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LETTERS

The X-ray crystal structure of linear [3]phenylene

Andreas Schleifenbaum,[a] Neil Feeder[b] and K. Peter C. Vollhardt[a,*]

[a]*Center for New Directions in Organic Synthesis, Department of Chemistry,
University of California at Berkeley and the Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley,
CA 94720-1460, USA*

[b]*University Chemical Laboratory, University of Cambridge, Lensfield Road, Cambridge CB2 1EW, UK*

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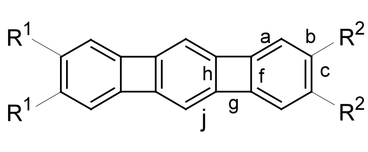
Abstract—The X-ray structure of the parent linear [3]phenylene (benzo[3,4]cyclobuta[1,2-*b*]biphenylene) has been obtained and is compared with those of its angular isomer and model compounds. The terminal rings reveal a relatively large degree of bond alternation while the center distorts to a cyclic bisallyl frame. © 2001 Elsevier Science Ltd. All rights reserved.

We report the X-ray structure of **1**,[1] the parent prototype of the linear phenylenes.[2] These molecules are exceedingly difficult to crystallize in suitable form for structural analysis, usually necessitating substitutional modification. As a consequence, only three pristine members of the series -**2**,[3] **3**,[4] and **4**[5]- have been, up to now, successfully scrutinized by this technique. The structure of **1** is important as **1** constitutes the linear complement to the angular and branched topologies in **3** and **4**, provides a further test of the accuracy of state of the art calculational procedures (which have had to rely on the experimental data of **5**[1] bearing distorting bulky substituents),[6] and allows for a first comparison of the effect of the respective central rings in **1**, **3**, and **4** on the geometry of their terminal counterparts.

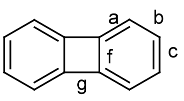
6[3]Phenylene (**1**) crystallizes in the triclinic space group $P\bar{1}$.[7] The unit cell contains two symmetrically independent molecules, each possessing an inversion center as single symmetry element. The packing adopts the simple herringbone motif (Fig. 1, left),[8] with nearest neighbor planes at an angle of 28°. The pentacyclic π frame of **1** (Fig. 1, right) is, like that of **3**,[4] virtually planar (Fig. 2), the fortuitous result of crystal packing as the phenylenes are 'floppy' and normally nonplanar.[5] Indeed, the substituted systems **5** and **6** are distinctly distorted from planarity (Fig. 2).[5] In **1**, the benzene ring dihedral angles are <0.7° and the cyclobutadiene nuclei strictly flat. Fig. 1 (right) depicts the bond lengths and angles of the molecule and Table 1 compares them with calculated values and similar data for various substruc-



1: $R^1 = R^2 = H$

5: $R^1 = R^2 = SiMe_3$

6: $R^1 = H$, $R^2 = SiMe_3$



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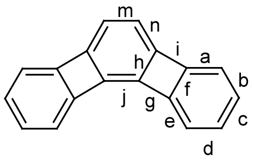

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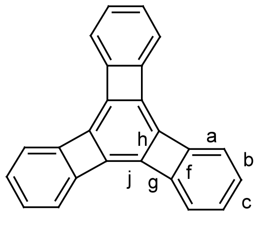

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Keywords: phenylenes; X-ray structure; bond alternation.

* Corresponding author. Fax: ++1 510 643-5208; e-mail: vollhard@cchem.berkeley.edu

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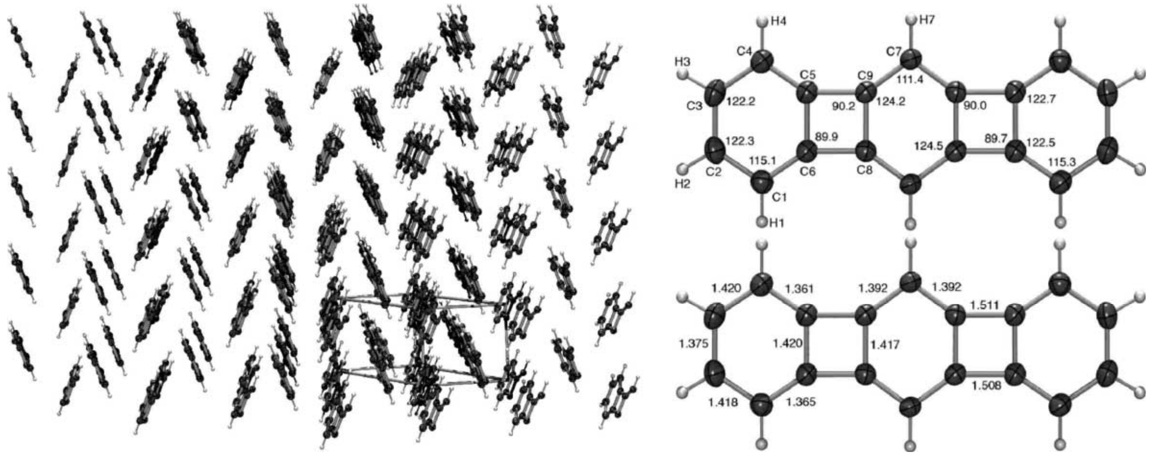


Figure 1. Crystal packing (left) and (averaged) structure of **1** [right; top: bond angles in degrees (±0.1); bottom: bond lengths in Å (±0.002)].

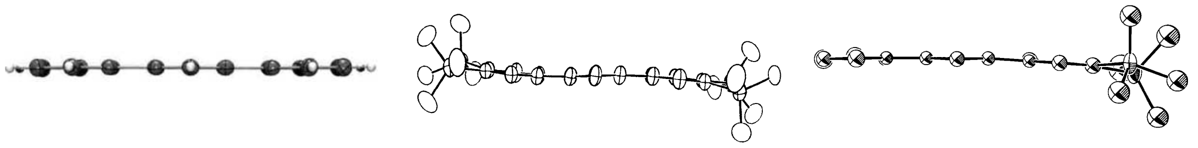
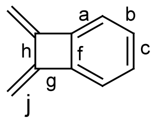


Figure 2. Side views of **1**, **5**, and **6**.

tures of **1**, as well as for phenylenes **2**–**5**. As expected, comparison of the terminal rings in **5** and **1**[11] confirms the distorting effect of the trimethylsilyl substituents, as noted for other phenylenes, substantially nullifying the normal direction of bond alternation induced by the $\sigma-$ (SIBL) and $\pi-$ frame.[1,2,4–6,12] On the other hand, the center substructure is relatively unaffected and exhibits the typical[1,5,13] deformation into two π allyl halves imposed by the linear 'double activation'. The bond localization index L[6c] for the center benzene ring is, however, only 0.07, allowing for significant diatropism, as shown by NICS calculations,[14] offset by the paratropism of the neighboring cyclobutadienoid rings. For calibration, the center (complete) cyclohexatriene in **4**[15] has $L=0.46$, that in the isomeric (to **1**) **3**, 0.30. The outer benzene rings reveal bond alternation in the cyclohexatriene sense with mean bond lengths of 1.42 and 1.37 Å for the long (C1–C2, C3–C4, C5–C6) and short bonds (C1–C6, C2–C3, C4–C5), respectively. The corresponding values for **2**–**4** are remarkably similar: 1.42, 1.38; 1.41, 1.37; and 1.41, 1.38, respectively, but the L values highlight a decreasing trend within the series **1**–**4**: 0.16, 0.14, 0.11, 0.10. This attenuation may be a reflection of the decreasing antiaromaticity of the adjacent four-membered ring along the series, in turn fine-tuned by the (decreasing) aromaticity of the central benzene, exactly as indicated by the NICS data.[14] Support for this notion is also gained from the observation of increasing deshielding of the terminal hydrogens in **1**–**4** [δ_{average} (CDCl$_3$) 6.53, 6.67, 6.95, 7.18 ppm, respectively]. In contrast, the average ^{13}C chemical shifts range only from 132.2–132.9 ppm. The ab initio bond lengths are in remarkable agreement with the experimental structure, verifying the validity of the predictive power of these methods,[5,6,15,16] with the density functional approach perhaps slightly superior. Attempts at structural predictions of **1** from component subunits,[17] e.g. **7**/**8**, **9**/**10**, and **11**/**12** (Table 1) fared best for **9**/**10** as a model for the terminal, **11**/**12** for the central rings. The pair **7**/**8**, with its acyclic diene components, significantly overestimates the length of bonds h and f in **1**.

In summary, the structural features of **1** are in accord with the predicted activated nature of the linear phenylene topology.



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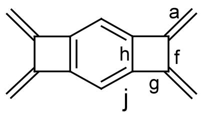

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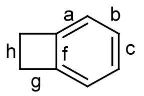

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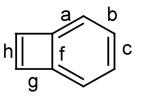

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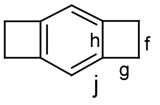

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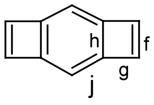

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Table 1. Selected calculated and/or experimental (in parentheses) bond lengths (Å) of **1** and related molecules[a]

	a	b	c	d	e	f	g	h	i	j	k	l	m	n
1	1.363	1.419	1.375	=b	=a	1.420	1.510	1.417	=g	1.392	=j	=h	=j	=j
HF/6-31G*[b]	(1.352)	(1.424)	(1.368)	=b	=a	(1.417)	(1.508)	(1.402)	=g	(1.383)	=j	=h	=j	=j
B3LYP/6-31G*[c]	(1.371)	(1.424)	(1.387)			(1.425)	(1.509)	(1.420)		(1.394)				
Substructures:														
7[d,e]	(1.388)	(1.404)	(1.404)	=b	=a	(1.411)	(1.489)	(1.516)	=g	(1.335)	–	–	–	–
8[e]	(1.335)	–	–	–	–	(1.513)	(1.486)	(1.423)	=g	(1.395)	=j	=h	=j	=j
M. v.[f] (**7**, **8**)	1.361					1.462	1.488	1.469		1.365				
9[g]	1.385	1.400	1.399	=b	=a	1.391	1.518	1.576	=g	–	–	–	–	–
10[c,e]	(1.361)	(1.437)	(1.379)	=b	=a	(1.425)	(1.525)	(1.352)	=g					
M. v.[f] (**9**, **10**)	1.373	1.419	1.389			1.408	1.522	1.464						
11[g]						1.575	1.521	1.399	=g	1.394	=j	=h	=j	=j
12[h]						(1.346)	(1.543)	(1.403)	=g	(1.394)	=j	=h	=j	=j
M. v.[f] (**11**, **12**)						1.460	1.532	1.401		1.394	=j	=h	=j	=j
[N]Phenylenes:														
2[i]	1.372	1.423	1.385	=b	=a	1.426	1.514	=f	=g	= a	=b	=c	=b	=a
3[j]	1.369	1.404	1.370	1.400	1.365	1.413	1.503	1.449	1.505	1.345	=h	=n	1.446	1.348
4[k]	1.371	1.403	1.389	=b	=a	1.427	1.499	1.497	=g	1.343	=h	=j	=h	=j
5[l]	1.358	1.438	1.397	=b	=a	1.397	1.513	1.407	=g	1.385	=j	=h	=j	=j

[a] The labeling scheme was devised to designate topologicaly similar bonds. The lengths of symmetry related bonds were averaged. Calculated values were obtained at the B3LYP/6-31G* level of theory, unless specified otherwise.

[b] Ref. 6c.

[c] Schleyer, P. v. R., private communication.

[d] Schulman, J. M., private communication.

[e] Stanger, A., private communication.

[f] M.v. = mean value.

[g] Ref. 9. Standard deviations ≦±0.001.

[h] Isomer **2a** in Ref. 10.

[i] Ref. 3. Standard deviations ≦±0.004.

[j] Ref. 4. Standard deviations ≦± 0.003.

[k] Ref. 5. Standard deviations ≦±0.004.

[l] Ref. 1. Standard deviations ≦±0.002.

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References

1. Berris, B. C.; Hovakeemian, G. H.; Lai, Y.-H.; Mestdagh, H.; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **1985**, *107*, 5670–5687.
2. Mohler, D. L.; Vollhardt, K. P. C. In *Advances in Strain in Organic Chemistry*; Halton, B., Ed.; JAI: London, 1996; Vol. 5, pp. 121–160.
3. Fawcett, J. K.; Trotter, J. *Acta Cryst.* **1966**, *20*, 87–93.
4. Diercks, R.; Vollhardt, K. P. C. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 266–268.
5. Holmes, D.; Kumaraswamy, S.; Matzger, A. J.; Vollhardt, K. P. C. *Chem. Eur. J.* **1999**, *5*, 3399–3412.
6. See, inter alia: (a) Maksić, Z. B.; Eckert-Maksić, M.; Mó, O.; Yáñez, M. In *Pauling's Legacy*: *Modern Modelling of the Chemical Bond*; Maksić, Z. B., Orville-Thomas, W. J., Eds.; Elsevier: Amsterdam, 1999; pp. 47–101; (b) Ma, J.; Li, S.; Jiang, Y. *J. Phys. Chem.* **1996**, *100*, 15068–15072; (c) Maksić, Z. B.; Kovaček, D.; Eckert-Maksić, M.; Böckmann, M.; Klessinger, M. *J. Phys. Chem.* **1995**, *99*, 6410–6416.
7. Crystal data for **1**: $C_{18}H_{10}$, $M = 226.26$, triclinic, space group: $P\bar{1}$, $a = 5.9470(6)$ Å, $b = 7.5860(10)$ Å, $c = 13.0780(13)$ Å, $\alpha = 102.345(6)°$, $\beta = 101.778(6)°$; $\gamma = 93.766(6)°$, $U = 560.52(11)$ Å^3, $Z = 2$, $D_{calcd} = 1.341$ g cm^{-3}; $T = 180(2)$ K, $\lambda = 0.71070$ Å, absorption coefficient: 0.076 mm^{-1}, $F(000)$: 236, crystal size: 0.20×0.18×0.02 mm^3, $\theta = 3.27$ to 25.07°, index ranges: $0 \leq h \leq 7$, $-8 \leq k \leq 9$, $-15 \leq l \leq 14$, reflections collected: 3058, independent reflections: 1935 ($R_{int} = 0.0285$), completeness to $\theta = 25.07°$: 97.9%, refinement method: full–matrix least-squares on F^2, data/restraints/parameters: 1935/0/163, goodness-of-fit on F^2: 1.026, final R indices [$I > 2\sigma(I)$]: $R_1 = 0.0450$, $wR^2 = 0.1136$, R indices (all data): $R_1 = 0.0637$, $wR^2 = 0.1281$. Crystallographic data (excluding structure factors) for the structure in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 157698. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44 (0) 1223–336033 or e-mail: deposit@ccdc.cam.ac.uk].
8. See: Desiraju, G. R.; Gavezzotti, A. *J. Chem. Soc., Chem. Commun.* **1989**, 621–623.
9. (a) Boese, R.; Bläser, D. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 304–306; (b) Boese, R.; Bläser, D.; Billups, W. E.; Haley, M. M.; Maulitz, A. H.; Mohler, D. L.; Vollhardt, K. P. C. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 313–317.

10. Boese, R.; Benet-Buchholz, J.; Stanger, A.; Tanaka, K.; Toda, F. *Chem. Commun.* **1999**, 319–320.
11. The quality of the X-ray structural data of **6** was insufficient to allow for accurate bond length and angle measurements.
12. See: (a) Stanger, A. *J. Am. Chem. Soc.* **1998**, *120*, 12034–12040; (b) Frank, N. L.; Siegel, J. S. In *Advances in Theoretically Interesting Molecules*; Thummel, R. P., Ed.; JAI: London, 1995; Vol. 3, pp. 209–261; (c) Faust, R.; Glendening, E. D.; Streitwieser, A.; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **1992**, *114*, 8263–8268.
13. Boese, R.; Matzger, A. J.; Mohler, D. L.; Vollhardt, K. P. C. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1478–1481.
14. Schulman, J. M.; Disch, R. L.; Jiao, H.; Schleyer, P.v. R. *J. Phys. Chem. A* **1998**, *102*, 8051–8055.
15. Beckhaus, H.-D.; Faust, R.; Matzger, A. J.; Mohler, D. L.; Rogers, D. W.; Rüchardt, C.; Sawhney, A. K.; Verevkin, S. P.; Vollhardt, K. P. C.; Wolff, S. *J. Am. Chem. Soc.* **2000**, *122*, 7819–7820.
16. (a) Schulman, J. M.; Disch, R. L. *J. Phys. Chem. A* **1997**, *101*, 5596–5599; (b) Schulman, J. M.; Disch, R. L. *J. Am. Chem. Soc.* **1996**, *118*, 8470–8474; (c) See, also: Eickmeier, C.; Holmes, D.; Junga, H.; Matzger, A. J.; Scherhag, F.; Shim, M.; Vollhardt, K. P. C. *Angew. Chem., Int. Ed.* **1999**, *38*, 800–804 and references cited therein.
17. See, for example: (a) Lin, C.-L.; Chu, S.-Y.; Ou, M.-C. *J. Chin. Chem. Soc.* **1998**, *45*, 13–16; (b) Jemmis, E. D.; Kiran, B. *J. Org. Chem.* **1996**, *61*, 9006–9008.