Source Function applied to experimental densities reveals subtle electron-delocalization effects and appraises their transferability properties in crystals

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❑ The Source Function (SF) [1] enables the electron density (ED) to be seen at a point as determined by source contributions from the atoms of a system, and it is therefore well linked to the chemist's awareness that any local property and chemical behaviour is to some degree influenced by all the remaining parts of a system [1-3].

❑ The key feature of the SF is that its evaluation requires only knowledge of the ED of a system, enabling a comparison of *ab initio* and X-ray diffraction derived ED properties on a common, rigorous basis.

❑ **We here apply the SF descriptor to X-ray derived EDs as a mean to reveal electron-delocalization effects (EDEs) in crystals**. Use of the SF to detect them has been firmly assessed for isolated molecules and for theoretically-derived EDs [2,4-5], but extending to crystals and experimental EDs, although being reported at two conferences [6-7] and in two papers discussing heteroaromaticity in a benzothiazol-substituted phosphane [8] or antiaromaticity in cyclopentadienone derivatives [9] needs to be fully demonstrated.

❑ Still unanswered questions are whether the EDs from X-ray data may be accurate enough **to reveal subtle features caused by electron pairing and whether these are not only detectable, but also reproducible and transferable, whenever appropriate.**

The Source Function

Views the ED at any point **r** as determined, in a cause-effect relationship, by a local source, LS(**r**,**r**'), which operates at all other points of the space,

$$\rho(\mathbf{r}) = \int LS(\mathbf{r},\mathbf{r}') \cdot d\mathbf{r}'$$
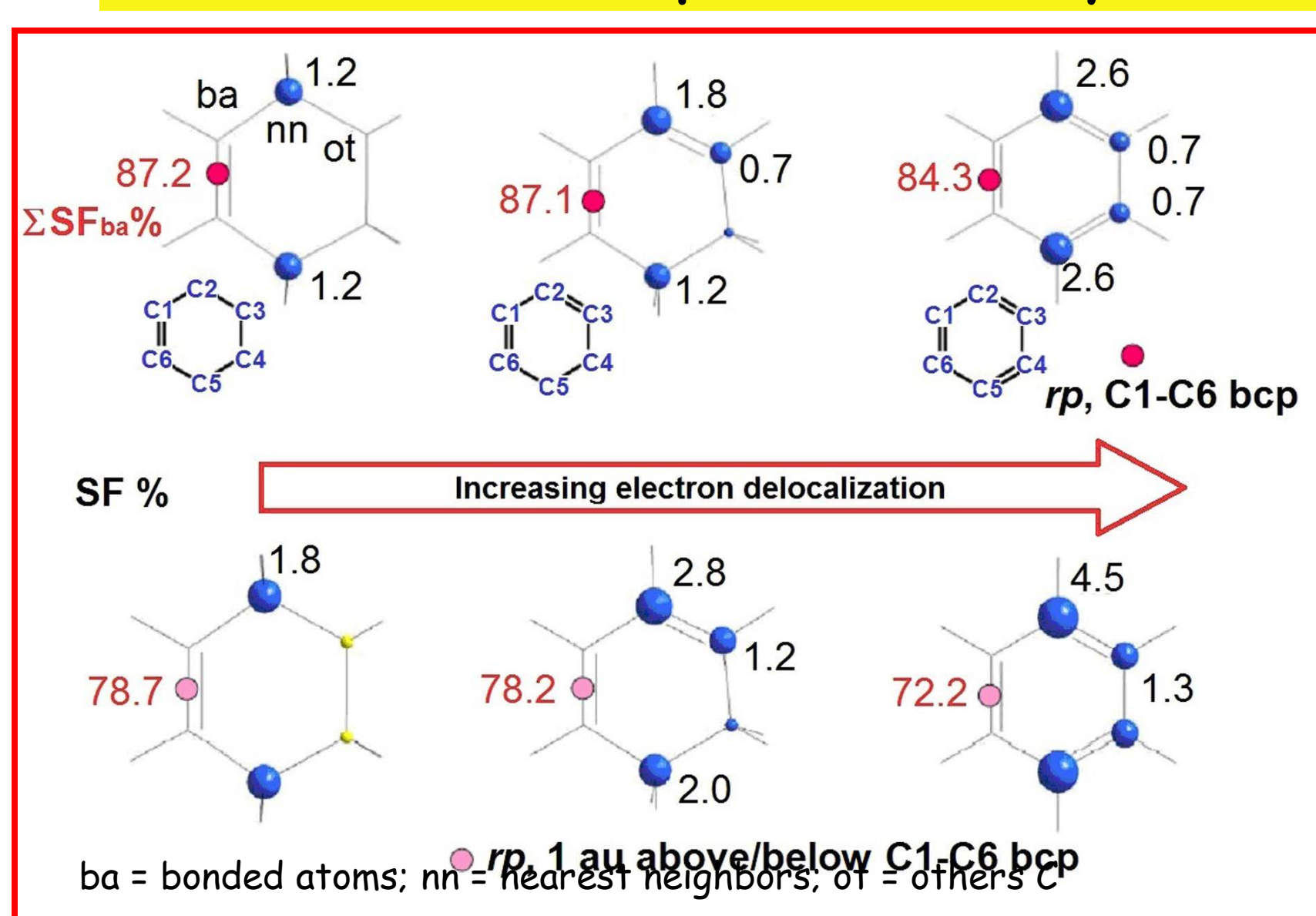
The local source is given by

$$LS(\mathbf{r},\mathbf{r}') = -(4\pi \cdot |\mathbf{r}-\mathbf{r}'|)^{-1} \cdot \nabla^2 \rho(\mathbf{r}')$$

where $(4\pi \cdot |\mathbf{r}-\mathbf{r}'|)^{-1}$ is a Green's function or an influence function representing the effectiveness of how the cause, the Laplacian of the density at r', $\nabla^2\rho(\mathbf{r}')$, gives rise to the effect, the electron density at r, $\rho(\mathbf{r})$.

The operation of the local source over the whole space may then be replaced by separate LS integrations over the atomic basins Ω defined by the Quantum Theory of Atoms in Molecules (QTAIM) and the ED at **r**, called the **reference point rp**, is so equated to a sum of contributions S(r;Ω), each of which called the *Source Function* (SF) from the atom Ω to ρ(**r**)
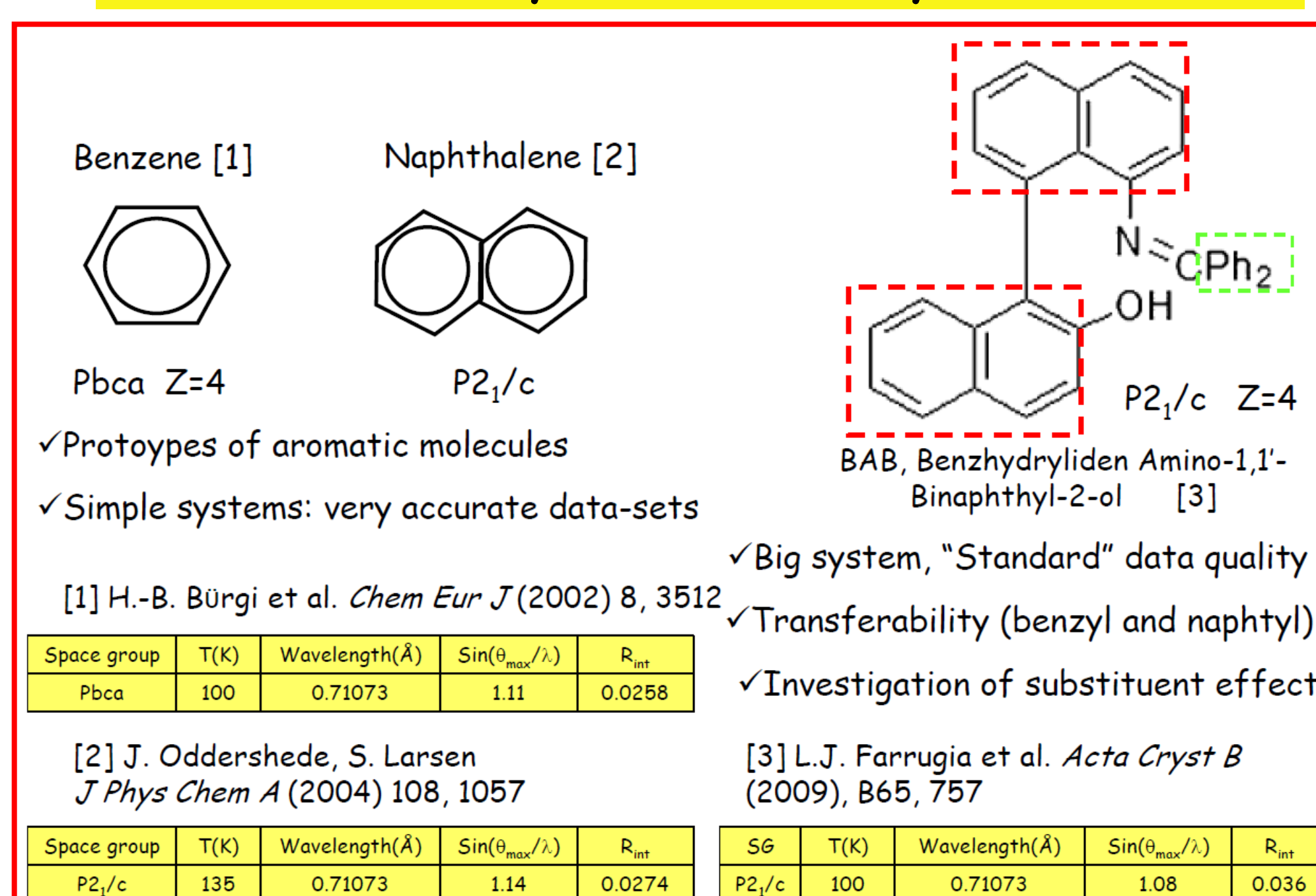
$$\rho(\mathbf{r}) = \int LS(\mathbf{r},\mathbf{r}')\ d\mathbf{r}' = \sum_{\Omega}\int_{\Omega} LS(\mathbf{r},\mathbf{r}')\ d\mathbf{r}' = \sum_{\Omega} SF(r,\Omega)$$
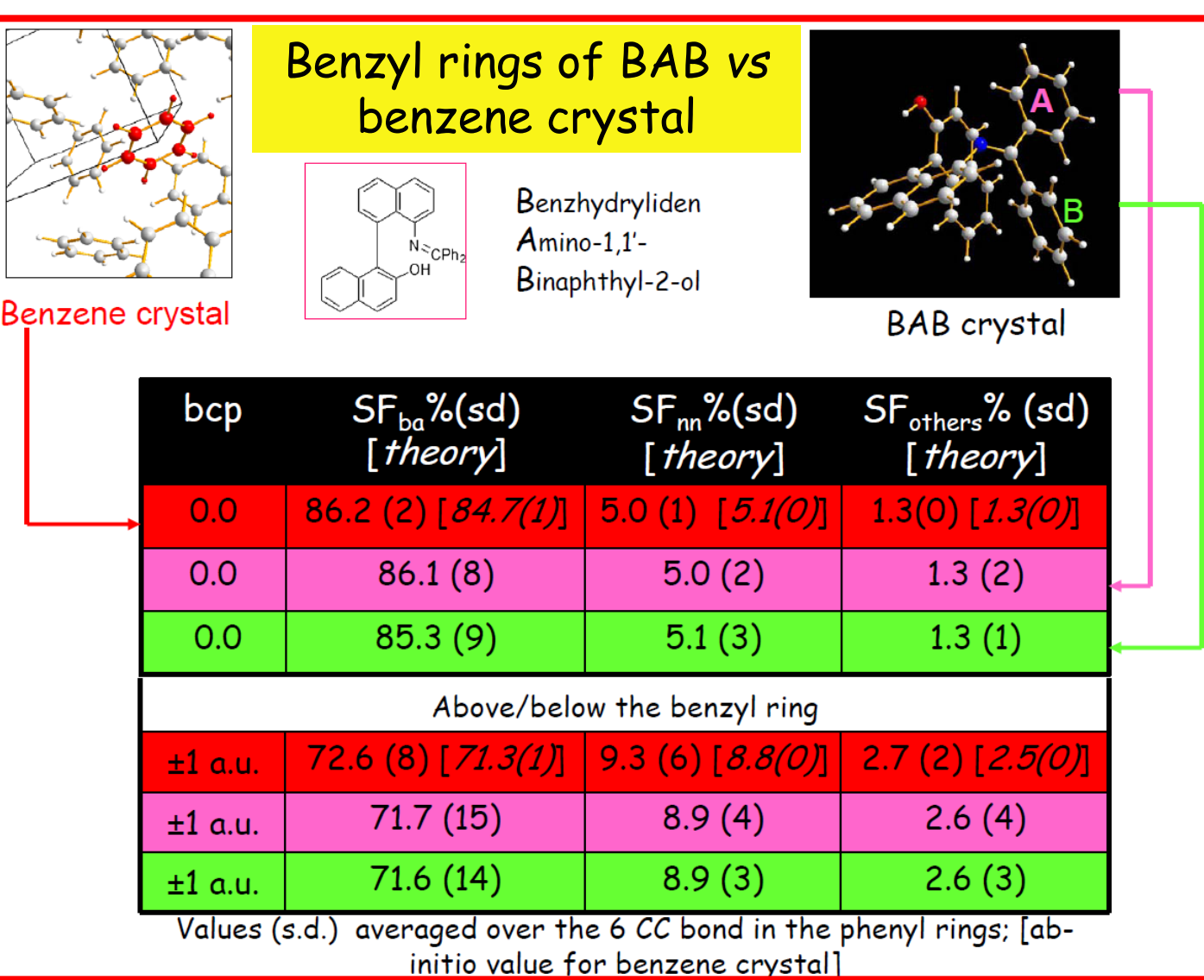
Proof of the concept : in vacuo systems

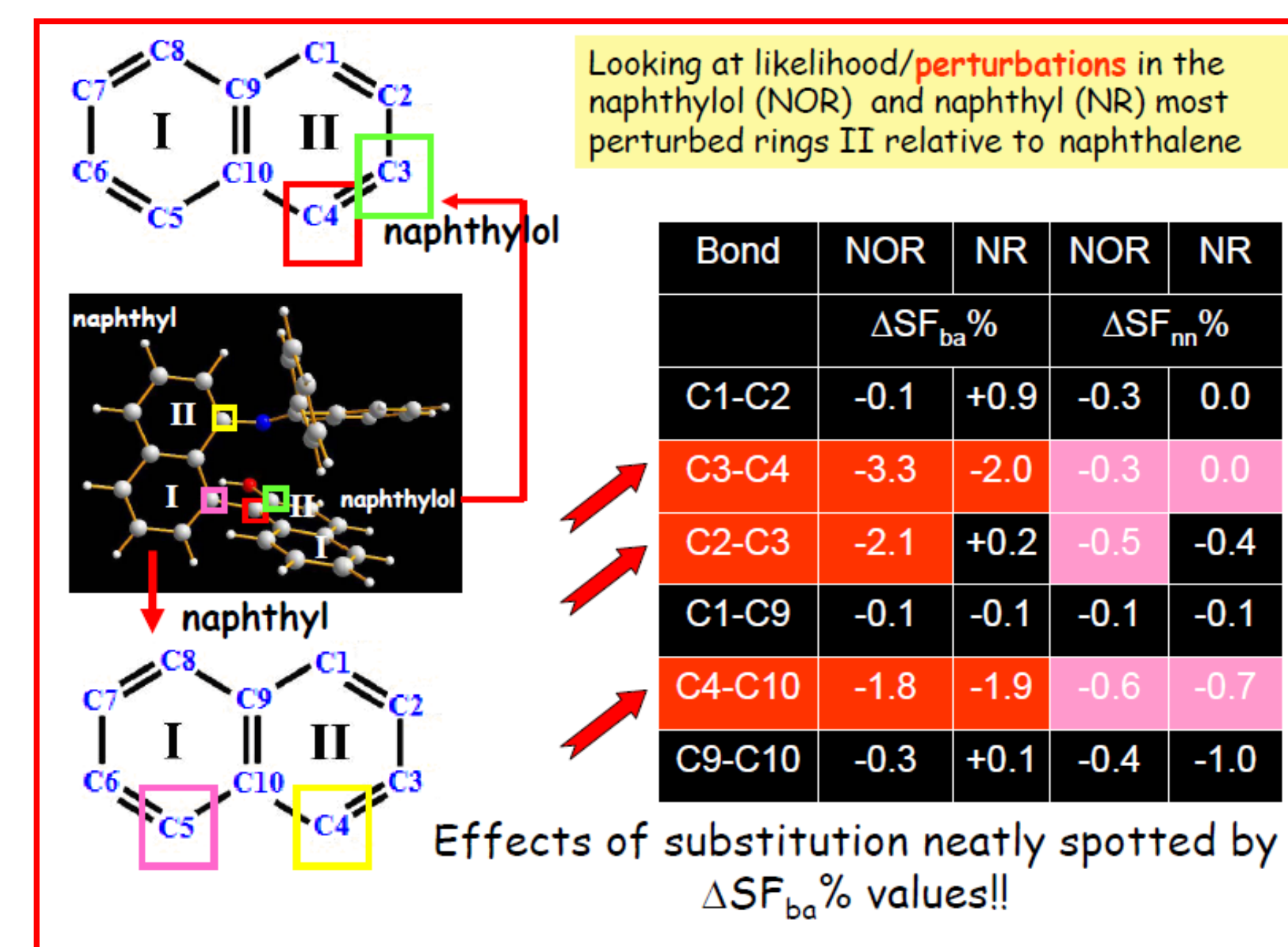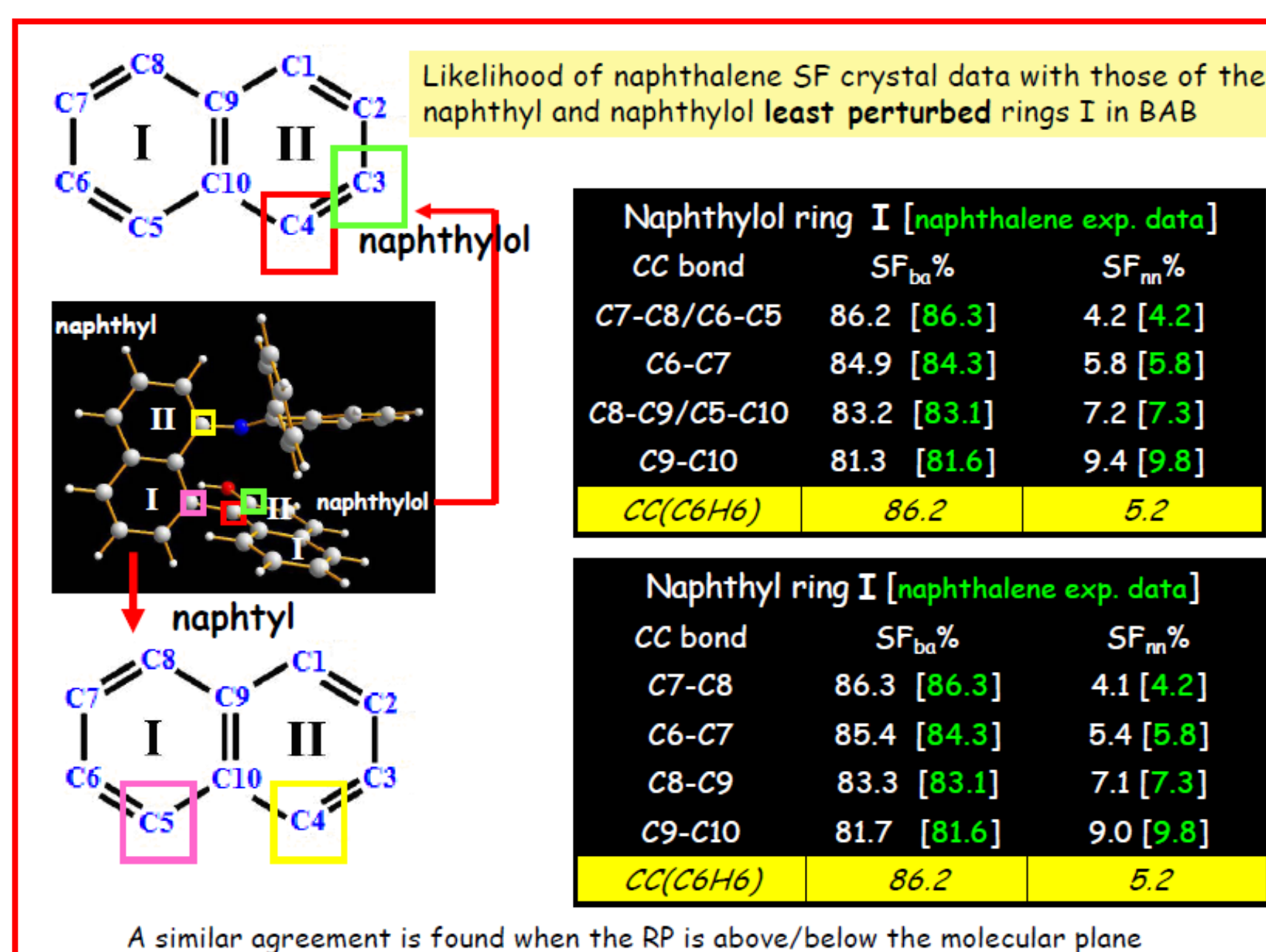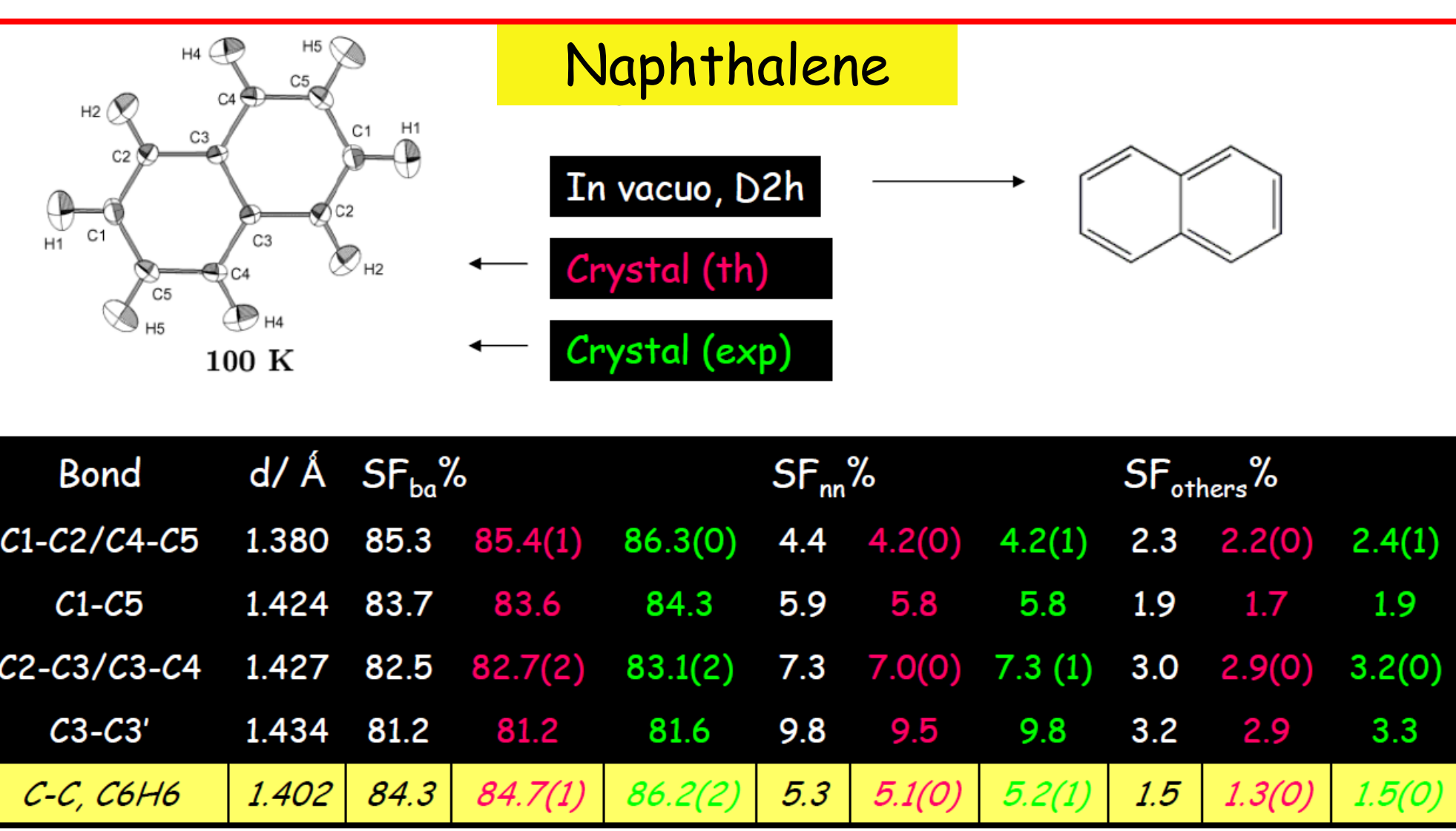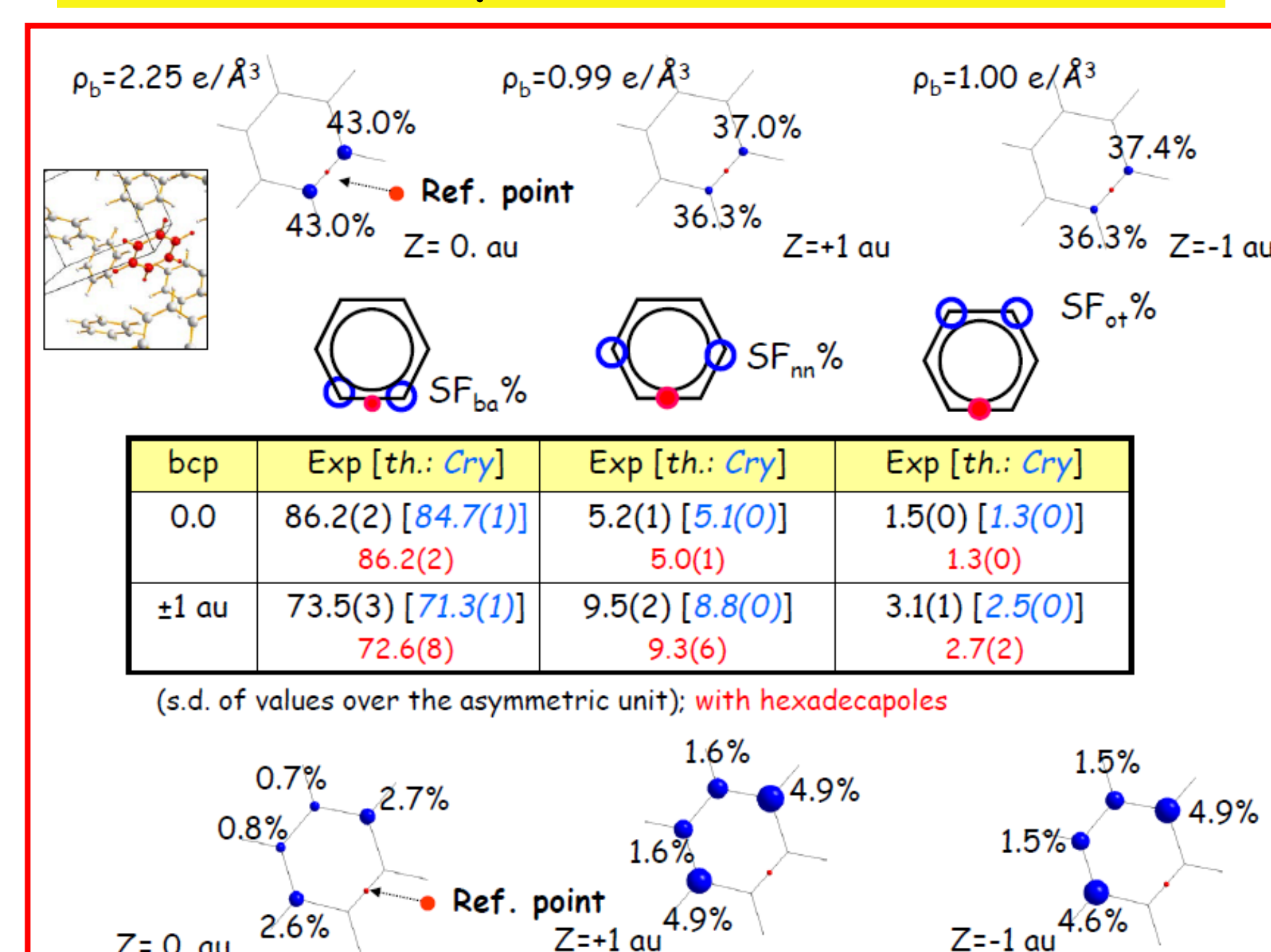SFba% decreases with increasing e delocalization
SFnn% & SFot% increase with increasing electron delocalization

Extension to crystals and X-ray derived EDs

Benzene [1]   Naphthalene [2]

Pbca Z=4   P2₁/c Z=4
✓ Prototypes of aromatic molecules
✓ Simple systems: very accurate data-sets

[1] H.-B. Bürgi et al. *Chem Eur J* (2002) 8, 3512

Space group	T(K)	Wavelength(Å)	Sin(θₘₐₓ/λ)	Rᵢₙₜ
Pbca	100	0.71073	1.11	0.0258

[2] J. Oddershede, S. Larsen *J Phys Chem A* (2004) 108, 1057

Space group	T(K)	Wavelength(Å)	Sin(θₘₐₓ/λ)	Rᵢₙₜ
P2₁/c	135	0.71073	1.14	0.0274

BAB, Benzhydryliden Amino-1,1'-Binaphthyl-2-ol [3]

✓ Big system, "Standard" data quality
✓ Transferability (benzyl and naphtyl)
✓ Investigation of substituent effect

[3] L.J. Farrugia et al. *Acta Cryst B* (2009), B65, 757

SG	T(K)	Wavelength(Å)	Sin(θₘₐₓ/λ)	Rᵢₙₜ
P2₁/c	100	0.71073	1.08	0.036

Benzene (X-ray vs ab-initio Periodic DFT)

bcp	Exp [th: *Cry*]	Exp [th: *Cry*]	Exp [th: *Cry*]
0.0	86.2(2) [*84.7(1)*] 86.2(2)	5.2(1) [*5.1(0)*] 5.0(1)	1.5(0) [*1.3(0)*] 1.3(0)
±1 au	73.5(3) [*71.3(1)*] 72.6(8)	9.5(2) [*8.8(0)*] 9.3(6)	3.1(1) [*2.5(0)*] 2.7(2)

(s.d. of values over the asymmetric unit); with hexadecapoles

Naphthalene

In vacuo, D2h
Crystal (th)
Crystal (exp)
100 K

Bond	d/Å	SFba%			SFnn%			SFothers%		
C1-C2/C4-C5	1.380	85.3	85.4(1)	86.3(0)	4.4	4.2(0)	4.2(1)	2.3	2.2(0)	2.4(1)
C1-C5	1.424	83.7	83.6	84.3	5.9	5.8	5.8	1.9	1.7	1.9
C2-C3/C3-C4	1.427	82.5	82.7(2)	83.1(2)	7.6	7.0(0)	7.3(1)	2.9	2.9(0)	3.2(0)
C3-C3'	1.434	81.2	81.2	81.6	9.8	9.5	9.8	3.2	2.9	3.3
C-C, C6H6	1.402	84.3	84.7(1)	86.2(2)	5.3	5.1(0)	5.2(1)	1.5	1.3(0)	1.5(0)

Benzyl rings of BAB vs benzene crystal

Benzene crystal   BAB crystal
Benzhydryliden Amino-1,1'-Binaphthyl-2-ol

bcp	SFba%(sd) [*theory*]	SFnn%(sd) [*theory*]	SFothers% (sd) [*theory*]
0.0	86.2(2) [*84.7(1)*]	5.0(1) [*5.1(0)*]	1.3(0) [*1.3(0)*]
0.0	86.1 (8)	5.0 (2)	1.3 (2)
0.0	85.3 (9)	5.1 (3)	1.3 (1)
Above/below the benzyl ring			
±1 a.u.	72.6 (8) [*71.3(1)*]	9.3 (6) [*8.8(0)*]	2.7 (2) [*2.5(0)*]
±1 a.u.	71.7 (15)	8.9 (4)	2.6 (4)
±1 a.u.	71.6 (14)	8.9 (3)	2.6 (3)

Values (s.d.) averaged over the 6 CC bond in the phenyl rings; [ab-initio value for benzene crystal]

Likelihood of naphthalene SF crystal data with those of the naphthyl and naphthylol least perturbed rings I in BAB

naphthylol

Naphthylol ring I [naphthalene exp. data]

CC bond	SFba%	SFnn%
C7-C8/C6-C5	86.2 [86.3]	4.2 [4.2]
C6-C7	84.9 [84.3]	5.8 [5.8]
C8-C9/C5-C10	83.2 [83.1]	7.2 [7.3]
C9-C10	81.3 [81.6]	9.4 [9.8]
CC(C6H6)	86.2	5.2

naphthyl

Naphthyl ring I [naphthalene exp. data]

CC bond	SFba%	SFnn%
C7-C8	86.3 [86.3]	4.1 [4.2]
C6-C7	85.4 [84.3]	5.4 [5.8]
C8-C9	83.3 [83.1]	7.1 [7.3]
C9-C10	81.7 [81.6]	9.0 [9.8]
CC(C6H6)	86.2	5.2

A similar agreement is found when the RP is above/below the molecular plane

Looking at likelihood/perturbations in the naphthylol (NOR) and naphthyl (NR) most perturbed rings II relative to naphthalene

naphthylol

naphthyl

Bond	NOR	NR	NOR	NR
	ΔSFba%		ΔSFnn%	
C1-C2	-0.1	+0.9	-0.3	0.0
C3-C4	-3.3	-2.0	-0.3	0.0
C2-C3	-2.1	+0.2	-0.5	-0.4
C1-C9	-0.1	-0.1	-0.1	-0.1
C4-C10	-1.8	-1.9	-0.6	-0.7
C9-C10	-0.3	+0.1	-0.4	-1.0

Effects of substitution neatly spotted by ΔSFba% values!!

Data at bcps. A similar behaviour is found for RPs above/below the molecular plane

Conclusions [10]

❑ The SF tool **recovers the characteristic SF% patterns caused by π-electron conjugation in benzene and naphthalene in almost perfect quantitative accord** with those from *ab initio* periodic calculations

❑ **The effect of chemical substitution on the transferability** of such patterns to the benzyl, naphthyl and naphthylol moieties of BAB **is neatly spotted by the observed systematic deviations**, relative to benzene and naphthalene of only those SF contributions from the substituted C atoms

❑ **The capability of the SF to reveal EDEs by using a promolecule ED (PED)**, rather than the "true" ED has been tested [10]. **The PED is unable to reproduce the SF trends** anticipated by the increase of electron delocalization

❑ The SF has wider applications than those related to the nature of chemical bonds in more or less conventional situations [2-3]. **Detection of EDEs is one such new direction, another being the extension of the SF machinery to retrieve the atomic sources of the spin ED [5,11]**

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