peri-Interactions in Naphthalenes, 12 [1]. The Significance of Linear and T-Shaped Arrangements in *peri*-Substituted Naphthalenes

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Nearly linear alignment and T-shaped arrangements of *peri*-substituents at the naphthalene and anthracene systems are common features which cannot serve to infer hypercoordinate bonding.

Key words: Octet Rule, Naphthalene *peri*-Interactions, 4c, 6e and 5c, 6e Bonds, S/S, Se/Se and Se/O Interactions

Introduction

Hypercoordination (or *hypervalence*) of the "higher" main group elements, *i. e*. their ability to violate the octet rule, continues to intrigue chemists. *E. g*., tetraphenylphosphonium salts exhibit electrophilic properties towards strong nucleophiles; with phenyllithium, pentaphenylphosphorane is formed [2], in which the P atom is in the centre of a trigonal bipyramid (TBP) with three equatorial and two axial covalent P–C bonds [3]. In TBP's, the apical atoms and the central atom are in linear alignment whereas each of the equatorial atoms forms a T-shaped arrangement with the central and the apical atoms. As a matter of course, the TBP is distorted when *different* ligands are attached to the central atom, the "linearity" being imperfect and the T's oblique [4, 5]. Search for linear and T-shaped arrangements has become a common procedure to trace hypercoordinate interactions [6 – 10]. Atomic arrangements amenable to a description as a distorted TBP may, however, be conditioned by molecular geometry so that the identification of linear and T-shaped alignments is insufficient to prove hypercoordination [4, 5, 11 – 13].

For considerable time, d-orbital participation was firmly believed to provide a solid "understanding" of pentacovalence [14]. Though even supported by extensive computations on prototype model molecules, the concept later fell into disgrace, and the theory of a three-centre, four-electron bond (3c, 4e), again resting on quantum chemical calculations, became the new favourite [15]. On the one hand, 3c, 4e-"half-bonds" continue to enjoy wide-spread approval [16], and the concept has even been extended to four- and five-centre, six-electron bonds (4c, 6e; 5c, 6e) [7 – 10]. On the other hand, Gillespie and Popelier pointed out some serious shortcomings and insisted that this is an unnecessary concept; according to these authors, the VB equivalent of the MO 3c, 4e description is a bond-no bond resonance which does not look attractive for compounds such as Ph_5P [17]. However, the pentaorgano-phosphoranes and hexaarylphosphates defy alternative explanations of hypervalence either. C–P bonds share with C–H bonds a very low polarity (Pauling electronegativities C 2.5, H and P 2.1, for comparison N and Cl 3.0, O 3.5, F 4.0), while such theories are based on a high polarity of the bonds in *hypervalent molecules* [17]. *Hypervalence* has therefore to be rated as a phenomenon which is still not adequately understood.

It seems therefore mandatory to scrutinize the alleged evidence adduced to support the various theories. It is tempting to suspect that at least the recent extensions of the three-centre, four-electron theory may eventually turn out to be as ephemeral as the theory of d-orbital participation. A countercheck whether the properties of the respective compounds resist a rationalization without recourse to hypercoordinate interactions and thus necessitate to invoke new types of bonding is indispensable.

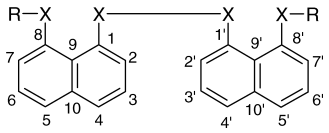
Discussion

Four- and five-centre, six-electron bonds (4/5c, 6e) have been claimed to play a decisive role in 1,8-disulfur-substituted naphthalenes [9] and related

Table 1. Comparison of **11** and **14a** [10] with **12** [60][a].

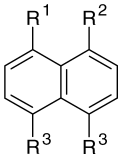
	11		**14a**			**12**	
Bonding distances [pm]							
Se(1)-C(1)	192.2		193.0		O(1)-C(1)	134.9	
Se(8)-C(8)	191.7		193.2		O(11)-C(11)	137.7	
					O(6)-C(6)	137.6	
O(9)=C(9)[b]	122.5		138.7		O(12)=C(12)	121.8	
O(10)-C(10)	120.9				O(5)=C(5)	121.4	
C(1)-C(9a)	141.1		144.4		C(1)-C(12a)	141.3	
C(9)-C(9a)	147.2		139.7		C(12)-C(12a)	148.8	
C(9)-C(8a)	148.7		140.0		C(12)-C(11a)	149.4	
C(8)-C(8a)	140.4		144.2		C(11)-C(11a)	140.0	
Non-bonding distances [pm] (%Σr(vdW))							
					C(1)···C(12)	254.5	(75)
					C(11)···C(12)	252.2	(74)
					C(5)···C(6)	253.7	(75)
Se(1)···O(9)	268.8	(78)	273.1	(79)	O(1)···O(12)	268.2	(84)
Se(8)···O(9)	267.3	(77)	274.4	(80)	O(11)···O(12)	277.7	(87)
					O(5)···O(6)	275.0	(86)
Angles at the hetero-atom [°]							
$C(1)^{Ph}$-Se(1)-C(1)	98.5		99.2		C^{Me}-O(1)-C(1)	118.9	
$C(1)^{Ph}$-Se(8)-C(8)	100.2		99.9		C^{Me}-O(11)-C(11)	116.3	
					C^{Me}-O(6)-C(6)	115.3	
Bay angles [°]							
Se(1)-C(1)-C(9a)	121.5		119.7		O(1)-C(1)-C(12a)	116.7	
C(1)-C(9a)-C(9)	121.1		125.6		C(1)-C(12a)-C(12)	122.7	
C(9a)-C(9)=O(9)[c]	120.3		117.8		C(12a)-C(12)=O(12)	121.8	
splay angle [°]	+2.9		+3.1			+1.2	
Se(8)-C(8)-C(8a)	121.7		120.8		O(11)-C(11)-C(11a)	119.9	
C(8)-C(8a)-C(9)	120.8		125.5		C(11)-C(11a)-C(12)	121.2	
C(8a)-C(9)=O(9)[d]	119.8		118.0		C(11a)-C(12)=O(12)	121.7	
splay angle [°]	+2.3		+4.3			+2.8	
					O(6)-C(6)-C(5a)	120.3	
					C(5)-C(5a)-C(6)	122.3	
					C(5a)-C(5)=O(5)	123.4	
					splay angle [°]	+6.0	
No-bond angles [°]							
Se(1)···O(9)···Se(8)	152.5		147.9		O(1)···O(12)···O(11)	124.3	
					C^{Me}-O(1)···O(12)	151.9	
					C^{Me}-O(11)···O(12)	87.5	
					C^{Me}-O(6)···O(5)	84.9	
Flattening of the anthraquinone skeleton[e] (upper part) [°]							
C(2)-C(1)-C(9a)	117.8		119.8		C(2)-C(1)-C(12a)	119.1	
C(1)-C(9a)-C(9)	121.1		125.6		C(1)-C(12a)-C(12)	122.7	
(C9a)-C(9)-C(8a)	119.8		124.2		C(12a)-C(12)-C(11a)	116.4	
C(9)-C(8a)-C(8)	120.8		125.5		C(11)-C(11a)-C(12)	121.2	
C(8a)-C(8)-C(7)	118.3		119.6		C(10a)-C(11)-C(11a)	120.3	
average	119.6		122.9		average	119.9[f]	
flattening?	no		yes		flattening?	no	
Flattening of the anthraquinone skeleton[e] (lower part) [°]							
C(3)-C(4)-C(4a)	120.2		121.2		C(3)-C(4)-C(4a)	118.4	
C(4)-C(4a)-C(10)	118.0		121.7		C(4)-C(4a)-C(5)	118.3	
C(4a)-C(10)-C(10a)	117.7		123.0		C(4a)-C(5)-C(5a)	116.9	
C(10)-C(10a)-C(5)	117.4		121.0		C(5)-C(5a)-C(6)	122.3	
C(10a)-C(5)-C(6)	119.1		120.4		C(5a)-C(6)-C(6a)	121.0	
average	118.5[g]		121.5[g]		average	119.4[f]	
flattening?	no		yes[g]		flattening?	no	
Torsional angles [°]							
$C(1)^{Ph}$-Se(1)-C(1)-C(9a)	−172.8		−163.1		C^{Me}-O(1)-C(1)-C(12a)	178.1	
$C(1)^{Ph}$-Se(8)-C(8)-C(8a)	−171.3		175.8		C^{Me}-O(11)-C(11)-C(11a)	101.5	
					C^{Me}-O(6)-C(6)-C(5a)	−91.7	

[a] Numbering of the ring systems according to IUPAC; atoms attached to ring C atoms are labeled with the same numbers as the latter. Ph = C_6H_5, Me = CH_3; $C(1)^{Ph}$=C(1) of a phenyl group; C^{Me}=the C atom of a methyl group. For e.s.d.'s, see ref. [10, 60]. [b] **14a**: O(9)-C(9). [c] **14a**: C(1a)-C(9)-O(9). [d] **14a**: C(8a)-C(9)-O(9). [e] **14a**: anthracene skeleton. [f] Though the decrease of 0.5° is hardly significant, the average angle is formally smaller than for the upper part, as predicted. [g] Although in **14a** this average angle exceeds 120° only slightly, the increase is presumably significant. The positive splay angles in the upper parts of **11**, **12** and **14a** trigger a compression of bond angles in the lower parts [4, 45, 53, 65], which counteracts the enlargement due to the flattening. In 1,8-disubstituted naphthalenes with intersubstituent repulsion, hence positive splay angles, the average of the angles C(3)-C(4)-C(10), C(4)-C(10)-C(5) and C(6)-C(5)-C(10) is consistently *ca.* $1-2^\circ$ smaller than that of the angles C(2)-C(1)-C(9), C(1)-C(9)-C(8) and C(7)-C(8)-C(9) though not smaller than 120° [45, 65], thus indicating ring flattening in addition to splaying to reduce steric repulsion.

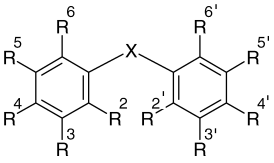


	X	R
1a	S	Ph
1b	Se	Ph
2	CH_2	H

selenium derivatives of naphthalene [7, 8] and anthracene [10]. Such bonding would be even more remarkable as the respective naphthalenes contain exclusively divalent heteroatoms bound to atoms of the same or almost the same electronegativity (Se 2.4, S and C 2.5 according to Pauling's scale) while elsewhere hypercoordination is largely restricted to the higher valence states and facilitated by electronegative groups attached to the atom in question [4]. In the anthracenes, two divalent selenium atoms each bound to two carbon atoms allegedly engage in hypercoordinate interactions with notoriously poor σ-donors, namely carbonyl and ether oxygen, by electron donation from one occupied p-orbital at the latter into the empty σ^*-orbitals of two Se–C bonds, hence dative interaction of C–Se←O→Se–C type [10]. In the naphthalenes, the same type of chalcogen atoms, *viz*. of a diarylchalcogenide partial structure, is claimed to exert the *opposite* effect, *viz*. to act as lone pair *donor* of electrons into the empty σ*-orbitals of a dichalcogenide bond, hence dative interaction of, *e. g.*, S→S−S←S type [9].



	R^1	R^2	R^3
3	Me	Me	H
6	PR^4R^5	H and ≠ H	H
7	CH_2Br	CH_2Br	H
8a	OMe	OMe	H
8b	OMe	OMe	NMe_2
13a	SeC_6H_4-OMe-4	F	H
13b	SeMe	SeC_6H_5	H
15	NMe_2	P^+(Me, Et, Ph) BPh_4^-	H



	-X-	R^2	R^3	R^4	R^5	R^6	$R^{2'}$	$R^{3'}$	$R^{4'}$	$R^{5'}$	$R^{6'}$
4a	-S-	H	H	NO_2	H	H	H	H	H	H	H
4b	-S-	H	OMe	OMe	H	H	H	OMe	OMe	H	H
4c	-S-	H	H	SH	H	H	H	H	SH	H	H
4d	-S-	Me	H	H	H	H	Me	H	H	H	H
4e	-S-	H	H	NH_2	H	H	H	H	NH_2	H	H
5a	-S-S-	H	H	H	H	H	H	H	H	H	H
5b	-S-S-	H	H	NO_2	H	H	H	H	NH_2	H	H
10a	-Se-Se-	a	H	H	H	a	a	H	H	H	a
10b	-Se-Se-	F	F	F	F	F	F	F	F	F	F

a = 2,4,6-$Me_3C_6H_2$-

*Di(8-phenylthio-naphth-1-yl) disulfide (***1a***)*

In **1a**, the four S atoms have been found to align nearly linearly, and it has been claimed that this alignment is stabilized by a four-centre, six-electron interaction (4c, 6e) [9]. For a reevaluation, **1a** is compared with simple diaryl sulfides and diaryl disulfides. Comparison with analogous oxygen compounds should provide an insight which properties might be ascribed to hypercoordinate interactions. For an assessment of steric hindrance in the *peri*-naphthalene part, comparison with 1,2-bis(8-methyl-naphth-1-yl) ethane (**2**) should be revealing. Compound **2** is not available, but its structural parameters can be estimated from the structure of 1,8-dimethyl-naphthalene (**3**) [18] and the tetrahedral valence angles at sp^3 carbon.

Disulfide **1a** *as a diaryl sulfide*: The S–C(1)^{Ph} bonds are approximately perpendicular to the respective C_{10} plane while the S–C(8) bonds are coplanar with the Ph planes. The S–C(1)^{Ph} as well as the S-C(8) bonds have the same lengths as in other diaryl sulfides (**1a**: 177.5/175.8 and 177.1/177.4 pm, respectively; average of 16 S–C^{Ar} bonds in symmetrical and unsymmetrical derivatives of Ph_2S including diaryl sulfides with *o*-substituents: 177.6 pm [19 – 23]). The angles C(8)–S–C(1)^{Ph}, 102.6° and 103.1°, are unconspicuous (average of 8 C^{Ar}–S–C^{Ar} angles ranging from 102.8° to 105.4°: 103.9° [19 – 23]).

A remarkable feature of **1a** is the inequality of the bond angles S–C(1)^{Ph}–C(2)^{Ph} and S–C(1)^{Ph}–C(6)^{Ph}, 116.6°/117.5° *vs*. 124.0°/123.9°. Though not general, this phenomenon is frequent in other diaryl sulfides Ar^{I}–S–Ar^{II} and related compounds such as anisoles, Ar–O–Me [24, 25]. For example, in **4a**, it is absent in the phenyl part (120°/120°), but significant in the nitro-phenyl part (116°/123°) [21]. Even in "symmetrical" diaryl sulfides Ar_2S, it may be present in one of the Ar groups and virtually absent in the other one (**4b**: 115.8°/124.9° and 119.6°/120.9° [23]). In **4c**, one of the S–C^{Ar} bonds behaves as the S–C^{Ph} bonds in **1a** while the other one is much less dissymmetric (116.7°/123.9° *vs*. 119.2/121.7° [26]). The phenomenon defies a straightforward explanation; *e.g.*, in **4d** the angle S–C(1)–C(2) is the larger one in one of the *o*-tolyl groups and the smaller one in the other (121.1/116.6° and 116.5/122.3° [22]). In **1a**, the dissymmetry of the S–C bonds is also apparent on the

C_{10} side. The angles S–C(8)–C(9) would be expected to exceed 120° for steric reasons (*vide infra*) and the angles S–C(8)–C(7) therefore to be the smaller ones. This is indeed the case (S–C(8)–C(7) 114.9°/114.5°, S–C(8)–C(9) 123.6°/123.8°). The angles S–C(8)–C(7) are somewhat smaller than the corresponding angles on the phenyl side; this is the consequence of a general flattening of the C_{10} systems which contributes to relieve the steric congestion in the *peri* space: The sum of the angles C(2)–C(1)–C(9), C(1)–C(9)–C(8) and C(7)–C(8)–C(9) exceeds 360° of the perfect C_{10} system by 9.5°/8.5°, 1.5°/1.7° being the share of C(7)–C(8)–C(9). Since the three angles around C(8) of the C_{10} parts and around C(1) of the phenyl groups add to 360°, this increase implies a decrease of the S–C–C angles, in fact at the sole expense of S–C(8)–C(7), because S–C(8)–C(9) is buttressed by the steric hindrance in the *peri* region.

The conformations of the S–C bonds – coplanarity of the S–C(8) bonds with the respective Ph planes, orthogonality of the S–$C(1)^{Ph}$ bonds with the respective C_{10} planes – comply with a pattern which is the predominant one in diaryl sulfides [23, 27]. Even in "symmetrical" sulfides Ar_2S the two S-$C(1)^{Ar}$ bonds behave differently. For example, in **4d** and **4e** one S–C bond resides in the synperiplanar (*sp*) sector, the other one in the synclinal (*sc*) sector with respect to the C(1)–C(2) bond [28]. In the tolyl compound, the deviations from coplanarity and orthogonality are 7.1° and 10.8°, respectively [22, 23]; in the aniline derivative, the deviations are larger (25.7° and 21.7° [20, 22]), but the *sc* bond is still closer to orthogonality than to the borderline between the *sc* and the *sp* sectors. In **4b** the S–C bonds are indeed very close to coplanarity and orthogonality (dihedral angles 3.6° and 90.9°, respectively [23]). While, then, in **1a** no prediction would have been possible which S–C bond would prefer coplanarity and which orthogonality, the conformations in the C–S–C parts of the molecule are as expected.

In conclusion, the S atoms of the diaryl sulfide parts do not exhibit any peculiar properties which might indicate their involvement in extra bonding.

Disulfide **1a** *as a diaryl disulfide*: The S–S bond of **1a** resides in the antiperiplanar (*ap*) sector with respect to the C(1)···C(8) connecting line of each C_{10} system. In **5a** and its substitution products, the bond lengths *d*(S–S) are 202.3 – 204.6 pm, *d*(S–C) 175 – 179 pm and the angles C–S–S 101 – 107° [29 – 34]. In **1a**, C–S–S, 104.4°/105.4°, is within these limits while the nominal deviation of < 1 pm for *d*(S–S) (205.5 pm) is too small to justify an interpretation. On the other hand, *d*(S–C(1))=181.6/181.9 pm is beyond the upper limit by *ca.* 3 pm. If it is assumed that S–C bonds are less resistant to bond stretching than, *e. g.*, O–C bonds [4, 5, 35], the phenomenon may be accounted for by steric relief: The splay angle of the S–C(1/8) bonds is considerably positive (*vide infra*). Stretching of the S–C bonds would therefore increase the S···S distance and thus reduce the steric congestion.

As for diaryl sulfides, it is common for diaryl disulfides that the S–C bonds assume an unsymmetrical position with respect to the phenyl rings (*e. g.* 115.4° *vs.* 124.4° in **5a** [29]). Though still recognizable, this phenomenon is remarkably small in **1a** (118.7° *vs.* 121.3° and 119.5° *vs.* 120.3°), but has been found even less pronounced in a substituted diphenyl disulfide [33]. Not surprisingly, the larger angle is the bay angle S–C(1)–C(9). As virtually the same angles, *viz.* 118.7° *vs.* 121.6°, have been observed in the S-C_6H_4-NH_2-4 part of **5b** [32, 36], the decrease defies an interpretation in favour of a new type of bonding.

For the dihedral angles about the S–S bond and the S–C bonds of diaryl disulfides no distinct preference is discernible [29, 31, 33, 34, 37]. Disulfide **1a** shares the *ap* conformation of the S–S bonds with **5a** [29, 31] while it had justly been pointed out that the torsional angle of −89.0° for $C(1)^{I}$–S–S–$C(1)^{II}$ is close to those usually observed in $Ar^{I}SSAr^{II}$ [9]. Hence, the C–S–S–C part of **1a** does not exhibit unusual properties either.

Disulfide **1a** *as a peri-disubstituted naphthalene*: Sulfur has a *van der Waals* radius *r*(vdW)= 180 pm [38]. An unconstrained non-bonding S···S distance would therefore require Σr(vdW)=360 pm. In the perfect naphthalene system, the available intersubstituent distance is only 247 pm [4, 5, 39 – 42] so that even strong distortion of the C_{10} system does not permit Σr(vdW) distances [1, 11, 42]. To accommodate bulky *peri*-substituents, the C_{10} system resorts to an enlargement of the bay angles substituent–C(1/8)–C(9) and C(1)–C(9)–C(8) (predominantly of the latter one [4, 5, 11, 12, 43]) whereas the C_{10} skeleton frequently remains virtually planar [12, 18, 42, 44, 45]. In **1a**, the planarity is borne out by the sum of the angles around C(1), C(8) and C(9), consistently 360°. All bay angles exceed 120° (one of the S–C(1)–C(9) angles, 120.3°, only formally); as elsewhere, the angles C(1)–C(9)–C(8) bear most of the burden of steric hindrance (128.1°/126.8°). The splay angles of the S–C bonds, 13.0°/10.9°, are very large and indicate severe intersubstituent repulsion, though the aforementioned

phenomenon of a dissymmetric conformation of the S–C^{Ar} bond even in Ph–S compounds may be responsible for part of the enlargement of the S–C(1/8)–C(9) angles. Intersubstituent repulsion is also evident from the long S···S distances, 298.8 pm, 52 pm (21%) longer than the ideal *peri* distance of equal substituents [46]. The splay angles are almost as large as in **3** (14.7° [18]); not surprisingly in view of d(H_3C–C(1/8)) in **3** < d(S–C(1/8)) in **1a**, d(S···S) in **1a** is even longer than d($H_3C\cdots CH_3$)=293.2 pm in **3**.

In conclusion, **1a** has all of the properties anticipated for *a)* a diaryl sulfide, *b)* a diaryl disulfide, *c)* a *peri*-disubstituted naphthalene with strong intersubstituent repulsion. It remains to investigate the "linear" alignment of the four sulfur atoms, *i. e.* that the S–S-bond lies approximately in the planes of both C_{10} systems, though the latter are almost perpendicular to each other. Each phenyl ring is nearly orthogonal to *both* C_{10} systems and thus minimizes steric interactions [47]. The "linearity" consists of two S···S–S angles of only 166.0° and 168.6° [9].

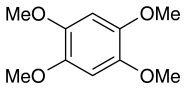
Both the antiperiplanarity of the S–S bond and the orthogonality of the S–$C(1)^{Ph}$ bonds are common features in 1- and 1,8-substituted naphthalenes. In naphth-1-yl phosphines **6** it is a frequent pattern that the P–R^4 bond is nearly orthogonal and the P–R^5 bond antiperiplanar close to coplanarity [4, 12, 42, 48, 49]. In 1,8-di(bromomethyl)naphthalene (**7**), both CH_2–Br bonds are perpendicular to the C_{10} plane, not surprisingly on different sides [50]. It is particularly interesting that methoxy groups have a pronounced tendency to place the H_3C–O bond coplanar with aromatic rings [25]. *E. g.*, this is the case in 1,8-dimethoxy-naphthalene (**8a**) [45], its 4,5-bis(dimethylamino) derivative **8b** and N-protonated **8b** [51] where both H_3C–O bonds adopt the same conformation as the S–S bond in **1a**. Similarly, in 1,2,4,5-tetramethoxybenzene (**9**) [52] and in bis(3,4-dimethoxyphenyl) sulfide (**4b**) [23], the *o*-methoxy groups are almost coplanar with the respective benzene ring and in *anti* conformations, thus avoiding steric interactions. In a *peri*-methoxy-substituted hetera-naphthalene, the H_3C–O bond adopts an almost perfect antiperiplanar conformation [53]. The phenomenon is not typical for the gas phase and therefore seems to depend on crystal packing effects which also account for the few exceptions [25]. Whatever the reason for this preference may be [24, 49], it is obvious that the phenomenon is not the consequence of hypercoordinate interactions. In **8a**, the (non-bonding) angle C(1/8)–O···O is 89.9°, the valence angle H_3C–O–C(1/8) 117.2°, so that the geometry of an oblique T, H_3C–O(C(1/8))···O, results with the angles H_3C–O···O 360° − (89.9° + 117.2°) = 152.9°. For the S–S···S angles in **1a**, this angle is a much better model than "linearity". In a 1,2-dimethoxybenzene of perfect shape (all angles 120°), the angle H_3C–O···O would even be 177.2° though a hypercoordinate interaction could be inferred neither from this linearity nor from the fact that the H_3C–O bonds lie in the C_6 plane.

In **3**, the splay angle of the H_3C–C(1/8) bonds, 14.7°, permits to estimate the angles $H_3C\cdots CH_3$–C(1/8) as *ca*. 82.7°. If the same angle and the antiperiplanar conformation of the H_2C–CH_2 bond are assumed for **2**, an oblique T $H_3C\cdots C(C(1))$–CH_2 results in which the $H_3C\cdots CH_2$–C(1) angle and the tetrahedral H_2C–CH_2–C(1) bond angle yield an angle of 167.9° for the alignment $H_3C\cdots CH_2$–CH_2 in perfect agreement with the average of the S···S–S angles in **1a**, 167.3°. With the splay angles of **1a**, 10.9°/13.0°, and 105° as a typical bond angle S–S–C in diaryl disulfides (average in **1a**: 104.9°), S···S–S angles of 171 ± 0.5° are obtained, even closer to linearity within a T consisting of S···S(C(1))–S. The linear alignment of the S atoms in **1a** thus turns out to be a trivial consequence of the geometry of a crowded naphthalene, and no evidence for the alleged hypervalent 4c, 6e bond is discernible.

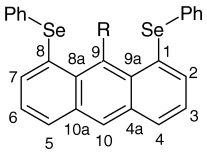
*Di(8-phenylseleno-naphth-1-yl) diselenide (***1b***)*

Diselenide **1b**, the selenium analog of **1a**, exhibits the same features, and the same explanation has been proposed [7, 8]. Alleged charge transfer from the Se^{Ph} atoms to the diselenide Se atoms [8] might be expressed by the symbol of a dative bonding interaction, hence Se^{Ph} →Se–Se←Se^{Ph}.

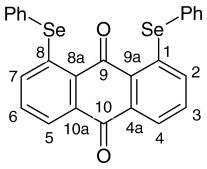
Again, the Se–C bond lengths in the diaryl selenide parts, 190.9 and 191.5 pm, compare well with those in other diaryl selenides (190.6 – 194.7 pm [54, 55]) and in methyl-phenyl-selenide (191.2 pm [56]). In the diselenide part, both the Se–C and the Se–Se bond length, 195.7/195.9 and 236.5 pm, respectively, exceed those in other diaryl diselenides by *ca*. 3 pm (d(Se–C)= 189.9 – 192.7 pm, d(Se–Se)= 231.9 – 233.9 pm [30, 57]). As for **1a**, this elongation may be ascribed to strain relief in the *peri* regions. No such elongation has been observed in bis(2,6-dimesityl-phenyl) diselenide (**10a**) [57] for which a trigonometric model calculation yields a Se···C distance of 314 pm (11.5%



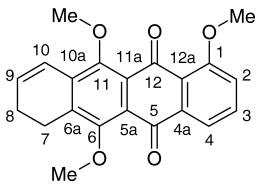
9



	R
14a	OMe
14b	H



11



12

less than $\Sigma r(\mathrm{vdW})[\mathrm{Se,C}] = 355$ pm [38]) between the Se atoms and C(1) of the mesityl substituents [58], indicating much weaker congestion. Considerable steric hindrance is borne out by the splay angles of the *peri* bonds, $+11.8^\circ$ and $+15.0^\circ$, even more than in **1a**, though again, part of the enlargement of the Se–C(1/8)–C(9) angles may be due to the tendency of Se–C^{Ar} bonds to adopt a dissymmetric conformation. This phenomenon is discernible in the Ph–Se parts of **1b** (Se–C(1)^{Ph}–C(2)^{Ph}/Se–C(1)^{Ph}–C(6)^{Ph} 118.2°/121.8° and 116.4°/123.0°), but more pronounced in the Se–C_{10} parts of the Ar_2Se substructure (Se–C(8)–C(7)/Se–C(8)–C(9) 115.0°/123.2° and 113.9°/124.7°), presumably because of the joint action of two effects, while in the diselenide substructure the dissymmetry is smaller (Se–C(1)–C(2)/Se–C(1)–C(9) 116.8°/122.6 and 117.8°/122.8° [59]).

The claim of a Se···Se–Se···Se 4c, 6e interaction rests exclusively on the fact that the Se–Se bond resides in the planes of both C_{10} skeletons with a nearly linear alignment of the four Se atoms. While the coplanarity is also shown by the O–C bonds and the S–S bond in the alkoxy-naphthalenes **8a**,**b** and in **1a**, respectively, the quasi-linearity is again a consequence of the bond and no-bond angles around the Se atoms. In a hypothetical **1b** with a planar C_{10} system and 120° angles, d(Se–C(1)) – d(Se^{Ph}–C(8))= 4.4 pm [8] and the angle Se–Se–C(1) 98.8° (as in **10b** [30]), the angle Se^{Ph}···Se–C(1) is 89.0°, hence the angle Se^{Ph}···Se–Se 172.2°, or *ca*. 175° if the enlargement of the angles (Se–)Se–C(1)–C(9) is taken into account. The experimental angles Se^{Ph}···Se–Se, 170.45/177.1° [8], then, provide no evidence for an additional type of bonding.

*1,8-Di(phenylseleno)anthraquinone (***11***)*

The results described above call for a closer inspection of the seleno-anthraquinone **11** and related compounds for which 5c, 6e bonds have been inferred [10]. The C_{14} system of the anthraquinone and the substituent atoms attached to it form a common plane from which the C(1)^{Ph} atoms of the phenyl rings deviate only slightly. Again the Se–C(1)^{Ph} bonds adopt an antiperiplanar conformation with respect to the quinone ring (dihedral angles C(1)^{Ph}–Se–C(1/8)–C(9a/8a) $-172.8^\circ/-171.3^\circ$). The alignment C(1)^{Ph}–Se···O···Se–C(1)^{Ph} has been called linear though the angle Se···O···Se is only 152.5°. The deviation of 27.5° from linearity, while called a "slightly bent alignment", has been recognized to be conditioned by the unequal bond lengths, d(Se–C(1/8))> d(C=O) [10].

A related structure, **12** [60], in which the PhSe groups are replaced by MeO groups and hence hypercoordinate interactions are precluded, may first be discussed for purposes of comparison (*cf*. Table 1). The anthraquinone system is virtually planar. The sum of the *van der Waals* radii of two O atoms, $\Sigma r(\mathrm{vdW})[\mathrm{O,O}] =$ *ca*. 320 pm [38], is much larger than the available *peri* space, so that there is substantial crowding (albeit no O→O dative bonding). Two ways of in-plane deformation can relieve the *peri* congestion: a flattening of the entire C_{14} system and in-plane distortions of the bay angles. A widening of the angles is recognizable neither in the upper part nor in the lower part of the C_{14} system (*cf*. Table 1). In-plane angle deformations result in positive splay angles for all three O···O interactions, $+1.2^\circ$, $+2.8^\circ$ and $+6.0^\circ$. Interestingly, the two splay angles in the upper part of the molecule are much smaller than that in the lower part; the equal angles O=C(12)–C(11a/12a) (121.7°/121.8°) in conjunction with the larger angle O=C(5)–C(5a) may indicate that the phenomenon is partly due to a reciprocal buttressing effect. The d(O···O) distances are significantly longer than the non-bonding distances d(C(1/11)···C(12))=254.5, 252.2 pm, *viz*. 268.2, 277.7 and 275.0 pm.

The H_3C–O bond of the 1-methoxy group lies virtually in the C_{14} plane and adopts an antiperiplanar conformation with respect to the C(1)–C(12a) bond (dihedral angle H_3C–O(1)–C(1)–C(12a) 178.1°, hence even closer to coplanarity than the Se–C(1)^{Ph} bonds in **11**). For the 11-methoxy group, the same conformation is rendered unfavourable by C(10) as an ortho-

substituent. The hydrogen atom C(10)-*H* resides in the C_{14} plane, too, and $\Sigma r(\mathrm{vdW})[\mathrm{H,O}] = 120 + 160 =$ 280 pm [38, 61] implies repulsive steric interaction. It is therefore not surprising that the H_3C–O bond is diverted into the anticlinal sector (dihedral angle H_3C–O(11)–C(11)–C(11a) 101.5°). The H_3C–O bond of the 6-methoxy group is positioned perpendicular to the C_{14} plane (dihedral angle H_3C–O(6)–C(6)–C(5a) −91.7°); it seems that the H–C(7)–H plane enforces an even greater deviation from coplanarity than C(10)–*H*. It emerges that the H_3C–O bond again adopts the antiperiplanar conformation unless steric interactions interfere.

As a consequence, the atoms C^{Me}–O(1)···O(12)··· O(11) are in the C_{14} plane, with much deformed T's C^{Me}–O(C(1))···O(12) and O(1)···O(=C)···O(11). The (non-bonding) angles H_3C–O(1)···O(12) and O(1)···O(12)···O(11) amount to only 151.9° and 124.3°, respectively rather than 180° as requested for the horizontal bar of a T.

As a whole, the structure of **11** is closely related (*cf.* Table 1). Steric interactions between Se and O are smaller than between S and S in **1a** (*cf.* Σr(vdW)[S,S]=360 pm, Σr(vdW)[Se,O]= 345 pm [38]). Accordingly, the splay angles between the Se–C(1/8) and C=O bonds are only 2.9° and 2.3°, in the same region as in **12**. Again, no flattening of the C_{14} system is apparent.

The bond lengths *d*(Se–C) range between 191.7 and 192.7 pm and are thus typical for aryl selenides (*vide supra*), as are the C–Se–C angles, 98.5° and 100.2° (PhSeMe: 99.6° [56], **13a**: 99.6°/100.8° [6e], **13b**: 97.8°/98.4° [8]). Unlike the S–C bonds in **1a**, the Se–C bonds deviate only very little from a symmetrical arrangement, hence from 120° angles to either side. This permits trigonometric model calculations with 120° angles. The bonds C(1)–C(9a) / C(8)–C(8a) are considerably shorter than C(9a)–C(9) / C(8a)–C(9); thereby C(9) comes into a position higher than the C(1)···C(8) connecting line so that the short C=O bond relative to the Se–C(1/8) bonds is partly compensated and the "linearity" improved. A simple trigonometric calculation leads to *d*(Se···O)=258.4 pm and an angle Se···O···Se of 150.1° as a consequence of natural bond lengths and valence angles and the geometry of the anthraquinone system. Since the splay angles had not been taken into account, it is not surprising that the experimental distances, *d*(Se···O)= 267.3 and 268.8 pm, are somewhat longer. The calculated angle Se···O···Se is in excellent agreement with the experimental value, 152.5°. The antiperiplanar conformation of the substituents PhSe and MeO is a common property of **11** and **12** and therefore no indicator of a hypervalent interaction either.

*9-Methoxy-1,8-di(phenylseleno)anthracene (***14a***)*

The anthracene derivative **14a** [10] has a closely related structure. Again, the C_{14} system is virtually planar. It is somewhat flattened (average of the five angles in the upper part 122.9°, in the lower part 121.5°). As part of this angle enlargement, C(9a)–C(9)–C(8a) is 124.2°. The planarity around C(9) requires the bay angles O–C(9)–C(8a/9a)$< 120°$ (117.8° + 118.0° + 124.2° = 360.0°). Nevertheless, splay angles of +3.1° and +4.3° result for the Se–C(1/8) and O–C(9) bonds, somewhat larger than in **11** and again indicative of steric repulsion. The proximity of the Se atoms forces the H_3C–O bond into a perpendicular conformation reminiscent of that of the 6-methoxy group in **12** (dihedral angle H_3C–O–C(9)–C(9a) 89.1°), whereas the Se–$C(1)^{Ph}$ bonds again reside in the antiperiplanar sectors (dihedral angles $C(1)^{Ph}$–Se–C(1/8)–C(9a/8a) −163.1° and 175.8°). While coplanarity of the five atoms $C(1)^{Ph[I]}$, Se, O, Se, $C(1)^{Ph[II]}$ with the C_{14} plane is a satisfactory description of their positions, they hardly qualify for a *linear alignment* in view of the experimental angle Se···O···Se, 147.9°, *ca.* 9° less than the angle resulting from a trigonometric model calculation using the bond lengths *d*(Se–C(1)), *d*(O–C(9)), *d*(C(1)–C(9a)), *d*(C(9)–C(9a)) and the angle C(1)–C(9a)–C(9) (see Table 1). The angles O···Se–C(1/8) can be estimated as *ca.* 75°, so that, in conjunction with the bond angles C–Se–C, 99.2° and 99.9°, *ca.* 174−175° are obtained for $C(1)^{Ph}$–Se···O, again on purely geometric grounds and therefore not indicative of hypercoordinate bonding.

The antiperiplanar conformation of the Se–$C(1)^{Ph}$ bonds in **11** and **14a** has been believed significant in view of a different conformation in **14b**. Even here, Σr(vdW)[H, Se]= 120 + 185 = 305 pm [38, 61] suggests some steric crowding; indeed, the splay angles of the Se–C(1/8) and H–C(9) bonds are positive (+3.9° and +2.4°). The Se–$C(1)^{Ph}$ bonds are virtually parallel, one residing in the synclinal sector and the other one in the anticlinal sector, both on the same side of the C_{14} plane (dihedral angles $C(1)^{Ph[I]}$–Se–C(1)–C(9a) 72.6°, $C(1)^{Ph[II]}$–Se–C(8)–C(8a) −103.0° = 77.0 − 180°).

All features of **14a,b** are met in many *peri*-disubstituted naphthalenes without hypercoordinate in-

tersubstituent interaction. As an example, in **15** [41] one of the H_3C–N bonds resides in the anticlinal sector and is parallel to the H_3C–P bond which resides in the synclinal sector on the same side of the C_{10} plane (dihedral angles H_3C–N–C(8)···C(1) -98.8°, H_3C–P–C(1)···C(8) $81.1^\circ = 180 - 98.9^\circ$). The other H_3C–N bond and the $C(1)^{Ph}$–P bond reside in the anticlinal and the synclinal sectors of the opposite side of the C_{10} plane, respectively, with *ca*. 8° deviation from a parallel alignment (dihedral angles H_3C–N–C(8)···C(1) 138.6°, $C(1)^{Ph}$–P–C(1)···C(8) $-49.7^\circ = 130.3 - 180^\circ$). The H_2C–P bond of the ethyl group is situated in the antiperiplanar sector; the dihedral angle H_2C–P–C(1)···C(8), -163.9°, compares well with the dihedral angle $C(1)^{Ph}$–Se–C(1)–C(9a) in **14a**, 163.1° [10, 62]. Even slight changes of the substituents at the phosphonium centre have a profound impact on the conformations [41] so that it is not surprising that the sole substituent at Se prefers a different conformation in **14a** and in **14b**.

Conclusion

The structural data of **1a**,**b**, **11** and **14a** can be fully rationalized without recourse to hypercoordinate interactions and are therefore not indicative of 4c, 6e and 5c, 6e bonds. The results of quantum chemical calculations [7 – 10], even if compatible with the experimental data, have no bearing on the problem as long as no properties are known which permit to experimentally distinguish between the conventional and the hypervalent bond model. The d orbital theory owed its temporary success to the predictive power of computations which took d orbitals into account but failed to recognize that their impact was only very small; the same may apply to the role of other types of hypervalent interactions. In the computations performed on the systems $H_2Se\cdots H$–Se–Se–$H\cdots SeH_2$, $H_2Se\cdots(H_2C{=})O\cdots SeH_2$ and $H_2Se\cdots(H_2)O\cdots SeH_2$ as simplified models of **1b**, **11** and **14a** [7, 8, 10], the most important parameter, *viz*. steric interactions, is completely ignored [11]. A similar computation of the system $H_3N + SiH_4$ [63] provides a *caveat* [4]: A shallow energy minimum at d(N···Si)= 300 pm had been identified. In 8-dimethylamino-naphth-1-yl-silanes no predilection for this distance is discernible; instead, the rigid geometry of the C_{10} system enforces shorter distances. If accidentally the computed energy minimum had coincided with the interatomic distance as imposed by the steric situation, no conclusion in favour of a dative N→Si interaction would have been possible in spite of the agreement between computation and experiment. While typical features of TBP's, quasilinear alignments and T-shaped arrangements are by no means restricted to them. Conditioned by molecular geometry, they are of wide-spread occurrence and can therefore not serve as straightforward indicators of hypervalence. Papers in which hypercoordinate interactions have solely been inferred from such geometries [64] may therefore require a reassessment.

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