Synthesis and Structure of Tetraarylcumulenes: Characterization of Bond-Length Alternation versus Molecule Length**

Johanna A. Januszewski, Dominik Wendinger, Christian D. Methfessel, Frank Hampel, and Rik R. Tykwinski*

Dedicated to Professor François Diederich on the occasion of his 60th birthday

Chains composed of sp-hybridized carbon atoms have been explored for decades because of their unique linear structure and interesting physical properties.^[1] More recently, the wirelike nature of sp-carbon oligomers has inspired a variety of studies that aim to evaluate these structures as components in nanometer-sized devices.^[2] Particularly interesting is the reported formation of such wires linking graphene nanoribbons, offering the prospect of all-carbon-based devices.^[2d-f,3]

Molecules composed of a skeleton of sp-hybridized carbon atoms can be constructed from a framework of either polyynes (alternating single and triple bonds) or cumulenes (cumulated double bonds). The chemistry of polyynes has been advanced to systems as long as 44 consecutive carbon atoms (22 acetylene units),^[4] and studies have shed considerable light on the physical and optoelectronic properties of polyynes.^[5] However, the study of cumulenes has lain essentially dormant since early work^[6,7] reported by Kuhn^[8,9] and Bohlmann.^[10,11] Thus, there remain many unanswered questions about the physical properties of this intriguing class of linear molecules. To date, UV/Vis spectroscopy has been the most useful method for the characterization of cumulenes,^[12] and analyses of cumulenes show a lowering of the lowest-energy electronic absorption (λ_{max}) as a function of length, such as that for [n]Ph and [n]Cy (n = 3, 5, 5)7, 9, Figure 1).^[9–11] Obviously, changes in λ_{max} versus molecular length are intricately dependent on structure and on the degree of bond-length alternation (BLA, defined as the bondlength difference between the two central-most double bonds of the cumulene chain). Recent theoretical studies predict that the BLA for cumulenes will rapidly approach zero $(BLA\!\leq\!0.01),^{[13-15]}$ that is, Peierls distortion is essentially absent.^[16] Experimentally, X-ray crystallographic analysis would provide an opportunity to confirm or refute theoretical

 [*] J. A. Januszewski,^[+] D. Wendinger,^[+] C. D. Methfessel, Dr. F. Hampel, Prof. R. R. Tykwinski
 Department of Chemistry and Pharmacy & Interdisciplinary Center of Molecular Materials (ICMM), University of Erlangen-Nuremberg Henkestrasse 42, 91054 Erlangen (Germany)
 E-mail: rik.tykwinski@chemie.uni-erlangen.de
 Homepage: http://www.chemie.uni-erlangen.de/tykwinski
 [⁺] These authors contributed equally to this work.



Figure 1. Structures of [n]cumulenes discussed in this paper.

trends in BLA as a function of cumulene length. Unfortunately, few solid-state structures have been reported for cumulenes, and data for [n]cumulenes with n > 5 are not available. The results presented herein offer an answer to the important question of BLA in long cumulenes.

It was clear from the onset of the study that the synthesis and solid-state analysis of long [n] cumulenes (n > 5) would be challenging, because available reports emphasized that these species were not typically stable enough for isolation.^[6] In order to stabilize the cumulene core through steric shielding, initial efforts targeted formation of the [n]tBuPh series of cumulenes (Figure 1). It quickly became clear, however, that the di(*tert*-butyl)phenyl (R = $tBu_2C_6H_3$) groups do not afford a sufficient stabilizing force to easily isolate the [7]- and [9]tBuPh cumulenes, and our attention then switched to the [n]Mes series.

Synthesis of [3]*t*BuPh began with the formation of **1a** through reaction of the Li–acetylide of **2a** with the diaryl ketone (Scheme 1). Reductive elimination of **1a** was then accomplished using $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ in the presence of hydrochloric acid, and pure [3]*t*BuPh was obtained by column chromatography in 76% yield as an intensely yellow solid. Unfortunately, the formation of **1b**, and thus [3]Mes, was not possible through the analogous route, because of the frustrating inability to form the methylether **2b**. Furthermore, all attempts to form a metal–acetylide directly from alcohol **3b** by reaction with either MgBrEt or *n*BuLi were unsuccessful.^[17]

[5]Cumulenes [5]*t*BuPh and [5]Mes were available through conventional methods,^[6] starting from alcohols **3a** and **3b**, respectively (Scheme 2). Formation of diols **4a**,**b** was achieved by oxidative homocoupling of **3a**,**b** under Hay conditions.^[18] While pure diol **4a** could be obtained, diyne **4b** was consistently contaminated with small amounts of by-

^[**] Funding from the University of Erlangen-Nuremberg and the Deutsche Forschungsgemeinschaft (DFG - SFB 953, Project A4 "Synthetic Carbon Allotropes") is gratefully acknowledged.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201208058.





Scheme 1. Synthesis of [3]cumulene [3]tBuPh.



Scheme 2. Synthesis of [5]cumulenes [5]tBuPh and [5]Mes. TME-DA = N, N, N', N'-tetramethylethylenediamine.

products, and the crude product was thus used directly for the formation of [5]Mes. Reductive elimination of **4a** and **4b** gave [5]*t*BuPh and [5]Mes.

For the synthesis of [7]tBuPh (Scheme 3), a Fritsch-Buttenberg-Wiechell (FBW) rearrangement was used to form the requisite trivue framework of 5a through the



Scheme 3. Synthesis of [7]cumulene [7]*t*BuPh.

reaction of ketone $6a^{[19]}$ with Colvin's reagent.^[20] Subsequent reduction of 5a gave [7]*t*BuPh. While attempts to directly isolate [7]*t*BuPh through precipitation resulted in decomposition, the pure cumulene could be isolated by slow crystallization from a solution of CH₂Cl₂/MeOH, and the crystalline solid was stable indefinitely in the absence of O₂.

The FBW route used to form **5a**, and ultimately [7]*t*BuPh, was not applicable to the synthesis of [7]Mes, because of the inability to form **6b**,^[21] thus, an alternative route was developed (Scheme 4). The synthesis of propargyl alcohol **7** was accomplished using a Cadiot–Chodkiewicz coupling (see the Supporting Information). Compound **7** was then converted to trivne **5b** in two steps, namely oxidation with PCC to ketone **8** and addition of lithiated mesitylene (Scheme 4). Reduction of **5b** to [7]Mes was accomplished with SnCl₂.



Scheme 4. Synthesis of [7]cumulene [7]Mes. PCC = pyridinium chloro-chromate.

Passing the reaction mixture through a column of basic alumina under a nitrogen atmosphere resulted in a red solution of the pure product [7]Mes in Et₂O. In solution, [7]Mes is stable for weeks when kept at circa -20 °C in a deoxygenated solvent, and crystals of [7]Mes from CH₂Cl₂/ hexane are stable for at least a week when stored at circa -20 °C in the absence of light and oxygen.

Homocoupling of diynes 9a,b gave tetraynes 10a,b, which were subjected to reductive elimination with $SnCl_2$ (Scheme 5). After formation of the desired cumulene



Scheme 5. Synthesis of [9]cumulenes [9]tBuPh and [9]Mes.

[9]*t*BuPh or [9]Mes was judged to be complete by TLC analysis, the reaction solution was neutralized by filtration through basic alumina under a nitrogen atmosphere. Attempted isolation of either [9]*t*BuPh or [9]Mes through precipitation led to decomposition of the product. [9]*t*BuPh and [9]Mes also decomposed rapidly in solution when exposed to oxygen, but they could be handled for hours ([9]*t*BuPh) or days ([9]Mes) when kept in a cold (-20° C), deoxygenated solution of Et₂O that was shielded from ambient light. Crystals of [9]Mes grown from a C₂D₂Cl₄ solution at -20° C are stable for at least a week when stored in the absence of light and O₂.

X-ray crystallographic analysis of [3]cumulenes is common (>20 structures), while data for [5]cumulenes is rare (three structures), and to our knowledge, no data exists for longer cumulenes.^[22] Herein, we report structural data for six new cumulenes ([3]*t*BuPh, [5]*t*BuPh, [7]*t*BuPh, [5]Mes, [7]Mes, [9]Mes), including the first known structures of [7]and [9]cumulenes (Figure 2).^[23]

While polyynes regularly show bending of the framework of sp-hybridized carbon atoms in the solid state,^[24] cumulenes appear to maintain a more linear structure. An examination of the known structures of [3]- and [5]cumulenes, as well as the cumulenes reported herein, shows that bond angles rarely vary by more than a few degrees from the ideal of 180°.^[25] An



Figure 2. ORTEP drawings (thermal ellipsoids at 20% probability level) for [3]-, [5]-, [7]tBuPh, and [5]-, [7]-, [9]Mes. For clarity, co-crystallized solvent molecules and hydrogen atoms are not shown.

exception to this tendency is the structure of [3]*t*BuPh, which shows cumulenic angles of 169.47° (C1-C2-C3) and 168.31° (C2-C3-C4). In addition to the likely influence of undefined crystal-packing forces, the bent shape of the [3]*t*BuPh might arise from favorable, intramolecular C-H/ π interactions between hydrogen atoms of one of the *tert*-butyl groups with the aromatic ring at the opposite terminus of the cumulene chain. This premise is supported by short C-H/ π distances of 2.81–3.27 Å,^[26] and these interactions are reminiscent of a recent study by Grimme and Schreiner highlighting dispersive forces in hexaphenylethane derivatives.^[27]

Steric congestion prevents coplanarity between the terminal aryl groups and the cumulene core for [n]tBuPh and [n]Mes cumulenes, although the extent of twisting differs quite substantially between the two series.^[28] Aryl twist angles of the mesityl groups are circa 50°, which limits conjugation between the aryl ring and the chain of sp-hybridized carbon atoms (Table 1, Figure 2). On the other hand, aryl twist angles for the [n]tBuPh cumulenes show an interesting pattern. At each terminus, the twist angle for one aryl ring is significantly smaller than that of the other, that is, 14.4–30.9° versus 40.4– 54.9°. In each case, therefore, two aryl rings are in a position

Table 1: Aryl twist angles [°] of aromatic ring relative to cumulenic framework. $^{\rm [a]}$

Ring ^[b]	[3]‡BuPh	[5]‡BuPh	[7]‡BuPh	[5]Mes	[7]Mes	[9]Mes
A	30.9	14.4	16.6	46.2	45.4	48.8
В	43.1	47.9	54.9	51.4	52.1	54.4
С	26.6		20.6			
D	40.4		43.6			

[[]a] Aryl twist angles were calculated as the difference between planes generated from 1) the six carbon atoms of the aryl ring and 2) the carbon atoms of the cumulene skeleton, along with the four *ipso*-carbon atoms of the aryl rings. [b] See Figure 2 for labeling of aryl rings.

to conjugate with the framework of sp-hybridized carbon atoms of the [n]tBuPh cumulenes.

One would predict that the ability of the aryl rings to interact with the cumulene core should have an effect on the bond-length pattern, as depicted in Figure 3 by the two resonance structures of a [5]cumulene. Indeed, bond lengths for [5]tBuPh and [7]tBuPh show an accentuated long/short bonding pattern in comparison to [5]Mes and [7]Mes (Table 2), although the difference is rather small.



Figure 3. Two canonical forms of a [5]cumulene that highlight the interconnection between BLA and conjugation of the terminal aryl groups to the cumulene core.

A key question to be answered based on structural analysis of cumulene bond lengths is: Do cumulenes show experimental evidence of reduced BLA as a function of increasing length? While this question has been answered for polyynes,^[29] to date there has been insufficient crystallographic data to offer an answer for cumulenes. Computational chemists have frequently studied BLA in cumulenes. From these theoretical studies, it seems clear that the basis set can have a remarkable effect on the results.^[15,30] In spite of these differences, however, theory suggests that BLA values converge quite rapidly to a value of nearly zero (Table 2, entries 7–13).^[13,14,31]

Experimental data for cumulenes show that the terminal double bond, C1–C2, is consistently the longest (1.33–1.35 Å; Table 2). The C1–C2 bond lengths do not show a significant

Angew. Chem. Int. Ed. 2013, 52, 1817–1821



Table 2: Selected bond lengths (Å) for [n]tBuPh and [n]Mes cumulenes and summary of BLA data.[a]

Entry	Cumulene	C1-C2	C2-C3	C3-C4	C4-C5	C5-C5′	BLA ^[b]	Ref.
1	[3]‡BuPh	1.334(3) 1.336(3) ^[c]	1.249(3)		_	-	0.086	
2	[5] <i>t</i> BuPh	1.342(2)	1.255(2)	1.309(3) ^[d]	-	-	0.054	
3	[7]tBuPh	1.345(3) 1.347(3) ^[e]	1.254(3) 1.252(3) ^[f]	1.302(3) 1.306(3) ^[g]	1.252(3)	-	0.052	
4	[5]Mes	1.339(2)	1.255(2)	1.303(3) ^[d]	-	-	0.048	
5	[7]Mes	1.334(3)	1.260(3)	1.299(3)	1.257(4) ^[h]	-	0.042	
6	[9]Mes	1.330(3)	1.255(3)	1.298(3)	1.260(4)	1.298(5)	0.038	
7[]	[7]H	1.319	1.274	1.289	1.275		0.014	[31]
8 ^[i]	[7]H	1.310342	1.266802	1.281530	1.267928		0.0136	[13]
9 ^[i]	[9]H	1.319	1.274	1.289	1.277	1.287	0.010	[31]
10 ^[j]	[9]H	1.310424	1.267176	1.281012	1.268959	1.279270	0.010	[13]
11 ^[k]	ΠΊΙΗ						0.009 ^[I]	[14]
12 ^[k]	[19]H–[39]H						0.006 ^[m]	[14]
13 ^[j]	[29]H						0.004 ^[n]	[13]

[a] See Figure 2 for numbering of atoms. [b] Calculated as difference in bond length between the two central-most bonds. For non-centrosymmetric structures, BLA was calculated using the average of positionally equivalent bonds. [c] C3-C4. [d] C3-C3'. [e] C7-C8. [f] C6-C7. [g] C5-C6. [h] C4-C4'. [i] Geometry optimization at B3LYP/6-31G* level. [j] Geometry optimization at PBE1PBE/cc-pVTZ level. [k] Geometry optimization at B3LYP/7ZVPP level. [l] Bond-length values of 1.280 Å and 1.271 Å. [m] Bond-length values of 1.278 Å and 1.272 Å. [n] Estimated value (bond lengths were not given for this value in Ref. [13]).

dependence on either end-group or cumulene length, suggesting that this bond is mainly dominated by the hybridization difference of the carbon atoms, that is, $C(sp^2)=C(sp)$. Bond lengths for the internal double bonds fall into a narrow range of 1.25–1.31 Å. BLA values for the [*n*]*t*BuPh cumulenes show a consistent decrease with increasing chain length from 0.086 Å ([3]*t*BuPh) to 0.052 Å ([7]*t*BuPh; Table 2, entries 1– 3). Cumulenes end-capped with mesityl groups show a similar decrease in BLA versus length, from 0.048 Å ([5]Mes) to 0.038 Å ([9]Mes; Table 2, entries 4–6). However, in comparison to [*n*]*t*BuPh, BLA values of [*n*]Mes are distinctively lower (Table 2). This observation is ascribed to the more pronounced twist angles of the aromatic rings in the cumulenes end-capped with mesityl groups.

A plot of cumulene BLA values versus the number of double bonds n and visual extrapolation to infinite length n suggests a limiting BLA value of 0.03–0.05 Å (Figure S1 in the Supporting Information). This prediction is relatively higher than that predicted by theory (Table 2, entries 7–13) for the "parent" series [n]H. While computational results can differ depending on the method of analysis, the trend appears clear that BLA \leq 0.01 Å for [9]H and longer cumulenes.

Similar to the investigation of polyynes, UV/Vis spectroscopy is an essential tool for the characterization of cumulenes. For the two series described herein, several tendencies are identified:

- In general, cumulenes exhibit two regions of absorption bands, one at higher and one at lower energy (Figure 4). Furthermore, fine structure increases with increasing chain length.
- 2) As described for other series of cumulenes, such as [n]Ph and [n]Cy, λ_{max} values shift significantly to lower energy as a function of chain length, that is, as conjugation is extended.
- 3) With the series of molecules accessible thus far, saturation has not yet been reached, that is, λ_{max} is further red-shifted as molecular length *n* increases.



Figure 4. UV/Vis spectra of [n]tBuPh and [n]Mes (Et₂O); spectra normalized to the most intense low-energy absorption (inset: lowest-energy absorption and energy values, λ_{max} and E_{g} , respectively).

End-groups have a dramatic effect on the λ_{max} values for [5]*t*BuPh and [5]Mes (λ_{max} = 500 and 460 nm, respectively). This correlates well with the diminished conjugation between the terminal aryl groups and cumulene



skeleton in [5]Mes, as documented by the increased aryl twist angle relative to [5]tBuPh (Table 1).

5) Effects of end-groups on λ_{max} values decrease rapidly with length, that is, the λ_{max} values of [7]*t*BuPh (564 nm) and [7]Mes (560 nm) are nearly identical, as are those of [9]*t*BuPh (664 nm) and [9]Mes (666 nm).

In summary, the synthesis of two series of [n]cumulenes has been accomplished in order to investigate the properties of these oligomers of sp-hybridized carbon atoms as a function of length. While the longer [n]cumulenes with n = 7 or 9 are not particularly stable in solution under ambient conditions, they show sufficient stability in the solid state so that X-ray crystallographic analysis could be accomplished for all derivatives except [9]*t*BuPh. This includes the first crystallographic analysis of [7]- and [9]cumulenes to date. Analysis of bond lengths for the cumulenes provides the first experimental evidence for reduced BLA as a function of cumulene length, and experimental values are distinctly higher than those predicted by computational studies for [n]H cumulenes.

Received: October 6, 2012

Keywords: bond-length alternation · carbyne · cumulenes · oligomers · polyynes

- a) Y. Tobe, T. Wakabayashi in Acetylene Chemistry: Chemistry, Biology, and Material Science (Eds.: F. Diederich, P. J. Stang, R. R. Tykwinski), Wiley-VCH, Weinheim, 2005, pp. 387–426;
 b) W. A. Chalifoux, R. R. Tykwinski, Chem. Rec. 2006, 6, 169– 182; c) A. L. K. Shi Shun, R. R. Tykwinski, Angew. Chem. 2006, 118, 1050–1073; Angew. Chem. Int. Ed. 2006, 45, 1034–1057;
 d) Polyynes: Synthesis, Properties, and Applications (Ed.: F. Cataldo), Taylor & Francis, Boca Raton, 2005.
- [2] a) I. E. Castelli, P. Salvestrini, N. Manini, *Phys. Rev. B* 2012, *85*, 214110; b) A. K. Nair, S. W. Cranford, M. J. Buehler, *Europhys. Lett.* 2011, *95*, 16002; c) J. Prasongkit, A. Grigoriev, G. Wendin, R. Ahuja, *Phys. Rev. B* 2010, *81*, 115404; d) Z. Zanolli, G. Onida, J.-C. Charlier, *ACS Nano* 2010, *4*, 5174–5180; e) L. Ravagnan, N. Manini, E. Cinquanta, G. Onida, D. Sangalli, C. Motta, M. Devetta, A. Bordoni, P. Piseri, P. Milani, *Phys. Rev. Lett.* 2009, *102*, 245502; f) B. Akdim, R. Pachter, *ACS Nano* 2011, *5*, 1769–1774.
- [3] C. Jin, H. Lan, L. Peng, K. Suenaga, S. Iijima, Phys. Rev. Lett. 2009, 102, 205501.
- [4] W. A. Chalifoux, R. R. Tykwinski, Nat. Chem. 2010, 2, 967-971.
- [5] For recent examples, see: a) L. D. Movsisyan, D. V. Kondratuk, M. Franz, A. L. Thompson, R. R. Tykwinski, H. L. Anderson, Org. Lett. 2012, 14, 3424-3426; b) N. Weisbach, Z. Baranova, S. Gauthier, J. H. Reibenspies, J. A. Gladysz, Chem. Commun. 2012, 48, 7562-7564; c) Y. Wada, T. Wakabayashi, T. Kato, J. Phys. Chem. B 2011, 115, 8439-8445; d) B. B. Frank, P. R. Laporta, B. Breiten, M. C. Kuzyk, P. D. Jarowski, W. B. Schweizer, P. Seiler, I. Biaggio, C. Boudon, J. P. Gisselbrecht, F. Diederich, Eur. J. Org. Chem. 2011, 4307-4317; e) F. Cataldo, L. Ravagnan, E. Cinquanta, I. E. Castelli, N. Manini, G. Onida, P. Milani, J. Phys. Chem. B 2010, 114, 14834-14841; f) C. Wang, A. S. Batsanov, K. West, M. R. Bryce, Org. Lett. 2008, 10, 3069-3072; g) S. Eisler, A. D. Slepkov, E. Elliott, T. Luu, R. McDonald, F. A. Hegmann, R. R. Tykwinski, J. Am. Chem. Soc. 2005, 127, 2666-2676.
- [6] Early work on cumulenes, see: a) H. Hopf, Classics in Hydrocarbon Chemistry, Wiley-VCH, Weinheim, 2000, chap. 9; b) H.

Fischer in *The Chemistry of Alkenes* (Ed.: S. Patai), Wiley, New York, **1964**, pp. 1025–1159.

- [7] For two notable exceptions, see: a) Y. Kuwatani, G. Yamamoto, M. Oda, M. Iyoda, *Bull. Chem. Soc. Jpn.* 2005, 78, 2188–2208;
 b) W. Skibar, H. Kopacka, K. Wurst, C. Salzmann, K.-H. Ongania, F. F. de Biani, P. Zanello, B. Bildstein, *Organometallics* 2004, 23, 1024–1041.
- [8] R. Kuhn, H. Krauch, Chem. Ber. 1955, 88, 309-315.
- [9] [n]Ph: a) R. Kuhn, K. Wallenfels, *Ber. Dtsch. Chem. Ges.* 1938, 71, 783-790; b) R. Kuhn, H. Zahn, *Chem. Ber.* 1951, 84, 566-570.
- [10] [n]Ph: F. Bohlmann, K. Kieslich, Abh. Braunschw. Wiss. Ges. 1957, 9, 147–160.
- [11] [n]Cy: F. Bohlmann, K. Kieslich, Chem. Ber. 1954, 87, 1363– 1372.
- [12] The electronic structures of [n]cumulenes are fundamentally different between two classes of molecules, that is, when *n* is even (n = 2, 4, 6...) or odd (n = 3, 5, 7...). π -Conjugation between the end-groups through the cumulene framework is only possible when n = odd. Only odd cumulenes are considered for the discussion in this manuscript.
- [13] F. Innocenti, A. Milani, C. Castiglioni, J. Raman Spectrosc. 2010, 41, 226–236.
- [14] M. Weimer, W. Hieringer, F. Della Sala, A. Görling, *Chem. Phys.* 2005, 309, 77–87.
- [15] U. Mölder, P. Burk, I. A. Koppel, J. Mol. Struct. THEOCHEM 2004, 712, 81–89.
- [16] R. Hoffmann, Angew. Chem. 1987, 99, 871–906; Angew. Chem. Int. Ed. Engl. 1987, 26, 846–878.
- [17] The reaction of 3b with either MgBrEt or nBuLi resulted in a retro-addition reaction, that is, deprotonation of the alcohol moiety of 3b, followed by expulsion of the acetylide (M-CCH, M=MgBr or Li) and formation of the ketone MesC(O)Mes.
- [18] A. S. Hay, J. Org. Chem. 1962, 27, 3320-3321.
- [19] For the synthesis of **6a**, see the Supporting Information.
- [20] For the use of Colvin's reagent for polyyne synthesis, see: a) P. Bichler, W. A. Chalifoux, S. Eisler, A. L. K. Shi Shun, E. T. Chernick, R. R. Tykwinski, Org. Lett. 2009, 11, 519-522; b) J. Kendall, R. McDonald, M. J. Ferguson, R. R. Tykwinski, Org. Lett. 2008, 10, 2163-2166.
- [21] Compound **6b** could not be formed because of the failure to synthesize the acetylenic precursor **3b**.
- [22] Based on a search of the CCDC, 18/09/12 (CSD version 5.33, Nov. 11) for [n]cumulenes with n = odd and alkyl or aryl endgroups.
- [23] For crystallographic data, see the Supporting Information.
- [24] S. Szafert, J. A. Gladysz, Chem. Rev. 2006, 106, PR1-PR33.
- [25] Exceptions include: a) T. Kawase, N. Nishigaki, H. Kurata, M. Oda, *Eur. J. Org. Chem.* **2004**, 3090–3096; b) Y. Kuwatani, G. Yamamoto, M. Iyoda, *Org. Lett.* **2003**, *5*, 3371–3374.
- [26] Calculated as the distance from H-atom to a plane generated from the six atoms of the aromatic ring.
- [27] S. Grimme, P. R. Schreiner, Angew. Chem. 2011, 123, 12849– 12853; Angew. Chem. Int. Ed. 2011, 50, 12639–12642.
- [28] Aryl twist angles calculated as the difference between planes generated from 1) the six carbon atoms of the aryl ring, and 2) the carbon atoms of the cumulene skeleton and the four *ipso*-carbon atoms of the aryl rings.
- [29] W. A. Chalifoux, R. McDonald, M. J. Ferguson, R. R. Tykwinski, Angew. Chem. 2009, 121, 8056–8060; Angew. Chem. Int. Ed. 2009, 48, 7915–7919.
- [30] Y. Zhao, D. G. Truhlar, J. Phys. Chem. A 2006, 110, 10478– 10486.
- [31] D. Nori-Shargh, F. Deyhimi, J. E. Boggs, S. Jameh-Bozorghi, R. Shakibazadeh, J. Phys. Org. Chem. 2007, 20, 355–364.