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Can Ring Strain Be Realized in Momentum Space?

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Abstract: An increased electron momentum density (EMD) at low momentum is proposed to be an indicator of ring strain, with the nature of the function tending toward a maximum. A **p**-space Hirshfeld atomic partitioning scheme is applied for analyzing the effect of strain on molecular EMDs. The Hirshfeld momentum densities for a strained system show an increase in the population for the carbons with the hydrogens becoming more positive in comparison with an unstrained reference molecule. The manifestation of strain in cage-like hydrocarbons such as tetrahedrane, cubane, prismane, etc. as well as their nitrogen-substituted analogues is clearly seen in terms of EMDs.

Introduction

Electron momentum density (EMD) of atoms and molecules has been of curiosity since the introduction of momentum space wave functions of hydrogen-like atoms by Podolsky and Pauling.[1] These theoretical studies found an experimental manifestation through the measurement of Compton line shapes.[2] In the years that followed, the interest in momentum distributions was catalyzed by their chemical interpretation by Coulson.[3] What makes the EMD unfamiliar to a chemist is the absence of nuclei-centric structure as opposed to the molecular electron density (MED) in coordinate space; a distribution which visually brings out bonds and nuclei. Coulson[3] had provided a means of interpreting the momentum distribution for hydrogen and some hydrocarbons, in terms of the maximum of the momentum density being in a direction perpendicular to bonding directions in coordinate space. Coulson's work remains as a milestone that brought out the chemical significance of a distribution that was otherwise obscure.

EMDs have had a potential interest in chemistry via an intimate connection with the valence behavior and kinetic energies of molecules. This has been exemplified with the monitoring of reactions in momentum space,[4] an information theoretic analysis of S_N^2 displacement reactions,[5] quantum mechanical similarity indices[6] from EMD, etc. On the experimental front, the technique of electron momentum spectroscopy (EMS) enables the measurement of spherically averaged momentum density distribution of an occupied molecular orbital. This has been recently exemplified by Zheng et al. by mapping the HOMO for glycine.[7] The absence of nuclei-centric structural information has indeed deterred chemists from venturing into momentum space. Hence, exploring further connections of EMDs with classical chemical concepts is still worthwhile. The purpose of the present work is to take a further step in this direction.

The EMD, $\gamma(\mathbf{p})$, is given by the following equation:

$$\gamma(\mathbf{p}) = \int \Phi^*(\mathbf{p},\mathbf{p}_2, ..., \mathbf{p}_N)\ \Phi(\mathbf{p},\mathbf{p}_2, ..., \mathbf{p}_N)\ d^3p_2\ d^3p_3\ ...\ d^3p_N$$

wherein the momentum space wave function, $\Phi(\mathbf{p}_1, \mathbf{p}_2, ..., \mathbf{p}_N)$ is a $3N$ dimensional Fourier transformation of the position-space wave function $\Psi(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N)$. It is to be noted that there does not exist a one to one correspondence between the MED and EMD. A recent review by Thakkar[8] gives an elaborate account of EMDs of atoms and diatomic molecules. The nature of EMD is complementary to its positional counterpart and requires in-depth analysis to establish a connection with the latter.[9a,b] The molecular EMDs have been analyzed via topographical principles by Gadre and co-workers[9c] who observed a certain hierarchical structure in the maximal and minimal characteristics of the distribution. An interesting feature of EMD is its inversion-symmetric nature that was proven by Löwdin[10a] and graphically shown by Thakkar and Smith.[10b] This enhanced symmetry led to a systematic classification of EMDs with the introduction of momentum space point groups for molecules by Gadre and co-workers.[11,12]

Techniques such as (e, 2e) and (e, γe)[13] give three-dimensional (3D) momentum density distributions of solids. Recent advances on the experimental side have been due to Weigold, McCarthy, and co-workers.[14] Strained organic mol-

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ecules probed by EMS have been a topic of their study during the past few years.[15−18] In particular, the strained systems such as [1,1,1]-propellane,[15] cubane,[16] and norbornane[17] have been analyzed by EMS and their bonding features interpreted via its position space counterpart, viz. the MED.

The classical definition of molecular strain originated in the work of Baeyer.[19] In modern terms, carbon atoms whose bond angles deviate substantially from standard bond angles 109.5°, 120°, and 180° respectively for sp^3, sp^2, and sp hybrid orbitals are said to be strained. Interestingly, the "bent banana bond" model of cyclopropane was introduced by Coulson and Moffit,[20] whose preliminary findings triggered the interest in molecular EMDs.[3] The topographical features of MED provide a visualization of molecular strain through angular deviations and bond ellipticities as put forth by Bader and co-workers.[21,22] Molecular strain has earlier been analyzed via heats of formation,[23] electrostatic force concepts,[24] etc. As noted earlier, EMDs have an interpretative problem in this respect since they lack an atom-centric visual description of molecular structure. However, EMDs are intimately connected to kinetic energy densities that in turn can be closely linked with strain, as is heuristically expected.[21] The current work is an attempt to explore the effect of ring strain on EMDs. This is done via a topographical analysis and a Hirshfeld partitioning[25] of the total EMD into atomic contributions.

Methodology

Topographical Analysis of EMD. The topographical analysis[21,26] of EMD is done by locating and characterizing its critical points (CP), viz. the points at which the gradient of the function vanishes, i.e., $\nabla\gamma(\mathbf{p}) = 0$. There can be only 4 types of nondegenerate CPs for a 3D function such as EMD,[33] and these are denoted as (i) (3, −3), a maximum in all directions, (ii) (3, −1), a saddle which is maximal in all directions except one, (iii) (3, +1), a saddle which is minimal in all directions except one, and (iv) (3, +3), a true minimum in all directions. Analysis of the topography of EMD is made convenient through the previously mentioned hierarchy of CPs. The hierarchy[9,27] in the CPs is as follows: (i) a (3, −3) maximum at $\mathbf{p} = 0$ is unique and no other CP is found, (ii) a (3, −1) saddle at $\mathbf{p} = 0$ is followed by only maxima anywhere else at small $\mathbf{p}$, (iii) a (3, +1) saddle at $\mathbf{p} = 0$ is followed by (3, −1)'s and maxima, and (iv) a (3, +3) minimum at $\mathbf{p} = 0$ implies the presence of all other CPs as well.

The molecular geometries of the systems investigated in the present work were optimized at the Hartree−Fock level of theory for the basis 6-311++G(2d, 2p), using the Gaussian 98 suite of programs.[28] The wave functions at the optimized geometry were used for evaluating EMD on a 3D grid using the property evaluation and visualization packages INDPROP[29] and UNIVIS-2000.[30] To assess the role of correlation on EMD, a few molecules were also treated by density functional theory. Mapping of the CPs was done using an algorithm[31] developed in our laboratory.

Partitioning of EMDs into Atomic Contributions.[32] A further analysis is provided by a Hirshfeld *Stockholder partitioning*[31] of the EMD into atomic contributions. The partitioning is carried out by evaluating the atomic contribution as $\gamma_A(\mathbf{p}) = [\gamma_A{}^0(\mathbf{p})/\Sigma_A\, \gamma_A{}^0(\mathbf{p})]\gamma(\mathbf{p})$ where $\gamma_A{}^0(\mathbf{p})$ is the momentum density of the free atom, $\gamma_A(\mathbf{p})$ is the Hirshfeld EMD,and $\gamma(\mathbf{p})$ is the total molecular EMD. The Hirshfeld charges are evaluated by integrating $\gamma_A(\mathbf{p})$, and the local kinetic energy contribution is estimated as $T_A = {}^1/_2\int p^2\, \gamma_A(\mathbf{p})\, d^3p$ using the numerical integration routine CUBINT.[33] The atomic wave function of the atom A in its ground state has been evaluated by keeping the positions of all atoms in the molecule fixed and setting the nuclear charges of the other atoms to 0 during the self-consistent calculation in GAUSSIAN 98.[28] Such a wave function evaluation for the free atom has been done in the spirit of Boys−Bernardi counterpoise correction for evaluation of basis set superposition error.[34] This wave function is subsequently employed to evaluate the EMD for the free atom in its ground state using the package INDPROP.[29]

Results

The EMD of the strained systems are examined with respect to an unstrained reference which has the same molecular formula. Table 1 lists the EMD values at $\mathbf{p} = 0$. Cyclopropane, a classic case of a strained system, with bent "banana bonds" reveals a maximum at $\mathbf{p} = 0$. It is conjectured that the presence of a strict (3, −3) maximum at $\mathbf{p} = 0$ (see Figure 1) is the first evidence of molecular strain. Its unstrained reference, which is a structural isomer, viz. 1-propene has lower energy with a (3, −1) CP at $\mathbf{p} = 0$ with the density itself being lower in comparison with cyclopropane.

A similar trend is observed for all the strained systems studied here. Generally, the EMD of a strained system is noticed to tend toward a maximum at $\mathbf{p} = \mathbf{0}$ along with an increased function value when compared to the unstrained isomer. This criterion may be taken as an indicator of molecular strain. The spherically averaged momentum densities, which have a direct connection with gas phase momentum density measurements, show a similar trend of increasing value and exhibiting the nature of a maximum, the only exception for this being cyclobutane which has a lower value at $p = 0$ when compared to 1-butene. It may be noted here that certain features of the

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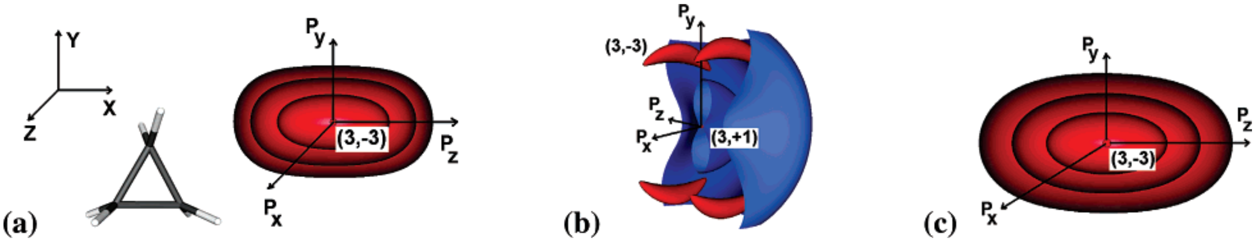

Figure 1. (a) Total EMD of cyclopropane with a (3, −3) at $\mathbf{p} = 0$. Isosurface values: 2.949, 2.994, and 3.042 a.u. (b) Hirshfeld EMD of the carbon in cyclopropane; blue isosurface of 0.468 a.u. at (3, +1) saddle value and four lobes (red, 0.479 a.u.) enclosing four maxima. (c) Hirshfeld EMD of the hydrogen in cyclopropane; red isosurfaces of 0.257, 0.267, 0.274 a.u., enclosing a maximum at $\mathbf{p} = 0$.

Table 1. Actual Molecular EMD at $\mathbf{p} = 0$, $\gamma(0)$ and Spherically Averaged Momentum Density at $\mathbf{p} = 0$, $\gamma(0)^a$

system	$\gamma(0)$ [S]	$\gamma(0)$	unstrained ref	$\gamma(0)$ at $\mathbf{p} = 0$	$\gamma(0)$
cyclopropane	3.076 [−3]	1.55 (max)	1-propene	3.013 [−1]	1.51 (min)
prismane	4.457 [−3]	2.23 (max)	benzene	4.117 [+3]	2.06 (min)
cyclopropene	2.690 [−1]	1.34 (max)	allene	2.454 [+1]	1.13 (min)
cyclobutane	3.895 [−3]	1.95 (max)	1-butene	4.021 [−1]	2.01 (max)
cubane	5.687 [−3]	2.84 (max)	styrene	5.532 [−1]	2.77 (min)
tetrahedrane	3.164 [−3]	1.60 (max)	butatriene	2.897 [+1]	1.40 (min)
[1,1,1]-propellane	4.324 [+1]	2.11 (max)	cyclopenta-1,3-diene	3.831 [+1]	1.92 (max)
bicyclobutane	3.525 [−3]	1.78 (max)	1,3-butadiene	3.504 [+1]	1.63 (min)
N_4 (tetrahedral)	2.229 [−3]	–	N_4 (planar)	2.190 [−1]	–

[a] The type of criticality denoted by S is given in square brackets: +3 denotes a strict minimum; +1 and −1, the saddles; and −3, a strict maximum. See Methodology section for details.

Table 2. Hirshfeld Charges $N_A = \int \gamma_A(\mathbf{p})\, d^3p$ and Local Atomic Kinetic Energies $T_A = {}^1/_2\int p^2 \gamma_A(\mathbf{p})\, d^3p$ of the Strained Systems and the Unstrained References^a

system	N_A	T_A	reference	N_A	T_A
cyclopropene	6.1153	37.8192	allene	6.1125	37.8413
	6.1146	37.8152		6.1123	37.8453
	0.9138	0.5940		0.9157	0.5837
	0.9137	0.5945			
			propene	6.1422	37.8096
				6.1430	37.8108
cyclopropane	6.1607	37.7729		6.1432	37.8116
	0.9197	0.6088		0.9286	0.6079
			1-butene	6.1499	37.8062
				6.1500	37.8063
cyclobutane	6.1664	37.8015		6.1511	37.8082
	0.9168	0.6137		6.1513	37.8091
				0.9247	0.6099
				0.9248	0.6100
prismane	6.0980	37.8064	benzene	6.0876	37.8362
	0.9020	0.6174		0.9123	0.6145
[1,1,1]-propellane	6.1146	37.8213	cyclopenta-1,3-diene	6.0856	37.8321
	6.1111	37.8195		6.0912	37.8401
	0.9056	0.6008		6.0914	37.8401
				0.9249	0.5992
bicyclobutane	6.1240	37.8389	1,3-butadiene	6.1123	37.8450
	6.1240	37.8398		6.1105	37.8448
	0.9173	0.5936		0.9257	0.5924

[a] See text for details.

3D momentum density distribution are lost on spherical averaging. Cyclobutane in its 3D momentum density distribution does possess a strict maximum at at $\mathbf{p} = \mathbf{0}$ which is greater than that of 1-butene which has a (3, −1) saddle at $\mathbf{p} = \mathbf{0}$ at 2.01 a.u. thus fulfilling the aforementioned criterion. It has been observed before that the nature of the momentum density distribution does not qualitatively change with higher basis and better level of theory.[35a] A further evidence is given for this via calculations of cyclopropane, cyclopropene, and tetrahedrane and their unstrained references. For this purpose, test calculations have been performed at density functional level of theory employing the Becke 3 parameter exchange and Lee, Yang, Parr (B3LYP)[28] correlation functional. The values of EMD at $\mathbf{p} = \mathbf{0}$ are seen to increase with the type of CP remaining unchanged. The values of $\gamma(\mathbf{0})$ in a.u. turn out to be (3.431, 3.149), (2.830, 2.530), and (3.327, 2.999) for the pairs (cyclopropane, 1-propene), (cyclopropene, allene), and (tetrahedrane, butatriene), respectively. Thus, the criteria for molecular strain are seen to hold true even on the inclusion of correlation.

An indication of solid-state effects may be brought out by a model calculation for oligomers of a weakly interacting system. We have examined the cyclopropane dimer to understand the effects of weak intermolecular interactions on EMD. The

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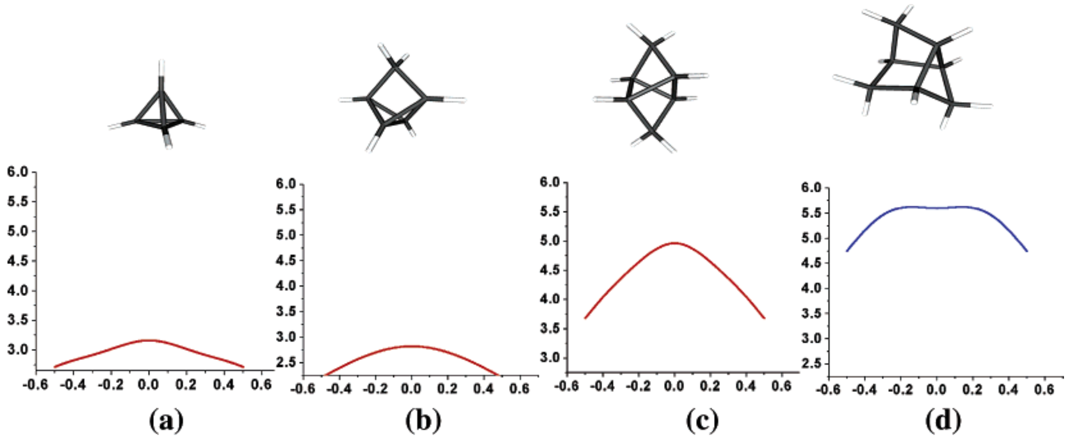

Figure 2. (a) Momentum density (in a.u.) of tetrahedrane along the p_z axis. Parts b, c, and d show the variation of the density for the same axis for a single, two, and three CH_2 insertion(s), respectively.

cyclopropane dimer EMD has a maximum (3,−3) CP at $\mathbf{p} = 0$ (EMD value 6.142), with the topography not changing for the dimer as compared to the noninteracting dimer (twice the monomer value) which has a maximum of 6.152 a.u. Including correlation effects at B3LYP/6-311++G(2d, 2p), the same trends are observed with the EMD values just increasing for the interacting (6.462 a.u..) and noninteracting system (6.447 a.u.). Water dimer also shows similar features, with its topography being similar to that of the monomer. A further detail on the nature of the momentum densities of strained systems/ unstrained references is clearly brought out by a Hirshfeld partitioning in momentum space.[32] The Hirshfeld charges and the partitioned local kinetic energies of the atoms are given Table 2.

It is clear that for all the strained systems the carbon atoms are *more populated* in comparison with those in the corresponding unstrained reference. At the same time, the hydrogens of the strained systems lose an amount of their density due to the strain and are rendered *less populated* in comparison with those in the reference molecules. It is generally known that the highly strained species such as cyclopropane and the caged tetrahedrane are more acidic than the corresponding less strained species, and this is seen from the depleted densities of hydrogens. The local kinetic energies of all the atoms of the strained systems are lower than those in the corresponding unstrained reference, which may be heuristically expected from the virial theorem since the electronic energies of the unstrained references are lower.

Furthermore, a comparison of the Hirshfeld charges of the atoms in momentum space for the strained systems within themselves shows a trend, which is as follows. Within the strained systems, the carbons become less negative as strain increases and the hydrogens become more positive. An examination of the bicyclobutane strained isomers methylcyclopropene and methylenecyclopropane which are decreasingly strained show the same trend with the carbon populations being 6.138 and 6.146, respectively. The values are seen to reflect the trend in the experimental strain energies.[22a] This is as expected since the greater the strain energy, the less bound is the atom and the more similar it is to a free atom. For instance, cyclopropene carbons have a population of 6.101 in comparison to the 6.161 Hirshfeld populations for cyclopropane. The experimental strain energies for cyclopropene and cyclopropane are 55.5 and 27.5 kcal/mol, respectively.

To summarize, the effects of ring strain are manifest in the momentum densities as follows. (i) The momentum density at $\mathbf{p} = \mathbf{0}$ is larger in magnitude for the strained system with the distribution tending to a maximum at low momenta. (ii) A partitioning of the total distribution into atoms reveals that the carbons accumulate more density in comparison with the unstrained reference and the hydrogens are more positive. (iii) Within the strained systems, the carbons become less negative with increasing strain. (iv) The spherically averaged values also seem to indicate a crowding of the density around $\mathbf{p} = \mathbf{0}$, although there is a loss of information on spherical averaging.

Discussion

The results of the present study pave the way for making a working hypothesis that the information in EMD at and around zero-momentum carries an effect of molecular strain. There exists adequate experimental evidence pointing to this inference. The results of EMS experiments on the strained systems such as cubane,[16] propellane,[15] norbornane,[17] and cyclopropane[18] highlight the peaks at small momenta in the spherically averaged densities of the individual orbitals. The EMDs of the individual orbitals when summed up yield the total molecular EMD. Thus, a peak in such a spherically averaged total EMD at $\mathbf{p} = 0$ is in conformity with our result. Furthermore, the long tail in the coordinate space densities has been observed by Penning ionization spectroscopy of cyclopropanes,[36] wherein the kinetic energy distributions have been analyzed by using noble gases as projectiles. The work gives evidence for the long tail in the density of cyclopropane in the plane of the ring.[36]

One may seek physical arguments as to why such build-up of density at low momentum values is a pointer to ring strain. Strain, as seen from position space, is evidenced in the form of bent bonds in the charge density. This closely connects with Baeyer's classical definition[19] of molecular strain. A bond in Bader's concept of AIM is characterized by a path of maximum electron density that passes through a (3, −1) criticality.[21] When the path is bent as seen in the case of strained systems, the maximum density is actually concentrated along a low potential region as compared to the case of an unstrained system where the path almost coincides with the internuclear axis which is a region of higher potential. This depletion of charge density from the bonding region results in a buildup of charge density in the

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long range. A corroborative evidence for this is supported by the topographical features of MESP of strained systems. Both tetrahedrane and cubane show low-valued (3, −1) CPs at large distances (8 and 13 a.u., respectively, from the center of mass).[31,37]

To reconfirm that the topographical feature of a strict maximum at $\mathbf{p} = \mathbf{0}$ in tetrahedrane and cubane is indeed due to strain, we have analyzed some more systems by inserting $-CH_2$ groups for the edges (C−C single bonds). For tetrahedrane, the EMD shows a change in criticality at $\mathbf{p} = \mathbf{0}$ for three $-CH_2$ insertions, i.e., the maximum at $\mathbf{p} = \mathbf{0}$ changes to a (3, −1) CP of EMD value 5.43 a.u. (2.92 on a normalization to 28 electrons as in tetrahedrane) which is lower in the hierarchy. Figure 2a displays the EMD for tetrahedrane along the p_z axis. It is seen that there is a subsequent decrease in EMD (2.25 a.u. normalized to 28) when a strain releasing $-CH_2$ group is inserted [cf. Figure 2b]. The nature of the criticality at $\mathbf{p} = \mathbf{0}$ itself changes to a minimum (2.77 au normalized to 28) in the p_z direction when three sides of tetrahedrane are strain-free by the substitution [cf. Figure 2d]. The nature of change in the criticality of EMD has a resemblance to the behavior of a function $f(x) = x^4 + ax^2 + bx$ as can be seen in Figure 2d. The change in the topography here is in general characterized by a cusp catastrophe according to catastrophe theoretic analysis, the details of which may be found elsewhere.[4,21,26] A similar analysis has also been done for cubane which yielded a change in the topography at $\mathbf{p} = 0$ for the first $-CH_2$ substitution itself. This behavior is also observed for the highly strained N_4 and N_8 systems on substituting the edges by −NH. It is indeed worthwhile noting that the EMDs of the strained systems could all exhibit the same qualitative behavior on parametrically releasing the strain.

Concluding Remarks

The molecular electron momentum densities have been elusive in their interpretation for a chemist. Apart from Coulson's work[3] and its extensions, a close connection for momentum density with chemistry has, in general, been conspicuous by its absence from the chemical literature. The advents in experimental techniques such as EMS, (e, 2e) and (e, γe) methods bring forth direct momentum density measurements warranting that a chemical interpretation of EMD has to come forth. We believe that the current work is an attempt in this direction. It is indeed worth noting that strained molecules, curiously, have attracted the attention of experimenters employing EMS.[15−18] The present work has attempted to establish a connection between the nature of the EMD at $\mathbf{p} = 0$ and ring strain. A concise statement of the results would be as follows: a buildup of the momentum density at low $|\mathbf{p}|$ values implies that the system is strained. It has been observed that an atomic partitioning of the EMDs through a Hirshfeld stockholder partitioning also reveals strain in the system. Analyzing the Hirshfeld contributions, it is noticed that the charges of the constituent atoms increase when compared to a strain-free isomer. The atoms in the strained molecules also tend to resemble "less bound" free atoms with increasing strain, the hydrogens being more acidic and decreasing kinetic energies for all the atoms. Further investigations on the Hirshfeld partitioning in momentum space are currently under way in our laboratory. Rich treasures of such basic chemical concepts buried in momentum space need a further in-depth exploration and exposition.

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Supporting Information Available: Complete reference 28. This material is available free of charge via the Internet at http://pubs.acs.org.

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