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Aryl-Aryl Interactions in (aryl-perhalogenated) 1,2-Diaryldisilanes

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

Three 1,2-diaryltetramethyldisilanes X_5C_6 -(SiMe₂)₂-C₆ X_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 -(SiMe₂)₂-C₆Cl₅ exists exclusively as eclipsed synconformer in the gas phase with strongly distorted Si-C₆Cl₅ units due to strong intramolecular interactions. In contrast, F_5C_6 -(SiMe₂)₂-C₆F₅ reveals weaker interactions. The contributions to the total interaction energy was analyzed by SAPT calculations.

London dispersion (LD) forces are basically the attractive part of van-der-Waals interactions^[1] 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···H-C fragments indeed interact weakly but for larger systems with multiple interaction partners, the contribution of dispersion increases rapidly.^[2] 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.^[3] Wagner and Schreiner recently underlined the importance of LD^[4] 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,^[5] whereas the introduction of even more sterically demanding substituents (like 'Bu, Ad) in all twelve meta-positions leads to isolable HPE derivatives, obviously due to stabilization by LD.^[6] A delicate balance between Pauli repulsion and LD attraction leads to unusually long C-C bonds observed in several diamondoid dimers;^[7] they were studied to evaluate a range of quantumchemical (QC) methods that take LD into account.[8]

Non-covalent intermolecular interactions between aromatic systems are of great importance for many supramolecular organization and recognition processes,^[9] for example for the side-chain

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interaction in proteins,^[10] intercalation of drugs into DNA,^[11] crystal engineering^[12] and in many host-guest recognition processes.^[13] In the history of QC calculations, the C₆H₆ (1) dimer was repeatedly studied. In contrast to the herringbone-like arrangement in the crystal structure of pure 1,[14-16] 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.^[17] Analogous to 1, Varadwaj et al. found twelve different structures for the dimer of hexafluorobenzene (C₆F₆, 2) by QC methods,^[18] the parallel displaced structure of the dimer being the most stable one. In contrast to the herringbone-like arrangements in solid 1 and 2,[14,15] the 1:1 co-crystal reveals columnar stacks of alternating C₆H₆ and C₆F₆ units.^[19] First attempts of explanation quoted interacting quadrupoles with their moments being of equal magnitude but of opposite sign (1: $-29.0 \cdot 10^{-40}$; 2: 31.7.10⁻⁴⁰ C m²).^[20] Later studies indicated that electrostatics alone cannot explain the intermolecular arrangement and that LD contributes at least as much to the total interaction energy.[21] 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 C₆H₆·C₆F₆ co-crystal.^[22] Several pentachlorophenyl compounds show a related behavior.^[23]

Recently, we investigated the effects of stacking interactions of three compounds with phenyl and perfluorophenyl rings bridged by (sila)propyl chains.^[24] In the solid state, these molecules receive stabilization by intermolecular aryl-aryl stacking interactions, whereas free molecules, determined by gas electron diffraction (GED), find their energetic minima as conformers bearing intra-molecular 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.^[25] Three symmetrically substituted 1,2-diaryl-1,1,2,2-tetramethyldisilanes X_5C_6 -(SiMe₂)₂-C₆X₅ [X = H(5), F(6), Cl(7)] were generated by salt elimination from 1,2dichlorodisilane 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** in the solid state were determined by Xray diffraction on single crystals obtained by slow evaporation of the solvent from saturated solutions.^[26] The twinning in crystals of **5** and **7** could be satisfactorily modelled. Figure 1 illustrates 1,2diphenyl-disilane **5** to reveal a *anti*-conformation with a torsion angle φ (CSiSiC) at 177.2(1)°. Substantial π -stacking to neighboring molecules is not observed, but the tilted T-like arrangement

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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) Å] lies within the typical range^[25] 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 $[\varphi_{\text{CSISIC}} = 173.7(1)^\circ]$, with a Si–Si distance [2.338(1) Å] being 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 [$d_{\text{centroids}} = 3.688(1)$ Å, 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.



Figure 3. a) View along the Si–Si axis of **7**; b) View on the distorted SiC₅ 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.

The crystal structure of the pentachlorophenyl disilane **7** shows a disorder (50:50, see SI) and adopts a rather unusual eclipsed conformation (Figure 3) described by a torsion angle φ_{CSISIC} of barely 6.0(1)°. This is the result of intramolecular C₆Cl₅···C₆Cl₅ stacking interactions [$d_{\text{centroids}} = 3.76(1)$ Å]. These are strong enough to distort the SiC₆Cl₅ units from planarity (Figure 3b), i.e. the angle Si(1)-C(3)-C(6) is 167.6(3)° and Si(2)-C(3)-C(6) is 168.1(3)°.

There are also slightly longer intermolecular aryl-aryl-interactions with a distance $d_{centroids}$ at 3.93(1) Å. The columnar stacks found in crystalline **7** resemble those in solid C₆Cl₆.^[22] The mean planes of the C₆Cl₅ units in **7** enclose angle of 63.9(2) and 65.5(2)° relative to the vector connecting the ring centroids. The corresponding tilt angle for solid C₆Cl₆^[22] was given as 63°. In addition to the stacking interactions, several other intermolecular Cl···Cl contacts below the sum of the vdW radii [3.347(1)–3.716(1) Å] are found.

Table 1. Selected experimental structures parameters for **5–7** in the crystalline state (XRD) and in the gas phase (GED, r_{h1} values, error 1σ).

	5 (XRD)	6 (XRD)	6 (GED) ^a	7 (XRD)⁰	7 (GED) ^c		
φ (CSiSiC) [°]	177.2(1)	173.7(1)	11.2(8)/	6.0(3)	8.0(5)		
			40.1(0)				
<i>d</i> (Si–Si) [Å]	2.342(1)	2.338(1)	2.386(4)/ 2.368(4)	2.381(2)	2.367(5)		
d _{c-c} inter. [Å]	-	3.688(2)	-	3.93(1)	-		
dc-cintra. [Å]	_		3.76(5) ^{b,c}	3.76(1)	3.82(5) ^b		
т (SiC,С _p) [°]	179.0(1)	179.4(1)) 172.8(6) ^b) 173.5(6) ^b	167.6(3) 168.1(3)	170.4(5) ^b		
	179.2(1)	178.4(1)					

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

Table 2. Energetic differences (ΔE) in kJ mol ⁻¹ relative to the most stable con-
former and dihedral angles φ (CSiSiC) for the conformers of 5, 6 and 7 at the
PBE0/TZVP level of theory, with and without GD3(BJ) corrections for dispersion.

		Dispersion corrected		Uncorrected for dispersion	
		φ (CSiSiC) [°]	⊿E	φ (CSiSiC) [°]	ΔE
5	gauche	57.9	6.8	64.9	4.6
	anti	179.9	0.0	180.0	0.0
6	syn	11.5	1.5	19.7	4.0
	gauche	48.2	0.0	54.1	0.0
	anticlinal	140.7	3.0	141.9	3.7
7	syn	8.4	0.0	11.2	0.0
	anticlinal	138.4	14.8	140.1	0.6

Using dispersion-corrected (D3BJ)^[8] energy scans (PBE0/TZVP) along the CSiSiC torsion angle, [27,28] the conformational landscapes of compounds 5-7 were explored; the generated structures were optimized at the PBE0/TZVP and PBE0(D3BJ)/TZVP levels of theory (see SI). 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-Cipso 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.^[29] usually observed for partially fluorinated ethanes^[30] and disilanes.^[31] Optimizing the

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syn-conformers of **6** and **7** under explicit consideration of dispersion, the dihedral angles φ_{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 kJ mol⁻¹ in the case of **7**.



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 $\bf{6}$ and the only occurring conformer of $\bf{7}$ (*syn*) as determined by gas electron diffraction (GED).

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, exptl. details see SI). 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.^[32] As predicted by the dispersion-corrected QC calculations for **7**, *syn* was the only

conformer found in the gas phase. Modelling the molecular scattering in this way resulted in a disagreement factor of 4.4%. The svn-conformer adopts a dihedral angle CSiSiC of 8.0(6)° and a centroid...centroid distance between the C_6Cl_5 rings of 3.82(5) Å. Both values are slightly larger than the corresponding parameters in the solid state (vide supra), but the Si–Si bond $[r_{h1} = 2.367(5) \text{ Å},$ 3o] is in a comparable range to the corresponding solid-state parameter [2.381(2) Å]. The gas-phase structure of the fluorinated 6 was fitted ($R_f = 3.6\%$) using a model comprising a synconformer $[\varphi_{CSiSiC} = 11.2(8)^{\circ}]$ and a gauche-conformer $[\varphi_{CSiSiC} =$ 48.1(8)°]. The preference for a conformer 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).^[33] The 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 kJ mol⁻¹, but a higher dispersion energy for the fluorinated **6** (**6**: –22.6, **5**: –13.2 kJ mol⁻¹), while the exchange repulsion energy behaves in a reverse manner (**6**: 13.1, **5**: 21.3 kJ mol⁻¹); the electrostatic contribution stabilizes **5** (–2.0 kJ mol⁻¹) but destabilizes **6** (3.4 kJ mol⁻¹). This can be rationalized to the parallel-displaced geometry for **5** (similar: benzene dimer in the gas^[17]) 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 kJ mol⁻¹ and **5** by 4.9 kJ mol⁻¹.



Figure 6. SAPT decomposition of energy in kJ mol⁻¹ of the interaction between the conformers found in the gas phase for **5–7**.

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 kJ mol⁻¹). The importance of electrostatic contributions for interacting aryl rings was recently high-lighted.^[34] The exchange repulsion in *syn*-**6** (36.4 kJ mol⁻¹) outweighs the dispersion energy (-31.3 kJ mol⁻¹) by 5 kJ mol⁻¹. In contrast to that, the large dispersion energy in **7** (-73.0 kJ mol⁻¹) stabilizes the intramolecular stacking interaction, while exchange is comparatively smaller 67.2 kJ/mol⁻¹.

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Our work demonstrates the strikingly different ability of phenyl, pentafluorophenyl and pentachlorophenyl substituents to exert arvl-arvl stacking interactions. We studied this between the 1.2aryl-substituents in tetramethyldilsilane units. While simple hydrogen substituted phenyl groups are too weak 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 Si-C₆Cl₅ units has to be overcome. The analysis of interaction contributions shows the increasing importance of London dispersion along the series $C_6H_5 < C_6F_5 < C_6CI_5$ 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.

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An eclipsed *syn*-conformation is exclusively observed for Cl_5C_6 -(SiMe₂)₂-C₆Cl₅ in the solid and gaseous phase with strongly distorted Si-C₆Cl₅ units; it demonstrates the strikingly different ability of phenyl, pentafluorophenyl and pentachlorophenyl substituents to exert aryl-aryl stacking interactions.

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Aryl-Aryl Interactions in (aryl-perhalogenated) 1,2-Diaryldisilanes