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Supporting information for article:

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

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Here we report details relative to the results presented in Section 2 of the manuscript. In particular, the Independent Atom Model (IAM) SF results for the cyclohexene, 1,3-cyclohexadiene and benzene series are listed in Section S1, along with some necessary computational details, while the strategy adopted for the multipolar refinement of the (experimental) X-ray structure factors is reported in Section S2. The theoretical level employed in theoretical calculations is discussed in Section S3 and Section S4 contains information relative to the procedure we used for numerical integration.

S1. IAM SF data for the cyclohexene, 1,3-cyclohexadiene and benzene series

IAM calculations on the cyclohexene, 1,3-cyclohexadiene and benzene series were performed with CRYSTAL09 code (Dovesi *et al*., 2009), using the PATO option in the *properties* section of the code and the same DZVP2 basis set (Godbout *et al.*, 1992), adopted by Monza *et al*. (2011). Molecular geometries were taken equal to those optimized *in vacuo* at the DFT/B3LYP level of theory, using DZVP2 basis set and the *GAUSSIAN 09* code. Source function calculations on the so obtained IAM electron densities (EDs) were performed with an updated version (Gatti, 2010) of the TOPOND-98 code (Gatti, 1999), interfaced to CRYSTAL09 and implementing the SF evaluation. SF calculations on the IAM ED were performed either using the "correct" determination of the QTAIM atomic boundaries obtained at the DZVP2/DFT/B3LYP level and then integrating the IAM ED within them, or evaluating the atomic boundaries through the IAM ED and then integrating such ED within the IAM boundaries. Hereinafter, the two approaches will be referred to as IAM_ONLY_INT and IAM_BOUND_INT. Their characteristic features and drawbacks (essentially of the IAM_sur_int approach) are fully explained in subsection 2.2 of the paper. Operationally, both approaches are made possible by the specific features of the TOPOND-98 code, which allow for separating the computational step of the atomic surface determination from the one of the ED integration within the surface boundaries. The latter may be taken equal to or different from those obtainable through the ED being integrated. The computational parameters adopted for the surface determination and the integration within atomic basins were the same as detilaed in section S4. SF and SF% results for the DZVP2/DFT/B3LYP, IAM_ONLY_INT and IAM_BOUND_INT models are listed in Table S1. Note that DZVP2/DFT/B3LYP results marginally differ from those reported by Monza *et al*. (2011) and in the Figure 1 of this paper, since they have been obtained through different software codes.

Table S1   SF and SF% contributions for the shortest bond in benzene, C_6H_6, 1,3-cyclohexadiene, C_6H_8, and cyclohexene, C_6H_{10}, using the DZVP2/DFT/B3LYP, IAM_ONLY_INT and IAM_BOUND_INT models at the bcp and at 1 au above/below the molecular plane[a,b,c,d]

Model	System	$\rho(rp)$	SF_{ba}	SF_{nn}	SF_{ot}	$SF_{ba}\%$	$SF_{nn}\%$	$SF_{ot}\%$	$\Sigma SF_H\%$
DZVP2/DFT/B3LYP	C_6H_6	0.301	0.253	0.016	0.004	84.0	5.4	1.5	8.7
		(0.144)	*(0.102)*	*(0.013)*	*(0.004)*	*(71.3)*	*(9.0)*	*(2.7)*	*(16.0)*
	C_6H_8	0.331	0.288	0.010	0.002	86.9	3.1	0.7	9.0
		(0.165)	*(0.129)*	*(0.008)*	*(0.002)*	*(78.1)*	*(4.9)*	*(1.2)*	*(15.9)*
	C_6H_{10}	0.334	0.291	0.008	0.000	87.2	2.5	0.1	10.0
		(0.168)	*(0.132)*	*(0.006)*	*(0.000)*	*(78.5)*	*(3.7)*	*(0.1)*	*(17.5)*
IAM_ONLY_INT	C_6H_6	0.215	0.184	0.021	0.010	85.6	9.7	4.5	-0.2 (-
		(0.116)	*(0.089)*	*(0.018)*	*(0.009)*	*(77.4)*	*(15.6)*	*(7.9)*	*2.0)*
	C_6H_8	0.235	0.208	0.022	0.011	88.4	9.3	4.5	-1.5 (-
		(0.125)	*(0.101)*	*(0.020)*	*(0.010)*	*(81.3)*	*(15.7)*	*(8.2)*	*4.3)*
	C_6H_{10}	0.238	0.210	0.025	0.013	88.5	10.7	5.5	-4.8 (-
		(0.126)	*(0.103)*	*(0.023)*	*(0.013)*	*(81.6)*	*(18.6)*	*(10.1)*	*10.1)*
IAM_BOUND_INT	C_6H_6	0.215	0.176	0.015	0.005	81.8	7.0	2.5	8.4
		(0.116)	*(0.081)*	*(0.012)*	*(0.005)*	*(70.5)*	*(10.6)*	*(4.2)*	*(14.1)*
	C_6H_8	0.235	0.200	0.011	0.004	85.0	4.7	1.5	8.9
		(0.125)	*(0.094)*	*(0.009)*	*(0.003)*	*(74.9)*	*(7.0)*	*(2.5)*	*(15.2)*
	C_6H_{10}	0.238	0.202	0.010	0.002	85.1	4.0	0.7	10.0
		(0.126)	*(0.099)*	*(0.008)*	*(0.001)*	*(75.5)*	*(6.1)*	*(1.2)*	*(17.0)*

a) the shortest bond is the C1-C6 bond in Figure 2 of the manuscript.

b) SF and ρ (ED) values are in atomic units.

c) Entries given in parentheses and in italic are for a reference point (*rp*) 1 au above/below the molecular plane. It lies along the direction of the major axis at bcp for the DZVP2/DFT/B3LYP model, while it lies along the minor axis for the IAM_ONLY_INT and IAM_BOUND_INT models.

d) SF_{ba}, SF_{nn}, SF_{ot} and the corresponding SF% symbols retain the same meaning as in the main paper. $\Sigma SF_H\%$ is the sum of the SF% contributions due to the H atoms.

S2. Multipolar refinement

All the multipolar refinements were performed using the XD2006 code (Volkov *et al.*, 2006). All the refinement were performed against the intensities (F^2) of the published datasets.

S2.1. Benzene

As mentioned in the main text, two multipole models were tested. For both of them, the atomic positions and Anisotropic Displacement Parameters (ADPs) were kept fixed at the published ones (Bürgi *et al.*, 2002), as they had been obtained from a neutron diffraction experiment and are therefore expected to be highly accurate. As in the original work, each C-H fragments of benzene was constrained to have a total valence charge (as defined my monopoles populations) of 5.0. Only Structure factors having a I/σ(I) ratio (*i.e.* the ratio between the intensity of a given reflection and its estimated standard deviation) greater than 2 were included in the refinement (like in the original work). For H atoms, the populations of all multipoles up to $l=2$ (quadrupole) were included in the refinement. Within the model labelled as 'No_Hex' in the main text, the populations of all multipoles of C atoms up to $l=3$ (octupole) were included in the refinement. For the 'Hex' model, instead, hexadecapole populations of C atoms and expansion contraction parameters for multipoles (the k and k' parameters, see Volkov *et al.*, 2006) of all atoms, were refined. The choice of not refining k/k' parameters in the 'No_Hex' model was dictated by the fact that this refinement was found to increase the dissimilarity among the corresponding eigenvalues of the electron density Hessian matrix at the bond critical points for the various C-C bonds (Table S2). This may clearly induce a large discrepancy among the bond ellipticity values, which although much lower than in the 'Hex' model, is at odds with the theoretical results (single-point periodical B3LYP/6-311G** calculations at experimental geometry, see *infra*), and with what expected from basic chemistry, given the absence of strong intermolecular interactions (see Sect. 2.3 of the main text).

Table S2   Eigenvalues of the Hessian charge density matrix and ellipticity at the C-C bond critical points for different multipolar models and for theoretical calculations. Atoms labels as in the main text.

model	Bond	Eigenvalues [e/Å^5]	Ellipticity
exptl, Hex	C1-C2	-15.99 -15.61 11.61	0.024
	C2-C3	-17.84 -15.61 11.44	0.143
	C3-C1'	-17.31 -14.92 11.44	0.160
exptl, No_Hex, k/k' default	C1-C2	-18.56 -15.09 11.73	0.230
	C2-C3	-18.80 -15.23 11.86	0.234
	C3-C1'	-18.04 -14.62 11.83	0.234
exptl, No_Hex, k/k' refined	C1-C2	-17.21 -14.76 13.36	0.166
	C2-C3	-17.55 -14.84 13.51	0.183
	C3-C1'	-16.60 -14.14 13.52	0.174
periodical calculations	C1-C2	-15.47 -12.94 7.81	0.196
	C2-C3	-15.57 -13.01 7.78	0.197
	C3-C1'	-15.40 -12.89 7.86	0.195

The agreement between the calculated (from the multipolar model) and measured structure factors was measured by three parameters (see Volkov *et al.* (2006) for details) R(F^2), wR(F^2) and the Goodness Of Fit (GOF). The obtained values were respectively, 0.0395, 0.0474 and 1.4466 for the 'No_Hex' model and 0.0240, 0.0337 and 1.0435 for the Hex model.

S2.2. Naphtalene

In the original work (Oddershede & Larsen, 2004), several X-ray diffraction experiments, at different temperatures, were performed. We used the dataset collected at 135 K, as it turned out to have the highest precision according to the Rint parameter, which measures the discrepancy among the hkl reflections measured more than once (see Volkov *et al.* (2006)). As in the original work a thorough analysis (which included also the exploitation of information from *ab-initio* calculations) was carried out to refine the ADPs, we kept these latter and the geometry fixed at the published values. All the data having I/σ(I)>3 were included in the refinement. Regarding the multipolar populations, we

refined the same multipole populations as in the original work, *i.e.* up to *l*=3 for C atoms and up to *l*=2 for H atoms. Contraction/expansion coefficients k and k' were refined as well. Agreement factors $R(F^2)$, $wR(F^2)$ and GOF were, respectively, 0.0165, 0.0239 and 0.9214.

S2.3. (±)-8'-benzhydrylideneamino-1,1'-binaphtyl-2-ol (BAB)

ADPs and atomic positions were kept fixed at the published values (Farrugia *et al.*, 2009). The latter were obtained through a careful refinement procedure involving extensive chemical constraints at the initial stages. We refined multipole populations up to hexadecapoles for C, N and O atoms and up to quadrupole for H against all the published data having I/σ(I)>1.5 (as in the original work). Following the same procedure adopted in the original work, we excluded from the refinement those multipoles on C atoms which break the (hypothetical) mirror plane of the aromatic rings. The *k/k'* expansion/contraction parameters were refined as well. We followed the procedure described in the original work, *i.e.* different sets of k/k' were assigned not only to different atom types, as normally done in XD2006, but each atom type was further divided into subgroups sharing the same connectivity. This led to 9 *k/k'* sets: 5 for C, 2 for H, 1 for O and 1 for N. Due to the complexity of the system (58 symmetry-independent atoms), it was not possible to jointly refine *k/k'* parameters and multipole populations (the least-square refinement did not converge). Therefore, we performed a block-refinement in which we optimized multipole populations at fixed k-parameters and then k-parameters at fixed multipole coefficients. After 6 steps, all the parameters were not changing more than their own e.s.d., hence we considered the least-square procedure converged. Agreement factors $R(F^2)$, $wR(F^2)$ and GOF were, respectively, 0.0198, 0.0288 and 1.6916.

S3. Theoretical calculations

Single-point periodical DFT calculations were performed at the experimentally estimated geometries using the CRYSTAL09 code (Dovesi *et al.*, 2009). The B3LYP exchange-correlation functional, along with the 6-311G** basis set were adopted. The SCF procedure was considered converged when the energy difference between two subsequent cycles was less than 10^{-7} atomic units. The reciprocal unit cell was sampled with a 4x4x4 grid of k-points. The adopted ITOL parameters, defining the truncation criteria for the evaluation of Coulomb and Exchange integrals (see Dovesi *et al.*, 2009) were 8, 8, 8, 8 and 14 for ITOL1-ITOL5.

S4. Integration of QTAIM basins and Source Function evaluation

The evaluation of the zero-flux surfaces defining the QTAIM atomic basins, the integration of quantities within them, and the calculation of Source Function contributions was carried out with

TOPOND (Gatti, 1999, Gatti 2010) and XDPROP (Volkov *et al.*, 2006) routine for theoretical and experimental electron density distributions.

The sampling accuracy for the evaluation of atomic properties is defined by two angular (θ and φ) and one radial parameters. For theoretically derived ED, the number of points used are 64,48 and 120 for φ,θ and radial coordinates, respectively. For the integration performed with XDPROP, instead, 972 angular and 400 radial points were used (Gauss-Chebyshev radial quadrature technique was used, see Volkov *et al.* (2006)). Another important parameter is the dimension of the β-sphere for each atoms, within which the electron density is expected to be more spherically symmetric and therefore a lower number of angular points are used. XDPROP determines automatically an appropriate value for all β-spheres. For TOPOND calculations, instead, we set the radii of the β-sphere as slightly lower than the distance between the nucleus and the nearest bond critical point. Finally, for experimentally derived electron densities, only the multipoles centred on atoms belonging to the molecule under investigation were considered. This choice is certainly reasonable considering the scarce perturbation on the molecular electron density distribution introduced by intermolecular interactions (see the discussion in subsection 2.3 of the main text).

The accuracy of integration was checked by three parameters: i) the difference between the value of the electron density at a reference point and that obtained by summing up all the SF atomic contributions ii) the total charge of the molecule (null, in principle) iii) the value of the Lagrangian, defined as $L(\Omega)=-1/4\nabla^2\rho(\Omega)$, where the symbol (Ω) is used to denote the integral of a quantity over the atomic basin Ω defined by zero-flux surfaces. By mathematical definition, $L(\Omega)=0$. In practice, values in the order of 10^{-3} au are considered acceptable. These values are reported in Table S3.

Table S3   Values of various parameters which measure the quality of the determination of atomic zero-flux surfaces and of the integration of scalar quantities within it.

Method	System	SF%err, average[a]	Molecular charge	L(Ω), average[b]
experimental	benzene[c]	0.10 (0.21)	9.5E-4	3.4E-4 (1.1E-3)
	naphthalene	0.37 (0.69)	1.8E-2	5.5E-4 (2.2E-3)
	BAB	0.73 (3.93)	2.7E-2	4.1E-4 (3.4E-3)

a) Difference between the electron density at the reference point and the sum of all SF contributions. The reported values are averaged over all reference points considered (see main text). The number in parenthesis represents the highest among all the values obtained

b) Value of the Lagrangian integrated over the QTAIM atomic basins. The reported values are averaged over all the atoms. The number in parenthesis represents the highest among all the values obtained

c) 'Hex model' considered, see discussion in Sect. S2

The values reported in Table S3 indicate a good quality of the integration, the exception being the reconstruction of electron density at reference points of BAB. We observed the same problems with *in-vacuo* DFT calculations, for which different grid settings were tested. A detailed comparison among various results led us to conclude that the erroneous reconstruction of electron density at reference points (see Saleh, 2014) is caused by errors on the (very small) contributions from atoms far away from the reference point. Indeed, the total molecular charges and L(Ω) values suggest a great accuracy for the results of the integrations (especially considering that BAB molecule contains as many as 236 electrons, hence the error on the total charge is about 0.01%). This means that the SF% values discussed in the main text were accurately determined.

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