-opposite positions.

Experimental Section

NMR spectra were recorded on a JEOL ECS-40 spectrometer, UV/visible spectra with a Unicam UV 4 spectrometer. Column chromatography was performed under compressed air using Fluka silica gel 60 for flash chromatography (pore size 60Å, particle size 35-75μm). Differential scanning calorimetry (DSC) was performed on a Perkin–Elmer DSC7 apparatus, and polarizing optical microscopy on a Olympus BH-2 microscope. Mass spectra were performed on a QStar Elite mass spectrometer (Applied Biosystems) in positive mode. Powder X-ray diffraction data were collected on a Rigaku Nanoviewer (XRF microsource generator, MicroMax 007HF), with a 1200-W rotating anode coupled to a confocal Max-Flux® Osmic mirror (Applied Rigaku Technologies, Austin, USA) and a MAR345 image plate detector (MARResearch, Norderstedt, Germany); samples were put in glass capillaries which were exposed to the X-Ray beam in a high temperature oven; the detector was placed at a distance of 309mm providing access to 2θ angles in the 0.5° to 29° range. Cyclic voltammetry and differential pulse voltammetry was performed in a three electrode cell, utilizing an Autolab PGStat20 potentiostat, driven by GPES software (General Purpose Electrochemical System, Version 4.4, EcoChemie B.V., Utrecht, the Netherlands), a platinum wire counter electrode, a 1.6 mm platinum disc working electrode, and a non-aqueous reference electrode comprised of a silver wire in a 0.01 M solution of AgNO_3 and 0.1 M tetrabutylammonium perchlorate in acetonitrile; the analyte (approximately 2 mmol) was dissolved in DCM supplemented with 0.1 M tetrabutylammonium hexafluorophosphate and degassed by bubbling argon prior to measurement. All potentials ($E_{1/2} = (E^\circ_a + E^\circ_c)/2$ in CV) are reported against the ferrocene/ferrocenium couple from an internal standard added at the end of the experiment.

Tetraethyl 1,4-phenylene-bis(phenylmaleate) **10**

1,4-phenylenediacetic acid **11** (7.5g, 194.2g/mol, 39mmol), phenylglyoxylic acid **12** (12.5g, 150.1g/mol, 84mmol), triethylamine (20g) and acetic anhydride (30g) were stirred at reflux in dry THF (300mL) under argon for 20h. The initially blue mixture turns quickly green. After cooling to room temperature, a mixture of ethanol (75g), bromoethane (75g) and 1,8-diazabicycloundec-7-ene (DBU) (75g) was added and the mixture was stirred at reflux under argon for 20h. After cooling to room temperature, the mixture was poured into 10% aqueous hydrochloric acid (1L), ethanol (200mL) was added, the mixture was stirred for 15min and the formed precipitate filtered off, yielding a first crop of crude product (18.5g after drying). A further crop (1.4g) was obtained by washing the aqueous filtrate with chloroform, evaporating the

chloroform and recrystallizing from a small amount of methanol. The two crops were united and recrystallized from methanol (300mL). Yield: 17.9g (570.6g/mol, 31mmol, 81%) of off-white solid.

¹H-NMR (CD₂Cl₂, 400MHz): δ = 7.26-7.16 (m, 6H), 7.05-7.00 (m, 4H), 6.91 (s, 4H), 4.25 (q, 7Hz, 4H), 4.24 (q, 7Hz, 4H), 1.27 (t, 7Hz, 6H), 1.26 (t, 7Hz, 6H) ppm.

¹³C-NMR (CD₂Cl₂, 100MHz): δ = 168.0, 167.8, 139.7, 138.1, 135.2, 135.0, 130.0, 129.9, 128.8, 128.5, 62.13, 62.12, 14.2 ppm.

FD-HRMS: *m/z* calcd for C₃₄H₃₄NaO₈ [*M*+Na]⁺: 593.2146; found: 593.2130.

Mp.: 135-137°C.

Tetraethyl [5]helicene-5,6,9,10-tetracarboxylate 4

A solution of tetraethyl 1,4-phenylene-bis(phenylmaleate) **10** (17.5g, 570.6g/mol, 31mmol) and iodine (400mg) in ethyl acetate (900mL) was stirred for 11 days at room temperature under air in a Peschl photoreactor with irradiation by a medium-pressure 150W mercury immersion lamp inside a borosilicate immersion tube in which cooling water circulates. The solvent was evaporated, and ethyl acetate was added and evaporated several times until the evaporated solvent appeared iodine-free. The crude product was purified by column chromatography on silica in chloroform containing ethanol (1%), followed by recrystallization from methanol (800mL). Yield: 13.3g (566.6g/mol, 23mmol, 77%) of pale yellow solid.

¹H-NMR (CD₂Cl₂, 400MHz): δ = 8.24-8.17 (m, 6H), 7.60 (t, 8Hz, 2H), 7.31 (t, 8Hz, 2H), 4.54 (q, 7Hz, 8H), 1.48 (t, 7Hz, 6H), 1.46 (t, 7Hz, 6H) ppm.

¹³C-NMR (CDCl₃, 100MHz): δ = 167.9, 167.8, 131.7, 130.7, 129.7, 129.2, 128.32, 128.28, 127.9, 127.8, 126.7, 126.0, 125.3, 62.4, 62.3, 14.4, 14.3 ppm.

FD-HRMS: *m/z* calcd for C₃₄H₃₀NaO₈ [*M*+Na]⁺: 589.1833; found: 589.1822.

Mp.: 148-152°C.

Tetraethyl benzo[ghi]perylene-3,4,11,12-tetracarboxylate 5

A solution of tetraethyl [5]helicene-5,6,9,10-tetracarboxylate **4** (10.5g, 566.6g/mol, 19mmol) in DCM (100mL) was added to a stirred suspension of aluminium trichloride (21g, 133.3g/mol, 158mmol) in DCM (400mL) in a 500mL flask, and the mixture was stirred at room temperature under exclusion of moisture for 3 days. The mixture was poured into a mixture of 10% aqueous HCl (500mL) and ice. DCM (600mL) and acetone (200mL) were added and the biphasic mixture was stirred until all solids were dissolved. The organic phase was separated and dried over sodium sulphate, and the solvent mixture was evaporated. Ethyl acetate (200mL), THF (100mL), ethanol (30g) bromoethane (30g) and DBU (15g) were added, and the mixture was stirred at reflux under argon for 16h. After cooling to room temperature, the mixture was poured into 10% aqueous hydrochloric acid (400mL), DCM (400mL) was added with stirring, the phases were separated, the organic phase was dried over sodium sulphate and the solvent was evaporated. The residue, which contains, besides other impurities, a ca. 3:1 mixture of product and starting material (determined by ¹H-NMR), was purified by recrystallization from butanol (300mL) (which eliminates the remaining starting material) and column chromatography on silica in DCM. Yield: 5.05g (564.6g/mol, 9mmol, 48%) of bright yellow solid.

¹H-NMR (CDCl₃, 400MHz): δ = 9.08 (d, 8Hz, 2H), 8.73 (s, 2H), 8.52 (d, 8Hz, 2H), 8.12 (t, 8Hz, 2H), 4.62 (q, 7Hz, 4H), 4.61 (q, 7Hz, 4H), 1.53 (t, 7Hz, 6H), 1.52 (t, 7Hz, 6H) ppm.

¹³C-NMR (CDCl₃, 100MHz): δ = 167.9, 131.4, 130.3, 129.6, 127.5, 127.4, 125.8, 125.5, 124.8, 124.4, 122.8, 62.34, 62.29, 14.4 ppm.

FD-HRMS: *m/z* calcd for C₃₄H₂₈NaO₈ [*M*+Na]⁺: 587.1676; found: 587.1648.

Mp.: 241-243°C.

***N,N'*-bis(1-hexyldecyl) benzo[ghi]perylene-3,4:11,12-tetracarboxdiimide 7**

Tetraethyl benzo[ghi]perylene-3,4,11,12-tetracarboxylate **5** (4.0g, 564.6g/mol, 7mmol), 7-aminohexadecane (4.8g, 241.5g/mol, 20mmol) and imidazole (20g) were stirred at reflux in 1,2-dichlorobenzene (40g) under argon for 5h. After cooling to room temperature, the mixture was poured into 10% aqueous hydrochloric acid (300mL), DCM (300mL) was added with stirring, the phases were separated, the organic phase was dried over sodium sulphate and the DCM was evaporated. The crude product was precipitated from the residual solution in 1,2-dichlorobenzene by adding methanol (300mL), filtered off, and purified by column chromatography on silica in a 3:1 mixture of petroleum ether and DCM, followed by reprecipitation from BuOH (300mL). Yield: 5.4g (863.2g/mol, 6mmol, 88%) of bright orange waxy solid.

¹H-NMR (CDCl₃, 400MHz): δ = 9.68 (s, 2H), 9.46 (d, 8Hz, 2H), 9.11 (d, 8Hz, 2H), 8.21 (t, 8Hz, 2H), 4.37 (tt, 10Hz, 5Hz, 2H), 2.30-2.18 (m, 4H), 1.92-1.80 (m, 4H), 1.48-1.31 (m, 16H), 1.31-1.13 (m, 28H), 0.83 (t, 7Hz, 6H), 0.80 (t, 7Hz, 6H) ppm.

¹³C-NMR (CDCl₃, 100MHz): δ = 170.1, 169.9, 129.5, 128.1, 127.3, 126.4, 125.34, 125.28, 124.5, 124.1, 123.5, 52.7, 32.9, 32.0, 31.9, 29.7, 29.6, 29.4, 29.3, 27.1, 22.8, 14.2 ppm.

FD-HRMS: *m/z* calcd for C₅₈H₇₄N₂O₄ [*M*]⁺: 862.5649; found: 862.5683.

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- [1] T. Hassheider, S. A. Benning, H.-S. Kitzerow, M.-F. Achard, H. Bock, *Angew. Chem. Int. Ed.* **2001**, *40*, 2060; *Angew. Chem.* **2001**, *113*, 2119.
- [2] a) D. Markovitsi, S. Marguet, J. Bondkowski, S. Kumar, *J. Phys. Chem. B* **2001**, *105*, 1299; b) T. Wöhrle, I. Wurzbach, J. Kirres, A. Kostidou, N. Kapernaum, J. Litterscheidt, J. C. Haenle, P. Staffeld, A. Baro, F. Giesselmann, S. Laschat, *Chem. Rev.* **2016**, *116*, 1139; c) S. Sergeyev, W. Pisula, Y. H. Geerts, *Chem. Soc. Rev.* **2007**, *36*, 1902; d) J. Eccher, G. C. Faria, H. Bock, H. von Seggern, I. H. Bechtold, *ACS Appl. Mater. Interfaces* **2013**, *5*, 11935; e) Y. Zhang, H. Wang, Y. Xiao, L. Wang, D. Shi, C. Cheng, *ACS Appl. Mater. Interfaces* **2013**, *5*, 11093; f) Z. Chen, V. Stepanenko, V. Dehm, P. Prins, L. D. A. Siebbeles, J. Seibt, P. Marquetand, V. Engel, F. Würthner, *Chem. Eur. J.* **2007**, *13*, 436; g) V. Dehm, Z. Chen, U. Baumeister, P. Prins, L. D. A. Siebbeles, F. Würthner, *Org. Lett.* **2007**, *9*, 1085; h) Z. An, J. Yu, S. C. Jones, S. Barlow, S. Yoo, B. Domercq, P. Prins, L. D. A. Siebbeles, B. Kippelen, S. R. Marder, *Adv. Mater.* **2005**, *17*, 2580.
- [3] a) A. Wicklein, A. Lang, M. Muth, M. Thelakkat, *J. Am. Chem. Soc.* **2009**, *131*, 14442; b) M. G. Belarmino Cabral, D. M. Pereira de Oliveira Santos, A. Bentaleb, E. A. Hillard, R. Cristiano, H. Gallardo, F. Durola, H. Bock, *Chem. Eur. J.* **2016**, *22*, 8043.
- [4] D. M. Pereira de Oliveira Santos, M. G. Belarmino Cabral, A. Bentaleb, R. Cristiano, H. Gallardo, F. Durola, H. Bock, *Chem. Eur. J.* **2016**, *22*, 7389
- [5] M. Ferreira, E. Giroto, A. Bentaleb, E. A. Hillard, H. Gallardo, F. Durola, H. Bock, *Chem. Eur. J.* **2015**, *21*, 4391.
- [6] H. Langhals, S. Kirner, *Eur. J. Org. Chem.* **2000**, 365;
- [7] J. Kelber, M.-F. Achard, B. Garreau-de Bonneval, H. Bock, *Chem. Eur. J.* **2011**, *17*, 8145.
- [8] A. A. Frimer, J. D. Kinder, W. J. Youngs, M. A. B. Meador, *J. Org. Chem.* **1995**, *60*, 1658.
- [9] a) E. V. Blackburn, C. E. Loader, C. J. Timmons, *J. Chem. Soc. C* **1970**, 163; b) N. Ito, T. Hirose, K. Matsuda, *Org. Lett.* **2014**, *16*, 2502.
- [10] E. Giroto, M. Ferreira, P. Sarkar, A. Bentaleb, E. A. Hillard, H. Gallardo, F. Durola, H. Bock, *Chem. Eur. J.* **2015**, *21*, 7603.
- [11] a) C. F. Koelsch, S. Wawzonek, *J. Org. Chem.* **1941**, *6*, 684; b) E. K. Fields, S. J. Behrend, S. Meyerson, M. L. Winzenburg, B. R. Ortega, H. K. Hall Jr., *J. Org. Chem.* **1990**, *55*, 5165; c) R. Wang, K. Shi, K. Cai, Y. Guo, X. Yang, J.-Y. Wang, J. Pei, D. Zhao, *New J. Chem.* **2016**, *40*, 113.
- [12] R. Weitzenböck, C. Seer, *Ber.* **1913**, *46*, 1994.