

## ■ Gas-Phase &amp; Solid-State Structures

## Aryl–Aryl Interactions in (Aryl-Perhalogenated) 1,2-Diaryldisilanes

Marvin Linnemannstöns,<sup>[a]</sup> Jan Schwabedissen,<sup>[b]</sup> Beate Neumann,<sup>[a]</sup> Hans-Georg Stammer,<sup>[a]</sup> Raphael J. F. Berger,<sup>[b]</sup> and Norbert W. Mitzel<sup>\*[a]</sup>

Dedicated to Professor Carlos Omar Della Védova on the occasion of his 65th birthday

**Abstract:** Three 1,2-diaryltetramethyldisilanes  $X_5C_6-(SiMe_2)_2-C_6X_5$  with two  $C_6H_5$ ,  $C_6F_5$ , or  $C_6Cl_5$  groups were studied concerning the importance of London dispersion driven interactions between their aryl groups. They were prepared from 1,2-dichlorotetramethyldisilane by salt elimination. Their structures were determined in the solid state by X-ray diffraction and for free molecules by gas electron-diffraction. The solid-state structures of the fluorinated and chlorinated derivatives are dominated by aryl–aryl interactions. Unexpectedly,  $Cl_5C_6-(SiMe_2)_2-C_6Cl_5$  exists exclusively as an eclipsed *syn*-conformer in the gas phase with strongly distorted  $Si-C_6Cl_5$  units due to strong intramolecular interactions. In contrast,  $F_5C_6-(SiMe_2)_2-C_6F_5$  reveals weaker interactions. The contributions to the total interaction energy were analyzed by SAPT calculations.

London dispersion (LD) forces are basically the attractive part of van-der-Waals interactions<sup>[1]</sup> and are generally regarded as weak compared to other types of molecular interactions. Accordingly, their importance for chemical reactivity and stability as well as their impact on molecular structure seem to have been underestimated in the past. Single pairs of  $C-H\cdots H-C$  fragments indeed interact weakly but for larger systems with multiple interaction partners, the contribution of dispersion increases rapidly.<sup>[2]</sup> Examples include the diverse phenomena, such as the variation in boiling points along the homologous series of *n*-alkanes, the greater stability of branched vs. linear isomers as well as the folded hairpin structure of gaseous *n*-alkanes longer than heptadecane.<sup>[3]</sup> Wagner and Schreiner re-


cently underlined the importance of LD<sup>[4]</sup> and suggested to revise the established understanding of the influence of steric effects on the stability of molecules in general. For instance, steric repulsion between phenyl groups in hexaphenylethane (HPE) is held accountable for its thermodynamic instability,<sup>[5]</sup> whereas the introduction of even more sterically demanding substituents (like *t*Bu, Ad) in all twelve *meta*-positions leads to isolable HPE derivatives, obviously due to stabilization by LD.<sup>[6]</sup> A delicate balance between Pauli repulsion and LD attraction leads to unusually long C–C bonds observed in several diamondoid dimers,<sup>[7]</sup> they were studied to evaluate a range of quantum-chemical (QC) methods that take LD into account.<sup>[8]</sup>


Noncovalent intermolecular interactions between aromatic systems are of great importance for many supramolecular organization and recognition processes,<sup>[9]</sup> for example, for the side-chain interaction in proteins,<sup>[10]</sup> intercalation of drugs into DNA,<sup>[11]</sup> crystal engineering<sup>[12]</sup> and in many host–guest recognition processes.<sup>[13]</sup> In the history of QC calculations, the  $C_6H_6$  (**1**) dimer was repeatedly studied. In contrast to the herringbone-like arrangement in the crystal structure of pure **1**,<sup>[14–16]</sup> the isolated benzene dimer exists in two equilibrium structures: a tilted T-shaped one and a parallel-displaced one. The complex dynamics and small difference in binding energies has caught the interest of experimentalists and theoreticians.<sup>[17]</sup> Analogous to **1**, Varadwaj et al. found twelve different structures for the dimer of hexafluorobenzene ( $C_6F_6$ , **2**) by QC methods,<sup>[18]</sup> the parallel displaced structure of the dimer being the most stable one. In contrast to the herringbone-like arrangements in solid **1** and **2**,<sup>[14,15]</sup> the 1:1 co-crystal reveals columnar stacks of alternating  $C_6H_6$  and  $C_6F_6$  units.<sup>[19]</sup> First attempts of explanation quoted interacting quadrupoles with their moments being of equal magnitude but of opposite sign (**1**:  $-29.0 \times 10^{-40}$ ; **2**:  $31.7 \times 10^{-40} \text{ C m}^2$ ).<sup>[20]</sup> Later studies indicated that electrostatics alone cannot explain the intermolecular arrangement and that LD contributes at least as much to the total interaction energy.<sup>[21]</sup> Pure hexachlorobenzene ( $C_6Cl_6$ , **3**) behaves differently than **1** or **2**. Its crystal structure comprises molecular stacks similar to the columnar structures of the 1:1  $C_6H_6$ : $C_6F_6$  co-crystal.<sup>[22]</sup> Several pentachlorophenyl compounds show a related behavior.<sup>[23]</sup>

Recently, we investigated the effects of stacking interactions of three compounds with phenyl and perfluorophenyl rings bridged by (sila)propyl chains.<sup>[24]</sup> In the solid state, these molecules receive stabilization by intermolecular aryl–aryl stacking interactions, whereas free molecules, determined by gas elec-

[a] M. Linnemannstöns, B. Neumann, Dr. H.-G. Stammer, Prof. Dr. N. W. Mitzel  
Lehrstuhl für Anorganische Chemie und Strukturchemie  
Fakultät für Chemie, Universität Bielefeld  
Universitätsstraße 25, 33615 Bielefeld (Germany)  
E-mail: mitzel@uni-bielefeld.de

[b] Dr. J. Schwabedissen, Dr. R. J. F. Berger  
Chemie und Physik der Materialien  
Paris-Lodron-Universität Salzburg  
Jakob-Haringer-Straße 2a, 5020 Salzburg (Austria)

 Supporting information and the ORCID identification number(s) for the author(s) of this article can be found under:  
<https://doi.org/10.1002/chem.201905727>.

 © 2019 The Authors. Published by Wiley-VCH Verlag GmbH & Co. KGaA. This is an open access article under the terms of Creative Commons Attribution NonCommercial-NoDerivs License, which permits use and distribution in any medium, provided the original work is properly cited, the use is non-commercial and no modifications or adaptations are made.

tron diffraction (GED), find their energetic minima as conformers bearing intramolecular aryl–aryl interactions.

We turn now to the interactions between symmetric pairs of perchlorinated, perfluorinated and parental phenyl groups, both in the solid and in the gas phase. Gases contain free molecules, independent of intermolecular forces omnipresent in both crystal and solution phases, and thus they are ideally suited for evaluating the results of QC methods. We chose the disilane backbone as a spacer linking the aryl groups due to its conformational flexibility observed in earlier investigations.<sup>[25]</sup> Three symmetrically substituted 1,2-diaryl-1,1,2,2-tetramethyldisilanes  $X_5C_6-(SiMe_2)_2-C_6X_5$  ( $X=H$  (**5**),  $F$  (**6**),  $Cl$  (**7**)) were generated by salt elimination from 1,2-dichlorodisilane **4** with the corresponding lithium phenyl species  $C_6X_5Li$  in good yields after purification by column chromatography and recrystallisation (**5**: 84%, **6**: 79%, **7**: 67%). Silanes **5–7** are insensitive towards water and can be stored under air for at least several months without decomposition.

The structures of **5–7** (Table 1) in the solid state were determined by X-ray diffraction on single crystals obtained by slow evaporation of the solvent from saturated solutions.<sup>[26]</sup> The

	<b>5</b> (XRD)	<b>6</b> (XRD)	<b>6</b> (GED) <sup>[a]</sup>	<b>7</b> (XRD) <sup>[c]</sup>	<b>7</b> (GED) <sup>[c]</sup>
$\phi(CSiSiC)$ [ $^\circ$ ]	177.2(1)	173.7(1)	11.2(8)/48.1(8)	6.0(3)	8.0(5)
$d(Si-Si)$ [ $\text{\AA}$ ]	2.342(1)	2.338(1)	2.386(4)/2.368(4)	2.381(2)	2.367(5)
$d_{c-c}$ inter. [ $\text{\AA}$ ]	–	3.688(2)	–	3.93(1)	–
$d_{c-c}$ intra. [ $\text{\AA}$ ]	–	–	3.76(5) <sup>[b,c]</sup>	3.76(1)	3.82(5) <sup>[b]</sup>
$\chi(SiC_p)$ [ $^\circ$ ]	179.0(1)	179.4(1)	172.8(6) <sup>[b]</sup>	167.6(3)	170.4(5) <sup>[b]</sup>
	179.2(1)	178.4(1)	173.5(6) <sup>[b]</sup>	168.1(3)	

[a] Values are given for the *syn*-/*gauche*-conformers. [b] Dependent parameters, not refined explicitly. [c] Only the *syn*-conformer is present.

twinning in crystals of **5** and **7** could be satisfactorily modelled. Figure 1 illustrates 1,2-diphenyl-disilane **5** to reveal an *anti*-conformation with a torsion angle  $\phi(CSiSiC)$  at  $177.2(1)^\circ$ . Substantial  $\pi$ -stacking to neighboring molecules is not observed, but the tilted T-like arrangement of phenyl groups of neighboring molecules resembles the crystal packing of benzene. The coordination geometry at the silicon atoms is almost tetrahedral and the Si–Si bond length ( $2.342(1)$   $\text{\AA}$ ) lies within the typical range<sup>[25]</sup> for 1,1,2,2-tetramethyldisilanes.

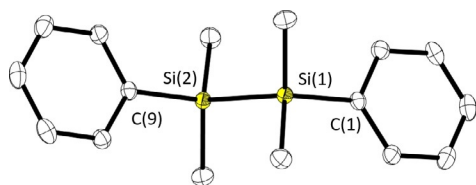


Figure 1. Molecular structure of **5** in the crystalline state. Displacement ellipsoids are drawn at 50% probability level. Hydrogen atoms are omitted for clarity.

The fluorinated **6** also adopts an *anti*-conformation in the crystal ( $\phi_{CSiSiC} = 173.7(1)^\circ$ ), with a Si–Si distance ( $2.338(1)$   $\text{\AA}$ ) identical within experimental error to that in **5**. In contrast to **5**, **6** consists of dimeric units of inversion symmetry. These dimers are stabilized by aryl–aryl interactions ( $d_{centroids} = 3.688(1)$   $\text{\AA}$ , Figure 2). However, there are no such interactions between these and neighboring dimers.

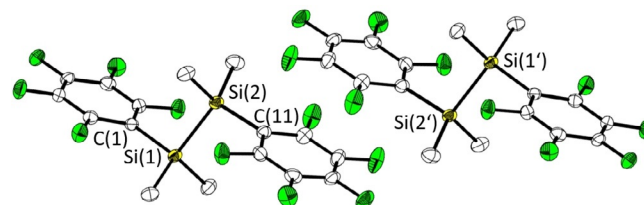


Figure 2. Molecular structure and primary aggregation of **6** in the crystal. Displacement ellipsoids are at 50% probability level. Hydrogen atoms omitted for clarity. Symmetry operation for generating equivalent positions:  $1-x, 1-y, 1-z$ .

The crystal structure of the pentachlorophenyl disilane **7** shows a disorder (50:50, see the Supporting Information) and adopts a rather unusual eclipsed conformation (Figure 3) described by a torsion angle  $\phi_{CSiSiC}$  of barely  $6.0(1)^\circ$ . This is the result of intramolecular  $C_6Cl_5 \cdots C_6Cl_5$  stacking interactions ( $d_{centroids} = 3.76(1)$   $\text{\AA}$ ). These are strong enough to distort the  $SiC_6Cl_5$  units from planarity (Figure 3b), that is, the angle  $Si(1)-C(3)-C(6)$  is  $167.6(3)$  and  $Si(2)-C(3)-C(6)$  is  $168.1(3)^\circ$ . There are also slightly longer intermolecular aryl–aryl-interactions with a distance  $d_{centroids}$  at  $3.93(1)$   $\text{\AA}$ . The columnar stacks found in crystalline **7** resemble those in solid  $C_6Cl_6$ .<sup>[22]</sup> The mean planes of the  $C_6Cl_5$  units in **7** enclose angle of  $63.9(2)$  and  $65.5(2)^\circ$  relative to the vector connecting the ring centroids. The corresponding tilt angle for solid  $C_6Cl_6$ <sup>[22]</sup> was given as  $63^\circ$ . In addition to the stacking interactions, several other intermolecular

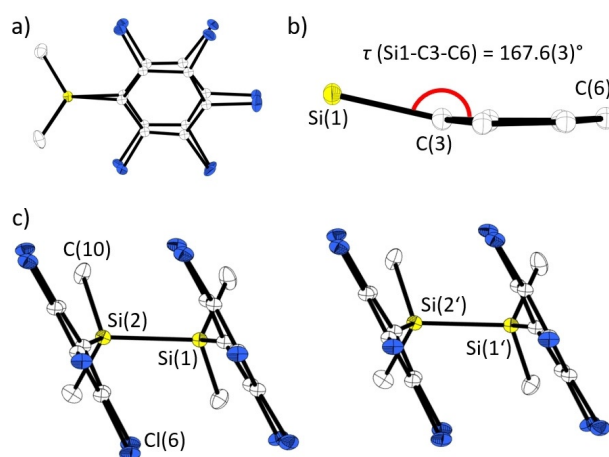


Figure 3. a) View along the Si–Si axis of **7**; b) View on the distorted  $SiC_5$  fragment; c) Molecular structure and primary aggregation motif of **7**. Displacement ellipsoids are drawn at 50% probability level. Hydrogen atoms are omitted for clarity. Symmetry operation for generating equivalent positions:  $2+x, +y, +z$ .

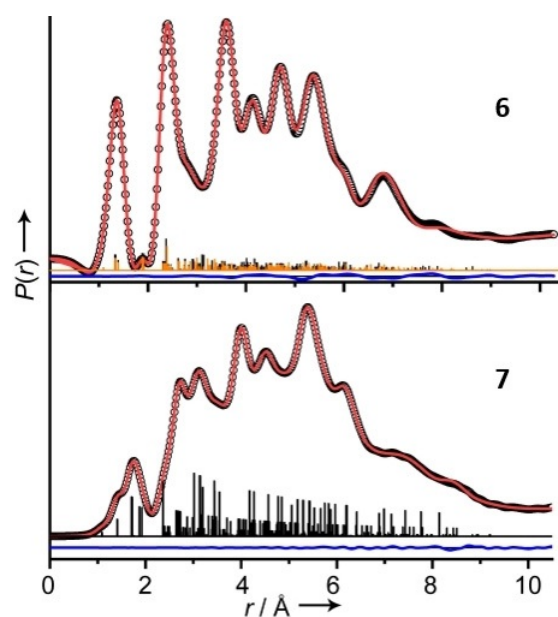
Cl...Cl contacts below the sum of the vdW radii (3.347(1)–3.716(1) Å) are found.

Using dispersion-corrected (D3BJ)<sup>[8]</sup> energy scans (PBE0/TZVP) along the CSiSiC torsion angle,<sup>[27,28]</sup> the conformational landscapes of compounds 5–7 were explored (Table 2); the

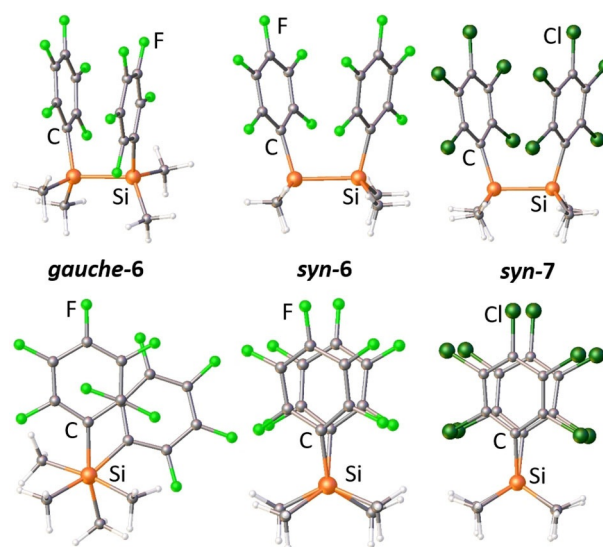
		Dispersion corrected		Uncorrected for dispersion	
		$\phi(\text{CSiSiC})$ [°]	$\Delta E$	$\phi(\text{CSiSiC})$ [°]	$\Delta E$
5	<i>gauche</i>	57.9	6.8	64.9	4.6
	<i>anti</i>	179.9	0.0	180.0	0.0
6	<i>syn</i>	11.5	1.5	19.7	4.0
	<i>gauche</i>	48.2	0.0	54.1	0.0
	<i>anticlinal</i>	140.7	3.0	141.9	3.7
7	<i>syn</i>	8.4	0.0	11.2	0.0
	<i>anticlinal</i>	138.4	14.8	140.1	0.6

generated structures were optimized at the PBE0/TZVP and PBE0(D3BJ)/TZVP levels of theory (see the Supporting Information). These potential energy scans predict two stable conformers for the parent phenyl-substituted disilane 5, three for the fluorinated species 6, and two for the chlorinated 7. Both predicted conformers of 5 are free of aryl stacking interactions and adopt, expectedly, stable *gauche*- and *anti*-orientations of the phenyl groups about the Si–Si bond. In contrast, energy scans for 6 and 7 forecast structures with *syn*-conformation of the aryl substituents stabilized by aryl–aryl stacking interactions. Optimizing the different suggested structures for 5 yielded *gauche*- and *anti*-conformers of  $C_1$ -symmetry, the latter one being the most stable conformer independent of including dispersion. The different tilt of the phenyl groups about the Si– $C_{ipso}$  bond reduces symmetry from the expected  $C_2$ . However, fluoro-compound 6 contains a *syn*-conformer and this is the sole conformer observed for 7. For 6 the *gauche*-conformer is lowest in energy. This is possibly a manifestation of the *gauche* effect,<sup>[29]</sup> usually observed for partially fluorinated ethanes<sup>[30]</sup> and disilanes.<sup>[31]</sup> Optimizing the *syn*-conformers of 6 and 7 under explicit consideration of dispersion, the dihedral angles  $\phi_{\text{CSiSiC}}$  become smaller and the silicon atoms bend out of the aryl planes (as described for the solid-state of 7 above). Dispersion corrections stabilize both *syn* conformers—by about  $14 \text{ kJ mol}^{-1}$  in the case of 7.

Experimental investigations of the conformational characteristics, relative abundances and structures of disilanes 5 to 7 in the gas phase were undertaken by means of gas electron diffraction (Figures 4 and 5; for exptl. details see the Supporting Information). Experimental scattering data of 5 were recorded, but could so far not be modelled satisfactorily due complicated dynamics related to large amplitude motions of the phenyl rings about the Si–C bonds. Related complications were described in other recent GED studies.<sup>[32]</sup> As predicted by the dispersion-corrected QC calculations for 7, *syn* was the only conformer found in the gas phase. Modelling the molecular scat-



**Figure 4.** Radial distribution curves for the GED refinements of disilanes 6 (top) and 7 (bottom): experimental values (circles), model (solid line) and difference curve (lower trace, exp.-model). Vertical sticks represent interatomic distances.

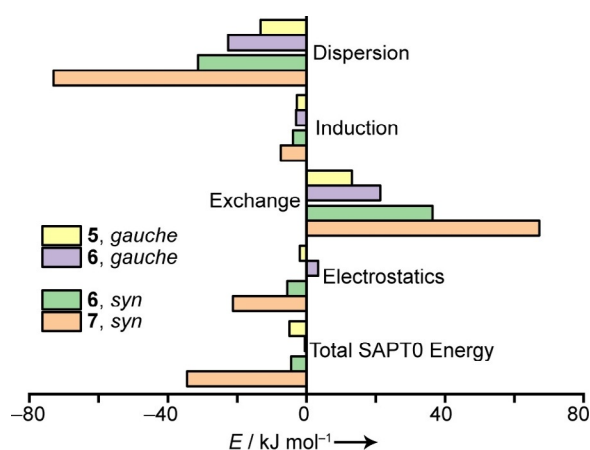


**Figure 5.** Two views of each of the structures of the *gauche*- and *syn*-conformers of 6 and the only occurring conformer of 7 (*syn*) as determined by gas electron diffraction (GED).

tering in this way resulted in a disagreement factor of 4.4%. The *syn*-conformer adopts a dihedral angle CSiSiC of  $8.0(6)^\circ$  and a centroid...centroid distance between the  $\text{C}_6\text{Cl}_5$  rings of  $3.82(5) \text{ \AA}$ . Both values are slightly larger than the corresponding parameters in the solid state (vide supra), but the Si–Si bond ( $r_{\text{H1}} = 2.367(5) \text{ \AA}$ ,  $3\sigma$ ) is in a comparable range to the corresponding solid-state parameter ( $2.381(2) \text{ \AA}$ ). The gas-phase structure of the fluorinated 6 was fitted ( $R_f = 3.6\%$ ) using a model comprising a *syn*-conformer ( $\phi_{\text{CSiSiC}} = 11.2(8)^\circ$ ) and a *gauche*-conformer ( $\phi_{\text{CSiSiC}} = 48.1(8)^\circ$ ). The preference for a con-

former remains ambiguous as the abundance of the *syn*-conformer is determined to be 43(13)% by GED. Thus, the two conformers are present in almost equal amounts in the gas phase. Despite the larger dihedral angle in the *syn*-conformer of **6**, the centroid...centroid distance is the same within experimental error (3.76(5) Å for **6**) between the two aryl substituents in **6** and **7**.

For breaking down the main contributions to the interactions between the aryl substituents in **5**–**7**, symmetry-adapted perturbation theory (SAPT) was applied (Figure 6).<sup>[33]</sup> The



**Figure 6.** SAPT decomposition of energy in  $\text{kJ mol}^{-1}$  of the interaction between the conformers found in the gas phase for **5**–**7**.

chosen conformers are those experimentally observed in the gas phase and additionally the *gauche* conformer of **5**. Comparing the two *gauche*-conformers of **5** and **6** gives similar induction stabilizations at about  $-3 \text{ kJ mol}^{-1}$ , but a higher dispersion energy for the fluorinated **6** (**6**:  $-22.6$ , **5**:  $-13.2 \text{ kJ mol}^{-1}$ ), while the exchange repulsion energy behaves in a reverse manner (**6**:  $13.1$ , **5**:  $21.3 \text{ kJ mol}^{-1}$ ); the electrostatic contribution stabilizes **5** ( $-2.0 \text{ kJ mol}^{-1}$ ) but destabilizes **6** ( $3.4 \text{ kJ mol}^{-1}$ ). This can be rationalized to the parallel-displaced geometry for **5** (similar: benzene dimer in the gas<sup>[17]</sup>) whereas electrostatic repulsion in **6** may be due to a fluorine atom located almost directly above the aryl substituent. Overall, aryl–aryl interactions stabilize **6** by  $0.5$  and **5** by  $4.9 \text{ kJ mol}^{-1}$ .

The aryl moieties in the *syn*-conformers are closer and interact more strongly. All energy contributions in **7** are about double as large as in **6**, except the electrostatic term: this is more than four times larger (**6**:  $-5.6$ , **7**:  $-27.2 \text{ kJ mol}^{-1}$ ). The importance of electrostatic contributions for interacting aryl rings was recently highlighted.<sup>[34]</sup> The exchange repulsion in *syn*-**6** ( $36.4 \text{ kJ mol}^{-1}$ ) outweighs the dispersion energy ( $-31.3 \text{ kJ mol}^{-1}$ ) by  $5 \text{ kJ mol}^{-1}$ . In contrast to that, the large dispersion energy in **7** ( $-73.0 \text{ kJ mol}^{-1}$ ) stabilizes the intramolecular stacking interaction, while exchange is comparatively smaller ( $67.2 \text{ kJ mol}^{-1}$ ).

Our work demonstrates the strikingly different ability of phenyl, pentafluorophenyl and pentachlorophenyl substituents to exert aryl–aryl stacking interactions. We studied this between the 1,2-aryl-substituents in tetramethyldisilane units.

While simple hydrogen substituted phenyl groups are too weak to predetermine aggregation in the solid state or conformers with aryl–aryl interactions in the gas phase, pentafluorophenyl and pentachloro-phenyl substituents do so. Interactions between pentafluorophenyl groups are strong enough to lead to intermolecular aggregation in the solid and to stabilize an otherwise unfavorable *syn*-conformer in the gas phase. Pentachlorophenyl substituents interact so strongly, that *syn* is the sole conformation present in the gaseous and solid states, despite the fact that substantial deformation of the  $\text{Si-C}_6\text{Cl}_5$  units has to be overcome. The analysis of interaction contributions shows the increasing importance of London dispersion along the series  $\text{C}_6\text{H}_5 < \text{C}_6\text{F}_5 < \text{C}_6\text{Cl}_5$  which is partially compensated by adversely acting exchange interactions and augmented by an electrostatic term, both also with increasing strength along the series. These results may serve to explain the practically often observed effect of low solubility of highly chlorinated aryl compounds.

## Acknowledgements

We thank Klaus-Peter Mester and Marco Wißbrock for recording NMR spectra and Barbara Teichner for elemental analyses. We gratefully acknowledge computation time and QC programs provided by the RRZK (Universität zu Köln) and the PC<sup>2</sup> (Universität Paderborn). This work was funded by DFG (German Research Foundation) in the Priority Program SPP1807 „Control of LD in molecular chemistry“, grant MI477/28-2 and BE4632/2-2, project no. 271386299) and the core facility GED@BI (grant MI477/35-1, project no. 324757882).

## Conflict of interest

The authors declare no conflict of interest.

**Keywords:** bridged arenes • dispersion • halogenated arenes • inter/intramolecular  $\pi$ -stacking • solid-state structures

- [1] F. London, *Z. Phys.* **1930**, *63*, 245.
- [2] S. Grimme in *The Chemical Bond* (Eds.: G. Frenking, S. Shaik), Wiley-VCH Verlag, Weinheim, Germany, **2014**, p 477.
- [3] N. O. B. Lüttschwager, T. N. Wassermann, R. A. Mata, M. A. Suhm, *Angew. Chem. Int. Ed.* **2013**, *52*, 463; *Angew. Chem.* **2013**, *125*, 482.
- [4] J. P. Wagner, P. R. Schreiner, *Angew. Chem. Int. Ed. Engl.* **2015**, *54*, 12274; *Angew. Chem.* **2015**, *127*, 12446.
- [5] M. Stein, W. Winter, A. Rieker, *Angew. Chem. Int. Ed. Engl.* **1978**, *17*, 692; *Angew. Chem.* **1978**, *90*, 737.
- [6] a) S. Rösel, C. Balestrieri, P. R. Schreiner, *Chem. Sci.* **2017**, *8*, 405; b) S. Rösel, J. Becker, W. D. Allen, P. R. Schreiner, *J. Am. Chem. Soc.* **2018**, *140*, 14421.
- [7] a) A. A. Fokin, T. S. Zhuk, S. Blomeyer, C. Pérez, L. V. Chernish, A. E. Pashenko, J. Antony, Y. V. Vishnevskiy, R. J. F. Berger, S. Grimme, C. Logemann, M. Schnell, N. W. Mittel, P. R. Schreiner, *J. Am. Chem. Soc.* **2017**, *139*, 16696.
- [8] a) S. Grimme, *J. Comput. Chem.* **2006**, *27*, 1787; b) S. Grimme, J. Antony, S. Ehrlich, H. Krieg, *J. Chem. Phys.* **2010**, *132*, 154104; c) S. Grimme, S. Ehrlich, L. Goerigk, *J. Comput. Chem.* **2011**, *32*, 1456; d) J. Řezáč, P. Hobza, *J. Chem. Theory Comput.* **2012**, *8*, 141.
- [9] E. A. Meyer, R. K. Castellano, F. Diederich, *Angew. Chem. Int. Ed.* **2003**, *42*, 1210; *Angew. Chem.* **2003**, *115*, 1244.

- [10] S. Burley, G. Petsko, *Science* **1985**, 229, 23.
- [11] L. S. Lerman, *J. Mol. Biol.* **1961**, 3, 18–IN14.
- [12] G. W. Coates, A. R. Dunn, L. M. Henling, D. A. Dougherty, R. H. Grubbs, *Angew. Chem. Int. Ed. Engl.* **1997**, 36, 248; *Angew. Chem.* **1997**, 109, 290.
- [13] C. A. Hunter, *Chem. Soc. Rev.* **1994**, 23, 101.
- [14] E. G. Cox, D. E. Cruickshank, J. A. S. Smith, *Proc. R. Soc. London Ser. A* **1958**, 247(1248), 1.
- [15] N. Boden, P. P. Davis, C. H. Stam, G. A. Wesselink, *Mol. Phys.* **1973**, 25, 81.
- [16] M. Pitoňák, P. Neogrady, J. Rezáč, P. Jurečka, M. Urban, P. Hobza, *J. Chem. Theory Comput.* **2008**, 8, 1829.
- [17] a) A. van der Avoird, R. Podeszwa, K. Szalewicz, C. Leforestier, R. van Harrevelt, P. R. Bunker, M. Schnell, G. von Helden, G. Meijer, *Phys. Chem. Chem. Phys.* **2010**, 12, 8219; b) M. Schnell, U. Erlekam, P. R. Bunker, G. von Helden, J.-U. Grabow, G. Meijer, A. van der Avoird, *Angew. Chem. Int. Ed.* **2013**, 52, 5180; *Angew. Chem.* **2013**, 125, 5288; c) M. Schnell, U. Erlekam, P. R. Bunker, G. von Helden, J.-U. Grabow, G. Meijer, A. van der Avoird, *Phys. Chem. Chem. Phys.* **2013**, 15, 10207.
- [18] P. R. Varadwaj, A. Varadwaj, B.-Y. Jin, *Phys. Chem. Chem. Phys.* **2015**, 17, 31624.
- [19] a) J. S. W. Overell, G. S. Pawley, *Acta Crystallogr. Sect. B* **1982**, 38, 1966; b) J. H. Williams, J. K. Cockcroft, A. N. Fitch, *Angew. Chem. Int. Ed. Engl.* **1992**, 31, 1655; *Angew. Chem.* **1992**, 104, 1666.
- [20] a) J. H. Williams, *Acc. Chem. Res.* **1993**, 26, 593; b) T. Dahl, D. Kozma, M. Ács, J. Weidlein, H. Schnöckel, G. B. Paulsen, R. I. Nielsen, C. E. Olsen, C. Pedersen, C. E. Stidsen, *Acta Chem. Scand.* **1994**, 48, 95; c) M. I. Cabaco, Y. Danten, M. Besnard, Y. Guissani, B. Guillot, *Chem. Phys. Lett.* **1996**, 262, 120; d) J. C. Collings, K. P. Roscoe, R. L. Thomas, A. S. Batsanov, L. M. Stimson, J. A. K. Howard, T. B. Marder, *New J. Chem.* **2001**, 25, 1410; e) M. R. Battaglia, A. D. Buckingham, J. H. Williams, *Chem. Phys. Lett.* **1981**, 78, 421.
- [21] a) M. O. Sinnokrot, C. D. Sherrill, *J. Am. Chem. Soc.* **2004**, 126, 7690; b) B. W. Gung, J. C. Amicangelo, *J. Org. Chem.* **2006**, 71, 9261; c) S. Tsuzuki, T. Uchimaru, M. Mikami, *J. Phys. Chem. A* **2006**, 110, 2027; d) R. G. Huber, M. A. Margreiter, J. E. Fuchs, S. von Grafenstein, C. S. Tautermann, K. R. Liedl, T. Fox, *J. Chem. Inf. Model.* **2014**, 54, 1371.
- [22] C. M. Reddy, M. T. Kirchner, R. C. Gundakaram, K. A. Padmanabhan, G. R. Desiraju, *Chem. Eur. J.* **2006**, 12, 2222.
- [23] a) M. V. Vener, A. V. Shishkina, A. A. Rykounov, V. G. Tsirelson, *J. Phys. Chem. A* **2013**, 117, 8459; b) S. Postle, V. Podgorny, D. W. Stephan, *Dalton Trans.* **2016**, 45, 14651; c) W. Zhao, Q. Yan, K. Tsutsumi, K. Nomura, *Organometallics* **2016**, 35, 1895; d) E. J. Fernández, A. Laguna, J. M. Lopez de Luzuriaga, M. E. Olmos, J. Perez, *Dalton Trans.* **2004**, 1801; e) C. P. Brock, Y. Fu, *Acta Crystallogr. Sect. B* **1997**, 53, 613.
- [24] S. Blomeyer, M. Linnemannstöns, J. H. Nissen, J. Paulus, B. Neumann, H.-G. Stammer, N. W. Mitzel, *Angew. Chem. Int. Ed.* **2017**, 56, 13259; *Angew. Chem.* **2017**, 129, 13443.
- [25] a) B. A. Smart, H. E. Robertson, N. W. Mitzel, D. W. H. Rankin, R. Zink, K. Hassler, *J. Chem. Soc. Dalton Trans.* **1997**, 2475; b) S. L. Hinchley, B. A. Smart, C. A. Morrison, H. E. Robertson, D. W. H. Rankin, R. Zink, K. Hassler, *J. Chem. Soc. Dalton Trans.* **1999**, 2303; c) S. L. Hinchley, H. E. Robertson, A. Parkin, D. W. H. Rankin, G. Tekautz, K. Hassler, *Dalton Trans.* **2004**, 759; d) J. Schwabedissen, P. D. Lane, S. L. Masters, K. Hassler, D. A. Wann, *Dalton Trans.* **2014**, 43, 10175; e) S. L. Masters, H. E. Robertson, D. A. Wann, M. Hölbling, K. Hassler, R. Björnsson, S. Ö. Wallewik, I. Arnason, *J. Phys. Chem. A* **2015**, 119, 1600.
- [26] CCDC 1965241, 1965242, and 1965243 contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.
- [27] a) J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* **1996**, 77, 3865; b) J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* **1997**, 78, 1396.
- [28] a) A. Schäfer, H. Horn, R. Ahlrichs, *J. Chem. Phys.* **1992**, 97, 2571; b) A. Schäfer, C. Huber, R. Ahlrichs, *J. Chem. Phys.* **1994**, 100, 5829.
- [29] a) S. Wolfe, *Acc. Chem. Res.* **1972**, 5, 102; b) C. Thiehoff, Y. P. Rey, R. Gilmore, *Isr. J. Chem.* **2017**, 57, 92; c) J. C. R. Thacker, P. L. A. Popelier, *J. Phys. Chem. A* **2018**, 122, 1439.
- [30] a) L. Fernholt, K. Hveseth, *Acta Chem. Scand. Sect. A* **1980**, 34, 163; b) D. Friesen, K. Hedberg, *J. Am. Chem. Soc.* **1980**, 102, 3987; c) F. Akkermann, J. Buschmann, D. Lentz, P. Luger, E. Rödel, *J. Chem. Crystallogr.* **2003**, 33, 969.
- [31] P. Ramasami, *Proc. Computer Sci.* **2010**, 1, 1139.
- [32] a) J.-H. Lamm, J. Horstmann, H.-G. Stammer, N. W. Mitzel, Y. A. Zhabanov, N. V. Tverdova, A. A. Otyotov, N. I. Giricheva, G. V. Girichev, *Org. Biomol. Chem.* **2015**, 13, 8893; b) Y. V. Vishnevskiy, D. S. Tikhonov, J. Schwabedissen, H.-G. Stammer, R. Moll, B. Krumm, T. M. Klapötke, N. W. Mitzel, *Angew. Chem. Int. Ed.* **2017**, 56, 9243; *Angew. Chem.* **2017**, 129, 9371.
- [33] a) R. M. Parrish, C. D. Sherrill, *J. Chem. Phys.* **2014**, 141, 044115; b) R. M. Parrish, T. M. Parker, C. D. Sherrill, *J. Chem. Theory Comput.* **2014**, 10, 4417; c) R. M. Parrish, C. D. Sherrill, *J. Am. Chem. Soc.* **2014**, 136, 17386; d) R. M. Parrish, J. F. Gonthier, C. Corminbœuf, C. D. Sherrill, *J. Chem. Phys.* **2015**, 143, 051103.
- [34] a) S. E. Wheeler, K. N. Houk, *J. Am. Chem. Soc.* **2008**, 130, 10854; b) S. E. Wheeler, K. N. Houk, *Mol. Phys.* **2009**, 107, 749; c) C. D. Sherrill, *Acc. Chem. Res.* **2013**, 46, 1020; d) S. E. Wheeler, J. W. G. Bloom, *J. Phys. Chem. A* **2014**, 118, 6133.

---

 Manuscript received: December 19, 2019

Accepted manuscript online: December 20, 2019

Version of record online: January 30, 2020