Electronic Supplementary Information for:

Efficient prediction of Nucleus Independent Chemical Shifts for polycyclic aromatic hydrocarbons

Dimitrios Kilymis,[1, 2] Albert P. Bartók,[3, 4] Chris J. Pickard,[5, 6] Alexander C. Forse,[7, 8] and Céline Merlet[1, 2]

[1])*CIRIMAT, Université de Toulouse, CNRS, Université Toulouse 3 - Paul Sabatier,*
118 Route de Narbonne, 31062 Toulouse cedex 9, France

[2])*Réseau sur le Stockage Électrochimique de l'Énergie (RS2E), Fédération de*
Recherche CNRS 3459, HUB de l'Énergie, Rue Baudelocque, 80039 Amiens,
France

[3])*Warwick Centre for Predictive Modelling, Department of Physics and School of Engineering,*
University of Warwick, Coventry, CV4 7AL, United Kingdom

[4])*Rutherford Appleton Laboratory, Scientific Computing Department,*
Science and Technology Facilities Council, Didcot, OX11 0QX, United Kingdom

[5])*Department of Materials Science and Metallurgy, University of Cambridge,*
UK

[6])*Advanced Institute for Materials Research, Tohoku University, Aoba, Sendai 980-8577,*
Japan

[7])*Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge, CB2 1EW,*
UK

[8])*Department of Chemistry, Department of Chemical and Biomolecular Engineering,*
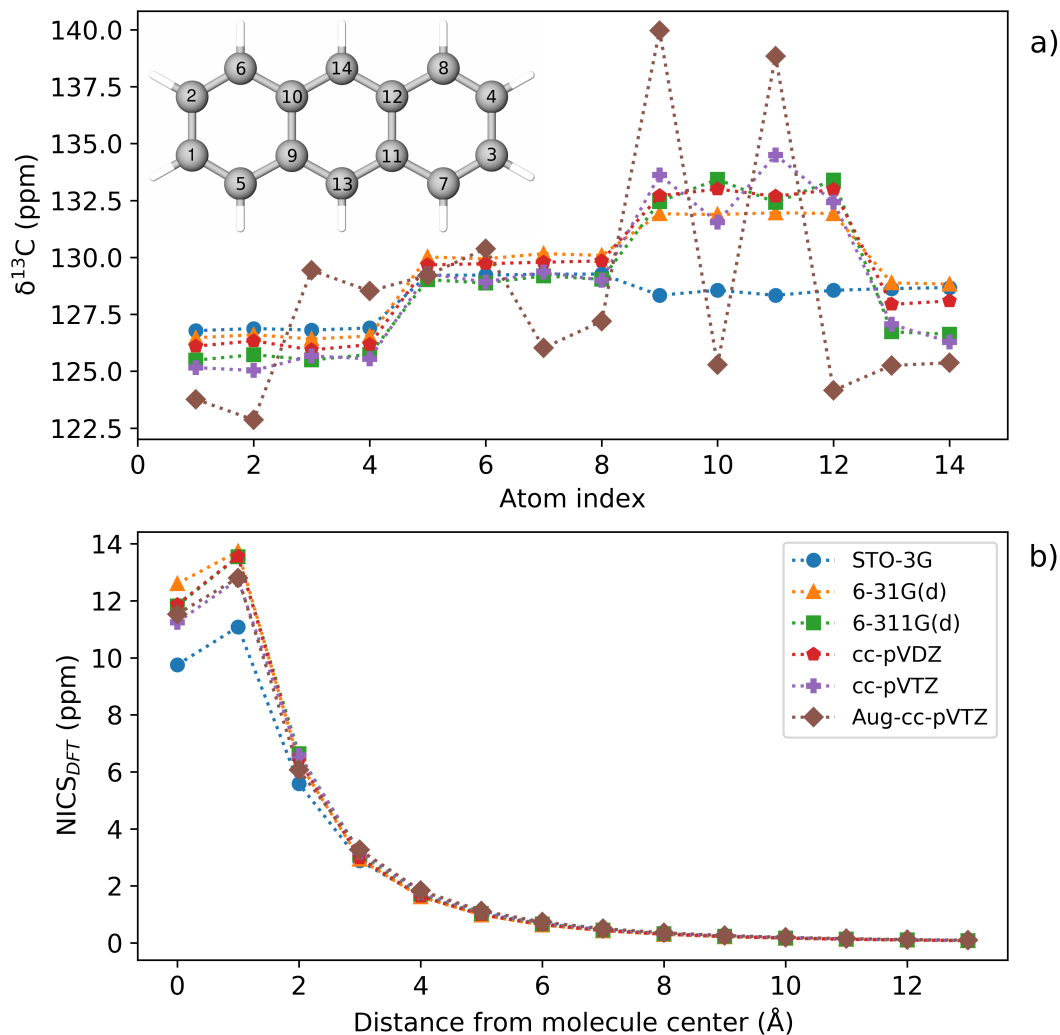*and Berkeley Energy and Climate Institute, University of California, Berkeley, CA94720,*
USA

FIG. S1. a) ^{13}C chemical shifts for carbon atoms in the anthracene molecule (**9**), calculated with different basis sets. Atoms have been numbered according to chemically equivalent positions. All basis sets reproduce the same trend for the chemical shifts, in good agreement with Ozubko *et al.*[1] (125.2 ppm for 1-4, 128.3 ppm for 5-8, 131.6 ppm for 9-12, 126.1 ppm for 13-14), with the exception of STO-3G and Aug-cc-pVTZ. b) NICS values on a vertical line from the molecule center using the same basis sets. All basis sets produce the same trend with the discrepancy at a distance of 3 Å being around 0.5 ppm. The NMR calculations have been performed on the geometry which was optimized using the 6-31G(d) basis set.
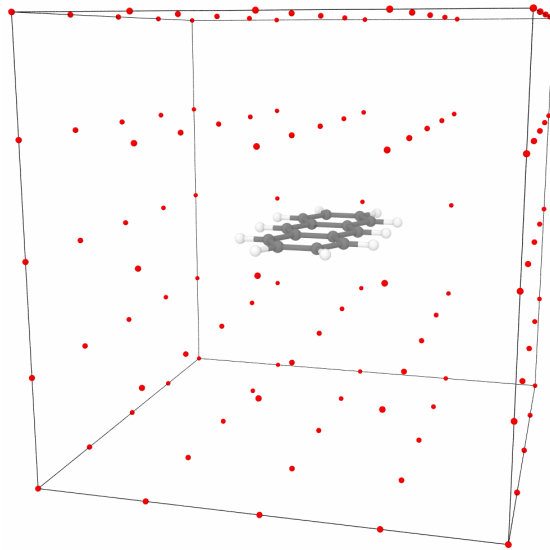
FIG. S2. Computational setup for the calculation of NICS values on a grid (red points) for the anthracene molecule.
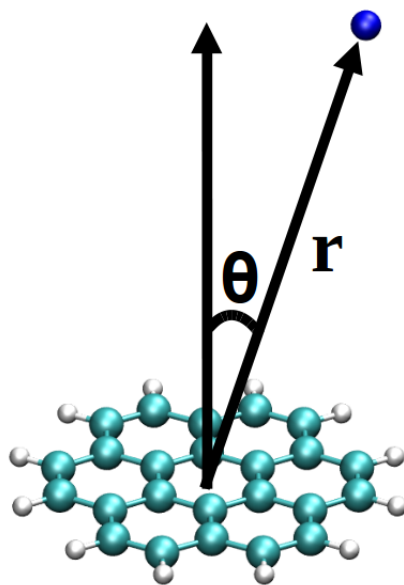

FIG. S3. Scheme describing the angle θ and the distance r considered for the dipolar model. For the coronene represented here, seven additive ring contributions are considered, each with their own θ and r.
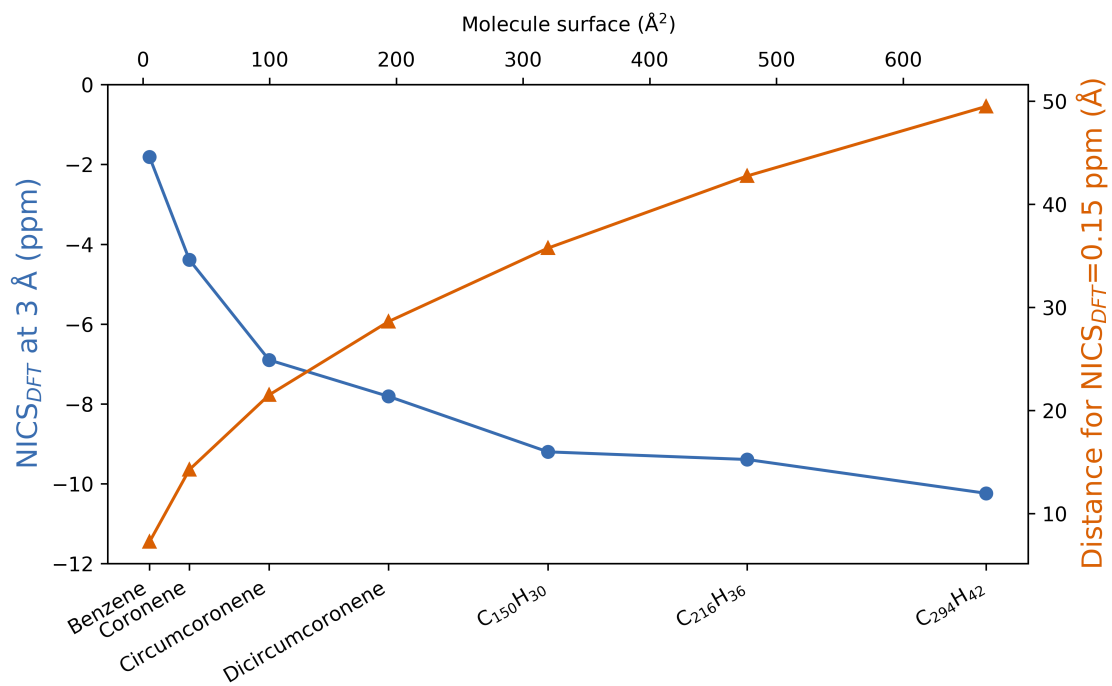
FIG. S4. Value of isotropic NICS using DFT for coronoids at a distance of 3 Å from the molecule center, as well as the distance from the molecule center where they reach a value of 0.15 ppm.

Molecular size effects for ^{13}C NMR shieldings calculated using DFT

We have examined molecular size effects on the ^{13}C NMR chemical shifts using the results for the coronoids which constitute a consistent series of molecules. While size effects have already been studied in such compounds[2–5], results have only rarely been reported on such a large range of molecules[6]. Comparison with experimental results is also limited to small coronoids. For coronene, our calculations yield chemical shift values of 124.2 ppm for the inner carbon atom, 129.8 ppm for the outer bridging, and 128.2 ppm for the protonated one. These values are found to be in good agreement with previous ^{13}C NMR experimental studies[7–9] and DFT calculations[6] which makes us confident that the chemical shifts calculated are reliable.
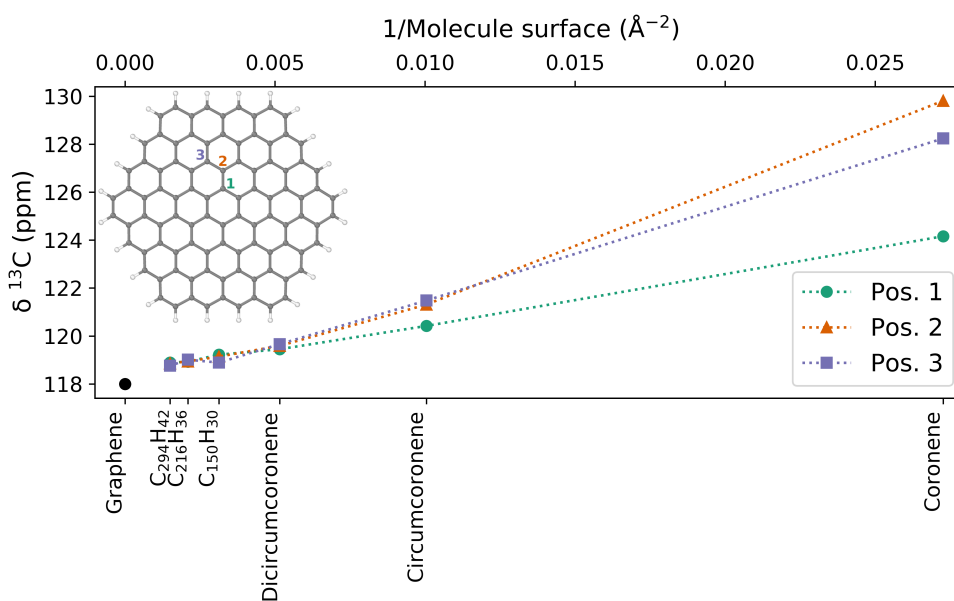

FIG. S5. Evolution of the ^{13}C NMR shift of three equivalent positions with respect to the inverse molecule size. The value for graphene is taken from Ref.[3].

In Fig. S5 we present the evolution of the ^{13}C chemical shifts for three equivalent positions in the series of coronenes. We observe that, as the molecule size increases, the chemical shifts for all equivalent positions decrease and eventually converge towards a single value which is found to be close to the 118.0 ppm value reported by Thonhauser et al. for bulk graphene[3]. The converged values for molecules larger than dicircumcoronene indicate that, as far as chemical shifts are concerned, an atom can be considered to be in the bulk if it is found at a distance of at least three hexagonal rings from the molecule edge.
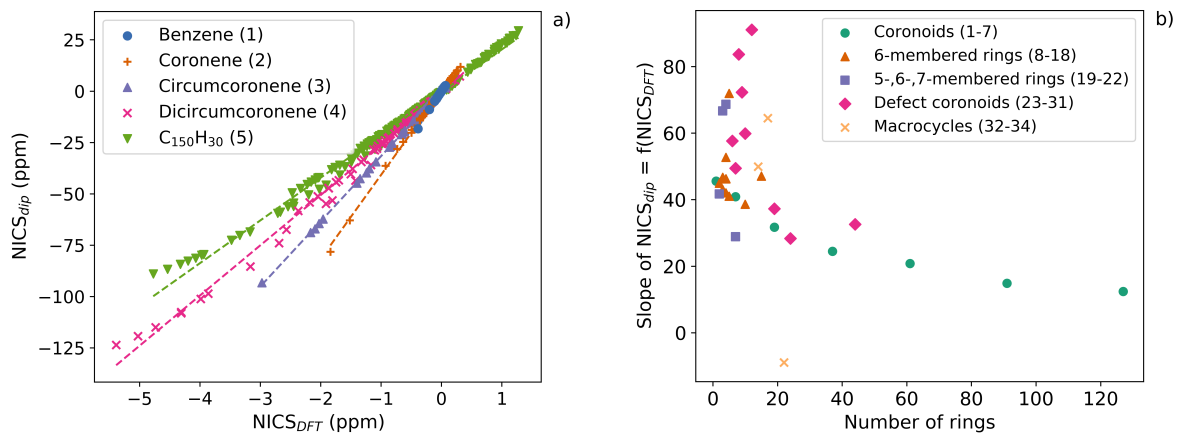
FIG. S6. a) Comparison of the NICS values calculated from a classical dipolar model with the values obtained by DFT for the coronene series and a distance cutoff of 5 Å. Dashed lines indicate the corresponding linear fits. b) Slopes of the linear fits with respect to the number of rings for all molecules in the study. The molecule number according to Fig. 1 is given in parentheses.
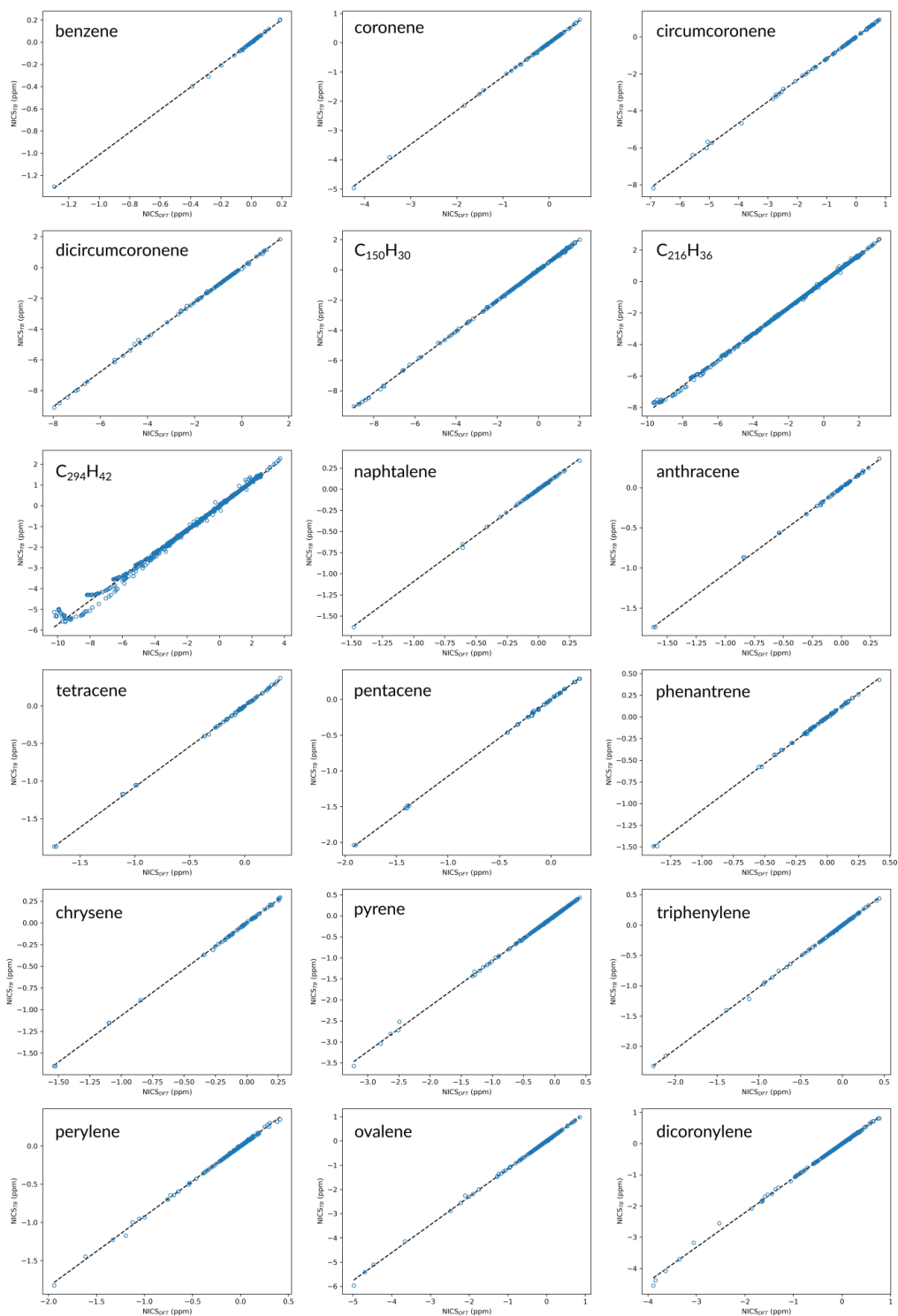
FIG. S7. Correlation between the isotropic NICS values calculated on external grid points with the tight-binding model and using DFT, for a cutoff distance of 3 Å, for all individual molecules. The fit is shown using dashed lines.

FIG. S8. (continued) Correlation between the isotropic NICS values calculated on external grid points with the tight-binding model and using DFT, for a cutoff distance of 3 Å, for all individual molecules. The fit is shown using dashed lines.
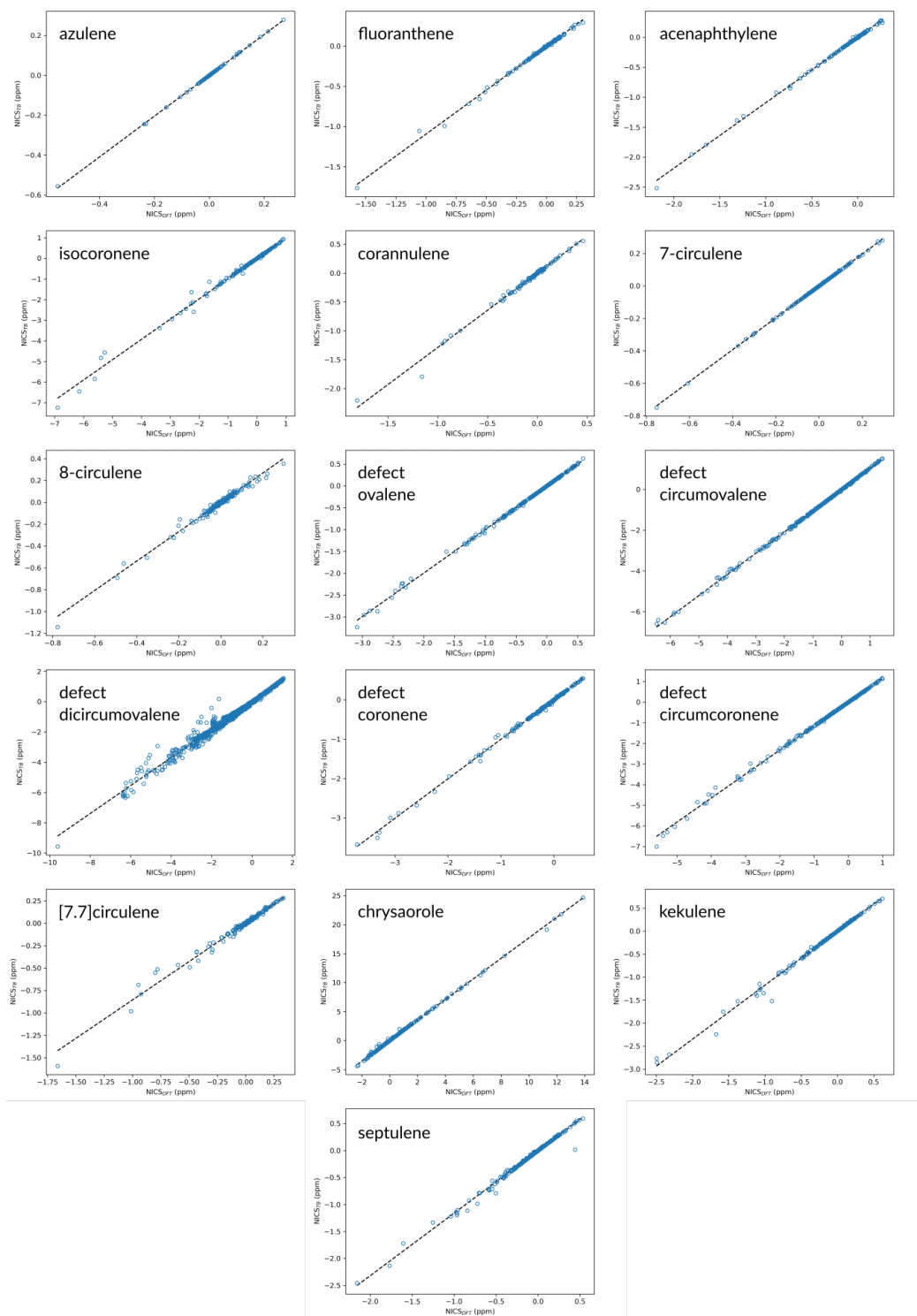
		slope	R^2	Err$_{max,iso}$ (ppm)	Err$_{max,ZZ}$ (ppm)
Coronoids					
1	benzene	1.014539	0.999313	0.028714	0.045475
2	coronene	1.158684	0.999652	0.742010	1.926015
3	circumcoronene	1.167102	0.999541	1.283446	3.537280
4	dicircumcoronene	1.131178	0.999556	1.147241	3.146512
5	C150H30	1.015562	0.999819	0.235541	0.426181
6	C216H36	0.830097	0.999587	1.945544	0.163704
7	C294H42	0.572531	0.996231	5.096041	15.434852
6-membered rings					
8	naphtalene	1.093967	0.999375	0.151856	0.285742
9	anthracene	1.072501	0.999402	0.136261	0.258124
10	tetracene	1.078143	0.999450	0.155158	0.305390
11	pentacene	1.073807	0.999586	0.143879	0.285264
12	phenantrene	1.077573	0.999282	0.135263	0.200893
13	chrysene	1.068886	0.999573	0.124523	0.190444
14	pyrene	1.076725	0.999357	0.352482	0.788974
15	triphenylene	1.025978	0.999583	0.101153	0.130273
16	perylene	0.920105	0.998690	0.168986	0.236475
17	ovalene	1.153149	0.999446	0.986912	2.577938
18	dicoronylene	1.107061	0.998522	0.659911	1.658967
5-,6-,7-membered rings					
19	azulene	1.023705	0.999727	0.012207	0.066505
20	fluoranthene	1.094339	0.996886	0.196028	0.376035
21	acenaphthylene	1.091623	0.998268	0.327544	0.140694
22	isocoronene	0.983508	0.992861	0.697601	2.246905
Defect coronoids					
23	corannulene	1.287611	0.991258	0.634562	1.975447
24	7-circulene	0.982344	0.999809	0.013011	0.184898
25	8-circulene	1.344067	0.980443	0.365990	1.021655

26	defect ovalene	0.998440	0.998935	0.149159	0.847554
27	defect circumovalene	1.043295	0.999413	0.344991	0.754204
28	defect dicircumovalene	0.923524	0.987508	1.823985	5.981987
29	defect coronene	1.002828	0.998134	0.171827	0.658572
30	defect circumcoronene	1.163116	0.998473	1.405776	4.062343
31	[7.7]circulene	0.856390	0.980649	0.268105	1.312503
Macrocycles					
32	chrysaorole	1.773138	0.998941	10.800381	32.693328
33	kekulene	1.175089	0.993768	0.613653	1.489056
34	septulene	1.345744	0.979818	0.664091	2.057950

TABLE S1: Slopes and correlation coefficients for the fit between the isotropic values of $NICS_{TB}$ and $NICS_{DFT}$ for all molecules under investigation and a cutoff distance of 3 Å, as well as the average maximal error encountered for the isotropic NICS and the ZZ component of the NICS tensor. Defects in molecules 26-30 are of Stone-Wales type.

		slope	R^2	$Err_{max,iso}$ (ppm)	$Err_{max,ZZ}$ (ppm)
Coronoids					
1	benzene	1.031421	0.999638	0.009506	0.019544
2	coronene	1.159235	0.999894	0.307054	0.743595
3	circumcoronene	1.183572	0.999859	0.777330	2.048938
4	dicircumcoronene	1.133898	0.999907	0.765759	2.006745
5	C150H30	1.015678	0.999885	0.085116	0.123001
6	C216H36	0.830722	0.999866	1.428500	0.102328
7	C294H42	0.571977	0.998406	3.902181	11.882342
6-membered rings					
8	naphtalene	1.074474	0.999772	0.043664	0.049926
9	anthracene	1.079373	0.999223	0.027698	0.037147
10	tetracene	1.085035	0.999282	0.036784	0.057747
11	pentacene	1.079434	0.999500	0.041370	0.067278
12	phenantrene	1.064587	0.998112	0.024445	0.021541
13	chrysene	1.072571	0.999336	0.028236	0.030704
14	pyrene	1.077867	0.999974	0.101239	0.186771
15	triphenylene	1.027825	0.999913	0.028604	0.050096
16	perylene	0.918941	0.999195	0.060895	0.091628
17	ovalene	1.149662	0.999951	0.403158	1.013466
18	dicoronylene	1.099419	0.999725	0.211126	0.461566
5-,6-,7-membered rings					
19	azulene	1.021174	0.999685	0.012207	0.066505
20	fluoranthene	1.091579	0.998943	0.073802	0.108069
21	acenaphthylene	1.081765	0.999401	0.077930	0.049896
22	isocoronene	0.976799	0.999335	0.117298	0.447217
Defect coronoids					
23	corannulene	1.288827	0.994347	0.113132	0.347932
24	7-circulene	0.978621	0.999920	0.007140	0.117130
25	8-circulene	1.337361	0.973934	0.101327	0.265234

26	defect ovalene	1.001091	0.999625	0.038107	0.297369
27	defect circumovalene	1.054937	0.999719	0.232383	0.410877
28	defect circumovalene	0.916278	0.993603	0.748081	2.624016
29	defect coronene	0.994509	0.999103	0.045824	0.237193
30	defect circumcoronene	1.162528	0.999588	0.622089	1.689619
31	[7.7]circulene	0.808601	0.978885	0.116159	0.536879
Macrocycles					
32	chrysaorole	1.790180	0.999678	6.377776	19.317687
33	kekulene	1.195793	0.998410	0.329350	0.794404
34	septulene	1.373432	0.993253	0.380396	1.252175

TABLE S2: Slopes and correlation coefficients for the fit between the isotropic values of $NICS_{TB}$ and $NICS_{DFT}$ for all molecules under investigation and a cutoff distance of 5 Å, as well as the average maximal error encountered for the isotropic NICS and the ZZ component of the NICS tensor. Defects in molecules 26-30 are of Stone-Wales type.

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