

Substituent effects in cation– π interactions revisited: a general approach based on intrinsic properties of the arenes†

Cite this: *Phys. Chem. Chem. Phys.*, 2014, 16, 1322

Received 1st October 2013,
Accepted 17th November 2013

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DOI: 10.1039/c3cp54147a

www.rsc.org/pccp

The controversial proposal that substituent effects in cation– π interactions can be attributed mainly to electrostatic effects between the ion and local dipoles has been theoretically studied by analyzing 171 aromatics interacting with Na^+ . Our results stress the importance of both electrostatic and π -polarization effects to properly describe cation– π interactions.

Cation– π bonding is an essential and widely recognized non-covalent interaction that involves aromatic rings.^{1,2} Numerous studies have reported the occurrence of cation– π interactions in protein structures^{1–7} and in protein–ligand^{8,9} and protein–DNA^{10,11} complexes.

The cation– π interaction is usually explained in terms of electrostatic effects^{1,6,12} that can be commonly rationalized by the first nonzero multipole moment of the arene that for benzene is the quadrupole, which is negative (the component perpendicular to the ring, Θ_{zz}) and, consequently, it is well suited for interacting favorably with cations. However other effects are also important; the polarization of the π -electron system by the cation has a significant contribution,¹³ whereas the reverse effect is expected to be small. The dispersion contribution is very small.¹⁴

Recently there has been some debate regarding the nature of a variety of interactions involving benzene rings,^{15,16} particularly the cation– π ¹⁷ interaction. Wheeler and Houk have examined substituent effects in 25 $\text{Na}^+ \cdots \text{C}_6\text{H}_5\text{X}$ complexes using DFT calculations. They found that the predicted interaction energies could be matched ($r^2 = 0.805$) using a model system in which the substituents are isolated from the aromatic ring. In contrast to the aforementioned physical explanations of the cation– π interactions, which rely on substituent-induced changes in the aryl π system through inductive and π -resonance effects, Wheeler and

Houk proposed that substituent effects in these systems can be attributed mainly to direct interactions between the cation and local C–X dipoles, suggesting that π -polarization models of cation– π interactions are flawed. It must be emphasized that the model of Wheeler and Houk applies only to substituted benzenes, and does not explain the nature of cation– π bonding in heteroaromatics.

Here our main purpose is to provide results that shed some light on the complete understanding of the physical nature of the forces governing the cation– π interaction. In this communication we present computational evidence supporting that substituent effects not only arise from local C–X dipoles but also from substituent-induced changes in the π -system as well, thus complementing Wheeler's proposal. Specifically, we show excellent correlations between quadrupole moments (Θ_{zz}) and dipole polarizabilities (α_{zz}) with the interaction energies for 104 substituted benzene rings (Chart 1) interacting with Na^+ . Moreover, we added 67 heteroaromatics (Chart 1), namely, pyrazine ($\text{C}_4\text{H}_{4-n}\text{N}_2\text{X}_n$, $n = 2, 4$) and triazine ($\text{C}_3\text{N}_3\text{X}_3$). These results are of utmost relevance since this is the first time that a correlation has been found for a combination of two intrinsic properties of the aromatic molecules, the molecular quadrupole moments and molecular polarizabilities, regardless of whether they are substituted benzenes or heteroaromatics. Moreover, correlations with σ_p rather than σ_m indicate the importance of resonance effects in cation– π interactions.

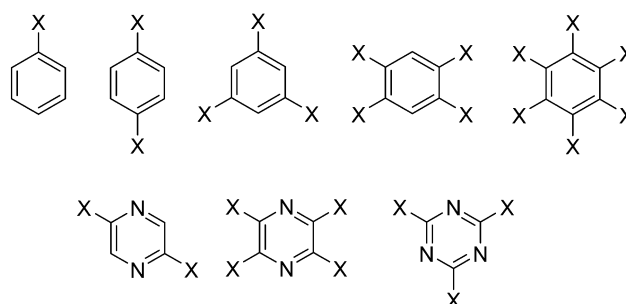


Chart 1 Studied aromatic systems.

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† Electronic supplementary information (ESI) available: Full computational details, Tables S1–S7, including E_{int} , R_c , Θ_{zz} , α_{zz} , E_c and E_p values of benzenes, pyrazines and triazines, Fig. S1–S9 and Cartesian coordinates of the complexes. See DOI: 10.1039/c3cp54147a

The interaction energies (E_{int} , not BSSE-corrected) and equilibrium distances (R_e) of all 171 cation- π complexes were obtained at the M06-2X/6-31+G* level following the same procedure as Wheeler and Houk,¹⁷ *i.e.*, by scanning the distance between Na^+ and the center of mass (COM) of the atoms forming the ring at 0.05 Å increments with the geometry of the substituted aromatics being frozen (see ESI† for more details). We used the same set of substituents as Wheeler and Houk with the addition of X = Cl, Br and NC. Θ_{zz} and α_{zz} were computed at the same level of theory, which are in excellent agreement with the experimental results (see ESI†). The zz component of the atomic dipole polarizability tensor was calculated as the set of first derivatives of the atomic z dipole moment component with respect to the z component of an applied electric field of 0.0025 a.u. along the z direction, the derivatives being evaluated at the zero-field point. BSSE correction was not taken into account because, when relatively small basis sets are used, its inclusion is not recommended in the calculation of interaction energies since it would lead to values with larger discrepancies with the accurate ones.¹⁸ All calculations were carried out using Gaussian09 package,¹⁹ apart from Θ_{zz} and the atomic dipole polarizabilities, which were calculated using GAMESS v. 11²⁰ and AIMAll²¹ program, respectively. Lowest sum of squared absolute error fitting calculations were performed using MATLAB. The plotting of noncovalent interaction regions was carried out using the NCIPLOT program.²²

In the present study we assume that the computed interaction energy of the cation- π complexes is the result of a linear combination of both electrostatic and polarization effects, *i.e.*, $E_{\text{int}} = a + bE_e + cE_p$ where a , b and c are constants, and E_e and E_p are the electrostatic and polarization contributions, respectively. E_e is computed from the central multipole expansion.^{23,24} More precisely we assume that the electrostatic interaction will be mainly governed by the quadrupole moment (despite not always being the first nonzero multipole moment), specifically Θ_{zz} . This results in eqn (1):²⁴

$$E_e = \frac{\Theta_{zz}(3 \cos^2 \theta - 1)}{2R_e^3} \quad (1)$$

Since Θ_{zz} is typically computed at the COM of the molecule, the angle θ (between the vectors Na^+ -COM of the molecule and Na^+ -COM of the ring, Fig. S1, ESI†) must be considered. E_p can be accounted for by considering the physics of the interaction between an ion and a nonpolar neutral molecule, which is attributed to the attraction between both to charge-induced dipole potentials. This is the essence of a theory which had first been sketched by Langevin²⁵ and further refined by Gioumousis and Stevenson.²⁶ This model assumes that the ion is a point charge and the molecule is a structureless sphere with polarizability α . In our case E_p is given by eqn (2).

$$E_p = -\frac{1}{2} \frac{\alpha_{zz}}{R_e^4} \quad (2)$$

In Table 1 and Tables S1-S7 (ESI†), we include the E_{int} , R_e , Θ_{zz} , α_{zz} , E_e and E_p values for the mono-, di-, tri-, tetra-, and hexasubstituted benzene, di- and tetrasubstituted pyrazine and trisubstituted triazine complexes. First we will focus on the

Table 1 Interaction energies of $\text{C}_6\text{H}_5\text{X}$ with Na^+ (E_{int} in kcal mol⁻¹), equilibrium distances (R_e in Å), Θ_{zz} (in B) and α_{zz} (in a.u.) of $\text{C}_6\text{H}_5\text{X}$, and electrostatic and polarization contributions (E_e and E_p , respectively, in kcal mol⁻¹) at the M06-2X/6-31+G* level of theory

X	E_{int}	R_e	Θ_{zz}	α_{zz}	E_e	E_p
H	-26.3	2.35	-8.6	38.9	-45.8	-31.4
CH ₂ OH	-29.6	2.30	-11.5	50.6	-51.6	-44.5
NHOH	-28.8	2.30	-10.6	47.4	-48.1	-41.7
N(CH ₃) ₂	-33.6	2.30	-11.0	64.5	-41.9	-56.7
NHCH ₃	-32.9	2.30	-11.4	54.6	-51.7	-48.0
OCH ₃	-27.9	2.35	-9.4	50.9	-40.7	-41.1
OH	-26.1	2.35	-9.0	42.2	-45.1	-34.1
CH ₃	-27.7	2.30	-8.2	48.2	-43.9	-42.3
NH ₂	-31.6	2.30	-11.5	45.0	-61.5	-39.6
SCH ₃	-28.0	2.30	-10.7	59.7	-39.7	-52.5
SH	-25.9	2.35	-9.8	51.4	-41.6	-41.5
CCH	-25.2	2.35	-11.5	47.1	-51.0	-38.0
SiH ₃	-25.6	2.35	-7.8	59.8	-33.0	-48.3
F	-21.2	2.35	-6.2	38.3	-30.8	-30.9
COOCH ₃	-23.3	2.35	-8.9	55.8	-24.8	-45.0
COOH	-21.3	2.35	-7.7	46.1	-28.1	-37.2
COCH ₃	-21.8	2.35	-5.0	53.3	-18.4	-43.0
OCF ₃	-20.2	2.40	-8.2	51.6	-16.5	-38.3
BF ₂	-19.8	2.35	-3.3	44.8	-11.1	-36.1
CHO	-19.4	2.35	-3.8	43.6	-16.5	-35.1
CF ₃	-18.3	2.40	-8.2	49.4	-21.6	-31.1
NO	-17.1	2.40	-3.2	42.1	-13.3	-31.2
SiF ₃	-18.4	2.40	-8.6	52.8	-17.8	-39.1
CN	-16.0	2.40	-1.8	43.7	-7.5	-32.4
NO ₂	-13.5	2.45	-2.0	43.3	-6.7	-29.6
Cl	-22.0	2.35	-8.1	44.2	-33.7	-35.6
Br	-23.1	2.35	-9.6	49.6	-26.0	-40.0
NC	-17.6	2.40	-2.6	45.8	-11.2	-33.9

results obtained for the monosubstituted benzenes (Table 1). In general E_{int} values agree with the common assumption that electron-donor/acceptor groups will strengthen/weaken the cation- π interaction. Fig. 1 shows E_{int} versus the linear combination of E_e and E_p .

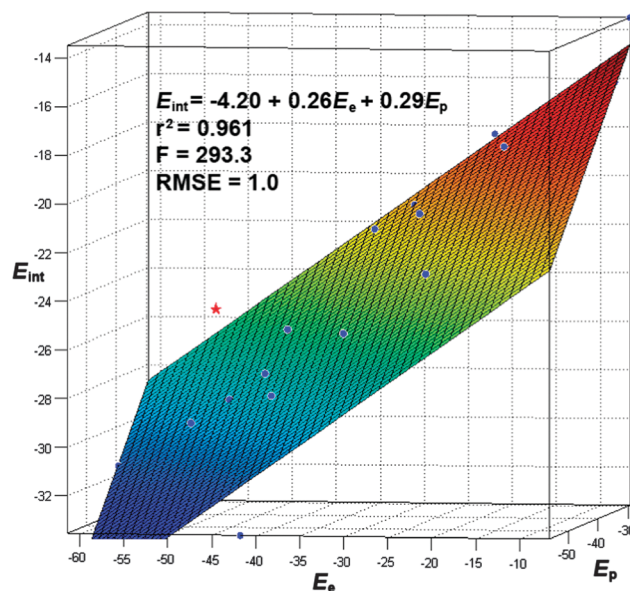


Fig. 1 Interaction energy, E_{int} , plotted versus a linear combination of electrostatic, E_e , and polarization, E_p , energies (in kcal mol⁻¹) for $\text{C}_6\text{H}_5\text{X}$. The star represents X = CCH.

The results from the fitting yield an excellent correlation with $r^2 = 0.949$ and an F statistic value of 232.3. F -statistics is used to compare the variance of two different set of values and thus tells us whether the overall regression is statistically significant. In our case F statistics is much larger than the F critical value of 3.403 confirming that there is a significant joint relationship for all the independent variables. Therefore, the computed E_{int} can be matched using simplified physical models for the calculation of electrostatic and polarization effects, indicating that both contributions are relevant. There are no outstanding outliers from the representation. However, there is one point ($X = \text{CCH}$) that slightly deviates from the general trend. E_{int} for ethynylbenzene is smaller than that for benzene, in agreement with the electron-withdrawing nature of the ethynyl group.^{27–33} Thus, a more positive Θ_{zz} value than that of benzene ($\Theta_{\text{zz}} = -8.6$ B) would be expected. However the opposite is observed [$\Theta_{\text{zz}}(X = \text{CCH}) = -11.5$ B]. Similar results are obtained for the di-, tri-, tetra- and hexaethynyl benzenes with increasingly much more negative Θ_{zz} values (-13.8 , -17.0 , -21.4 and -30.6 B, respectively, Tables S1–S4, ESI[†]). This peculiar behavior of the ethynyl-substituted benzenes has been reported very recently.³⁴ The reason behind this is that the central multipole expansion fails to describe the true electrostatic nature of ethynyl-substituted aromatic π -systems due to the size of the substituent. Removal of other large substituents, such as COOCH_3 and COCH_3 , does not significantly improve the correlations as the removal of CCH does. Hence, from now on we will only discuss the results without considering $X = \text{CCH}$. If we remove the faulty $X = \text{CCH}$ from Fig. 1 the correlation moderately increases up to $r^2 = 0.961$ and $F = 293.3$. Wheeler and Houk, using almost the same set of compounds and their equation for a model system based on local C–X dipoles interacting with Na^+ , obtained a worse correlation value of $r^2 = 0.805$. The value of the intercept (-4.20 kcal mol⁻¹) may reflect the BSSE, which was not corrected for the calculation of E_{int} , and may also arise from the small contribution of dispersion forces and Na^+ polarization.

The fitting representations of E_{int} versus a linear combination of E_e and E_p for di- and trisubstituted benzenes also yield very good correlations ($r^2 = 0.936$ and 0.935 , Fig. S2 and S3, ESI[†] respectively). The correlations for the tetra- and hexasubstituted benzenes are also excellent ($r^2 = 0.967$ and 0.943 , Fig. S4 and S5, ESI[†] respectively). No energy minimum was found during the scanning of $X_6 = (\text{CN})_6$.

With the aim of completing our study, it is imperative to take into account non-benzene aromatics. In this regard pyrazine and triazine heteroaromatics were included. In Tables S5–S7 (ESI[†]) we summarize the results of di- and tetrasubstituted pyrazines and trisubstituted triazines, respectively. First it is worth mentioning that no energy minima were found during the scanning of pyrazines $X_2 = (\text{NO}_2)_2$ and $X_4 = (\text{NO})_4$ and triazines $X = \text{F}$, CF_3 , NO , SiF_3 , CN , NO_2 and NC . This is understandable considering the large and positive Θ_{zz} and relatively small α_{zz} values of those molecules. The representations of the fitting of E_{int} versus the linear combination of E_e and E_p (Fig. S6 and S7, ESI[†]), for di- and tetra substituted pyrazines, give very good correlations of $r^2 = 0.913$ and 0.934 ,

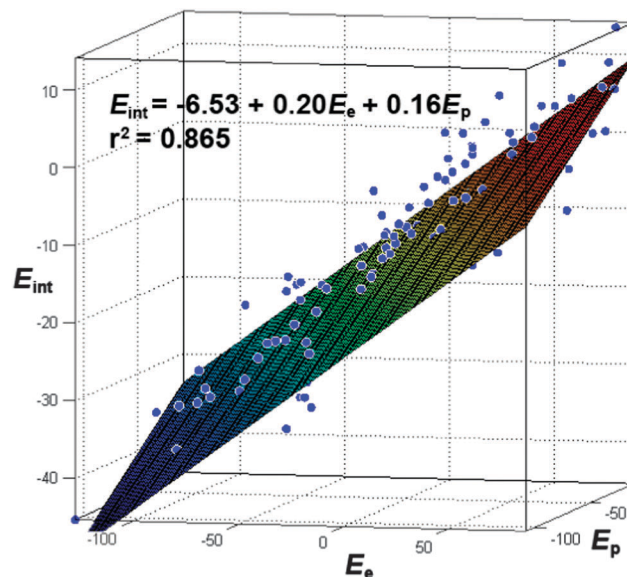


Fig. 2 Interaction energy, E_{int} , plotted versus a linear combination of electrostatic, E_e , and polarization, E_p , energies (in kcal mol⁻¹) for all aromatic systems without ethynyl groups.

respectively. Furthermore, an excellent fitting is achieved ($r^2 = 0.952$) for the triazine derivatives (Fig. S8, ESI[†]). According to our energy scheme the relative weight of E_e is more important than E_p for di-, tri- and hexasubstituted benzenes whereas tetrasubstituted benzenes and heteroaromatics yield similar relative weights for both contributions.

Moreover, if E_{int} for all 161 cation– π complexes is plotted against the linear combination of E_e and E_p , one single relationship is obtained with a good correlation coefficient $r^2 = 0.865$ (Fig. 2). Therefore all the above-mentioned results stress the significance of both electrostatic and polarization effects for an appropriate description of the cation– π interaction, regardless of whether the aromatic ring is either benzene or heterocyclic.

Since noncovalent interactions are characterized by low density and reduced density gradient (RDG) values, they can be located using the NCIPLOT program.²² These regions are mapped in real-space by plotting an RDG isosurface for a low value of RDG, providing a rich visualization of noncovalent interactions as broad regions of real space rather than simple pairwise contacts between atoms. In addition, the sign of the second eigenvalue of the density Hessian times the density is color-mapped onto the isosurfaces. Fig. 3 shows the gradient isosurfaces for the electron-donor $\text{C}_6\text{H}_3(\text{N}(\text{CH}_3)_2)_3 \cdot \text{Na}^+$ and the electron-withdrawing $\text{C}_6(\text{NC})_6 \cdot \text{Na}^+$ complexes. There is an area of noncovalent interaction (larger for the former than for the latter) between the aromatic system and the cation that covers the ring, just where the cation– π interaction is expected. The location and extension of the noncovalent interaction areas coupled with the bluish (indicative of a relatively strong and attractive interaction) and green (indicative of a weak interaction) colors of those regions for the former and latter complexes, respectively, support the idea that the π -system is polarized due to substituent effects. Similar gradient isosurfaces are obtained for other cation– π complexes.

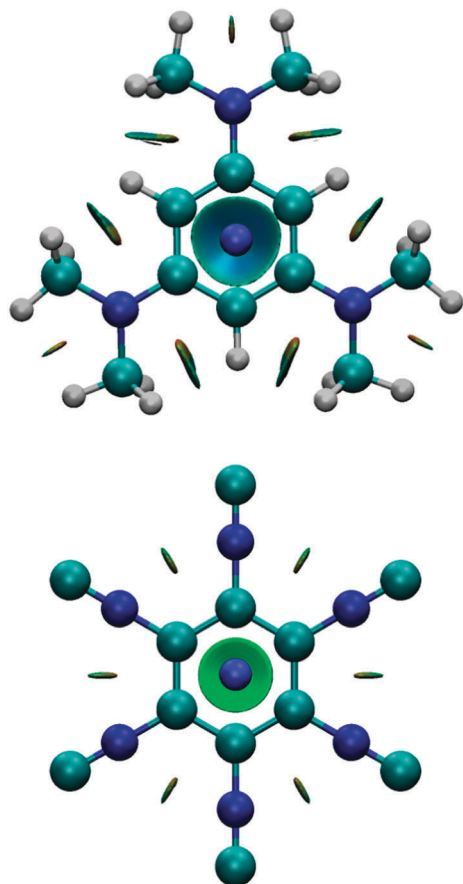


Fig. 3 Top views of the NCIPlot gradient isosurfaces for $C_6H_3(N(CH_3)_2)_3 \cdot Na^+$ (top) and $C_6(NC)_6 \cdot Na^+$ (bottom) complexes. Blue, green and red indicate strongly attractive, weak and strongly repulsive interactions, respectively.

To dig deep into the relative importance of polarization effects due to the induced-dipole of the aromatics, we plotted E_{int} against E_e for the monosubstituted benzenes (Fig. S9, ESI†). We observed that there is a good linear relationship ($r^2 = 0.850$) but not as strong as that shown in Fig. 1 ($r^2 = 0.961$) when both polarization and electrostatic contributions are considered. Very similar results are observed for the rest of the molecules, indicating that the polarization effects of the aromatic systems play an important role. This can be clearly anticipated by analyzing the α_{zz} values in Table 1 and Tables S1–S4 (ESI†). The polarizability of the arenes is influenced by the substituents with α_{zz} values spanning from 36.9 a.u. for C_6F_6 to 113.0 a.u. for $C_6H_3(N(CH_3)_2)_3$. Since consideration of polarization is important to properly describe the cation- π interaction it must also be important for the description of the substituent effects that, consequently, cannot be rationalized using only electrostatic considerations, as suggested by Wheeler.¹⁷ Of course, it could be argued that the E_p values reported here are simply capturing the polarizability of the substituents. However we could consider that this polarization contribution may also come from the polarization of the aromatic π density.

To further corroborate that π -polarization of the ring is important to properly describe substituent effects, we computed

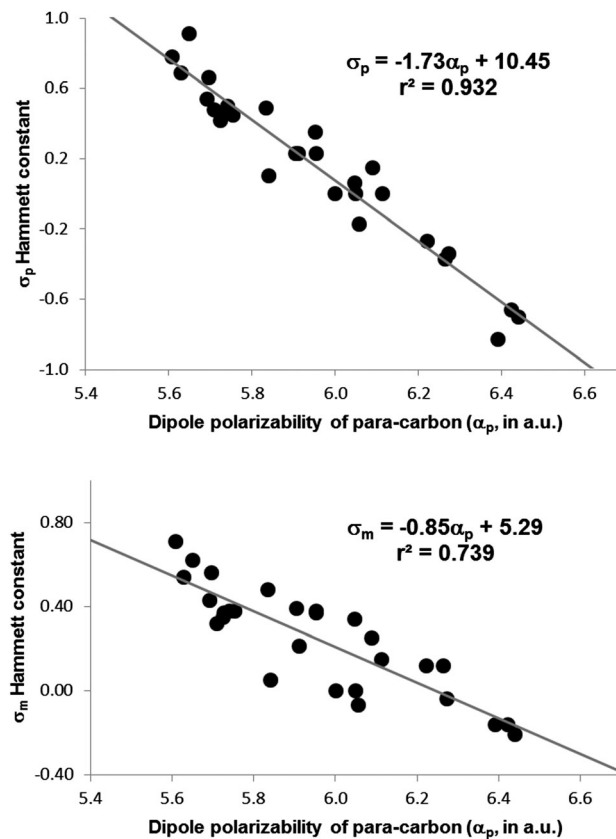


Fig. 4 Dipole polarizability of the C atom at the *para* position, α_p , plotted versus the Hammett constants, σ_p (top) and σ_m (bottom) for C_6H_5X .

the dipole polarizability (perpendicular to the ring) of the C atom at the *para* position for monosubstituted benzenes, and we have plotted it against Hammett constants σ_p and σ_m (Fig. 4). The excellent linear correlation results obtained for σ_p rather than σ_m clearly demonstrate the direct implication of substituents in the polarization of the aromatic ring. Moreover, our results are in excellent agreement with Mandolini's experimental results³⁵ claiming the importance of resonance effects in cation- π interactions.

Conclusions

The present study shows excellent correlations between the computed interaction energies of 161 cation- π complexes and a linear combination of electrostatic and polarization terms, leading to a general approach to describe and predict cation- π interactions. These results are outstanding if we take into account that these two terms were obtained from simple models based on intrinsic properties of molecules, namely, the quadrupole moment, Θ_{zz} , and the molecular polarizability, α_{zz} . Therefore, Θ_{zz} and α_{zz} are key to describe the cation- π interaction in benzene and heteroaromatic rings. Moreover we have proven that the polarization of the aromatic molecule plays an important role in providing an appropriate description of the cation- π interactions. Indeed the implication of these ion-induced dipole effects is remarkable. In fact, our results

support that the polarization of the ring π -density is important to properly describe substituent effects, throwing no doubt on the notion that resonance effects do not play a negligible role. We would like to emphasize that the model of Wheeler and Houk is a fair approximation to tackle the study of substituent effects in cation– π interactions and that our results are complementary and do not contradict their conclusions.

Acknowledgements

We thank CONSOLIDER-Ingenio 2010 (CSD2010-0065), the MICINN of Spain (project CTQ2011-27512/BQU, FEDER funds) and the Direcció General de Recerca, Desenvolupament Tecnològic i Innovació del Govern Balear (project 23/2011, FEDER funds) for financial support. We thank the CESCA for computational facilities. D.Q. thanks the MICINN of Spain for a “Ramón y Cajal” contract.

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