Influence of the substitution on the inversion barrier of corannulene: a theoretical study.

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1. Introduction.

Since the discovery of fullerenes contemporary chemists have been stimulated to investigate properties of this promising class of compounds.[1] The attempts to achieve the synthesis of C_{60} have opened an exciting area in the synthetic organic chemistry in the form of buckybowl chemistry.[2] A large number of interesting bowl-like structures, also known as "geodesic polyarenes", that can be mapped on the C_{60} molecule, have been synthesized and were shown to exhibit interesting structural, chemical, and physical properties.[3] In that way, the interest in the science of these nonplanar π-conjugated carbon molecules, including C_{60}, carbon nanotubes and molecular bowls, has greatly expanded due to their potential for application in interdisciplinary fields such as electrical materials science, catalysis, and pharmaceutics.[4]

The structures of such molecular bowls are expected to be quite rigid. Nevertheless, the smaller members of the family, in spite of its substantial curvature are surprisingly flexible undergoing rapid bowl-to-bowl inversion in solution as evidenced by the dynamic NMR behavior of $C_{20}H_{10}$ (**1** = corannulene) and several of its derivatives. This inversion process is represented in Fig. 1, highlighting the transformation of the curved molecule in a planar transition state as well as the energy barrier associated to the inversion process. Scott and coworkers demonstrated for the first time that the bowl-to-bowl inversion of a mono-substituted corannulene derivative occurs rapidly with an activation barrier of 10–11 kcal/mol.[5] Further elaboration of the structure gave more detailed insight into the inversion dynamics, for example, the introduction of a rigid five-membered ring to the rim of corannulene was found by Sygula and coworkers to slow the inversion.[6] Siegel and coworkers investigated the relationship between the inversion energy barrier and the bowl depth.[7] In the same direction, the synthesis and inversion process of heterobuckybowls (C_{60}-related molecular bowls with some of its carbon atoms replaced by O, N, S or P) was investigated by Priyakumar and Sastry finding trends similar to the ones of its parent systems.[8]
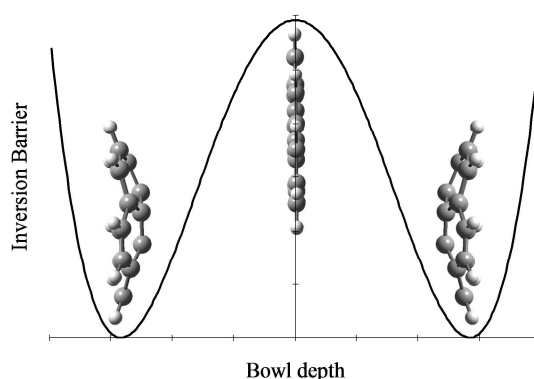
Fig. 1. Energy diagram of the inversion process of corannulene. The structures of the bowl-shaped minima and the planar transition state are showed.

Computational chemistry plays a fundamental role in understanding and modeling the novel properties of buckybowls complementing and sometimes guiding the work of the experimentalists. This tool achieves more importance in the studies of the inversion process of molecular bowls because the experiments by the NMR technique are limited to molecules with atoms that undertake a diasterotopic–enantiotopic conversion during the bowl inversion. With the aim of gaining understanding in this subject, we performed this theoretical study as an exploration of the effect that substitution of some of the hydrogen atoms has on the bowl-to-bowl inversion of corannulene derivatives applying DFT methods to model systems with the formula $C_{20}H_{10-n}R_n$ with n = 0, 2, 4, 5, 6, 8, and 10. The homogeneous and gradual substitution of the hydrogen atoms by different "R" groups, allow the analysis of structurally related families testing the structure–energy relationships previously applied to heterogeneous groups of compounds.
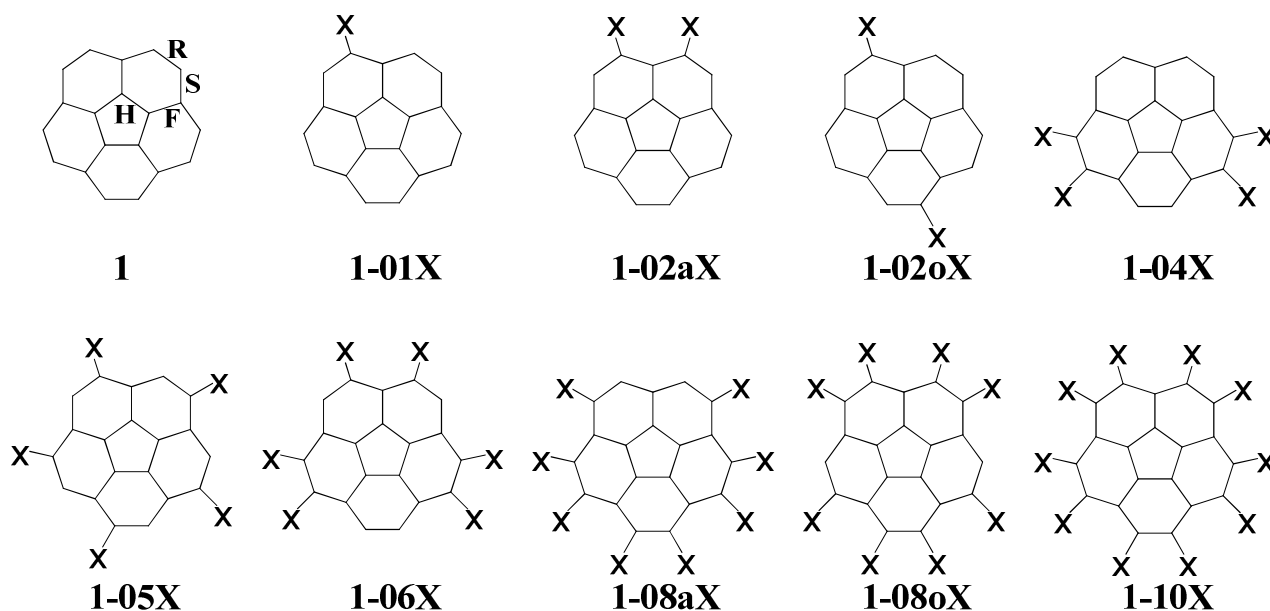

| 1 | 1-01X | 1-02aX | 1-02oX | 1-04X |
| 1-05X | 1-06X | 1-08aX | 1-08oX | 1-10X |

Fig. 2. Corannulene (**1**) and the corannulene substitution pattern studied in this work (hydrogen atoms were omitted for simplicity). Rim (**R**), Spoke (**S**), Flank (**F**) and Hub (**H**) bonds of corannulene are identified in **1**. In the labels of the structures, the "X" is replaced by a letter that stands for the nature of the substituent: **A** = –C≡CH, **B** = –Br, **C** = –Cl, **M** = –CH$_3$.

2. Computational Details.

Carbon-carbon bonds in **1** are conveniently classified as Rim, Flank, Hub, and Spoke (see the labels of **1** in Fig. 2). The hydrogen atoms attached to the rim of **1** were progressively substituted by chlorine, bromine, acetylene or methyl groups, conforming families of derivatives which structures are shown in Fig. 2. Not all positions were explored with all the substituents and mixed substitution was not considered.

The geometries of the bowls and the corresponding structures of the transition states were optimized at various levels of theory using the Turbomole[9] and Gaussian09[10] Quantum Chemistry program packages. Different DFT methods (B3-LYP, B-LYP and PBE) with double and triple-zeta plus polarization basis sets were employed in all of the calculations. With pure functionals the resolution of the identity (RI) approximation was utilized. In the optimized structures of the minima the depth of the bowls (**h**) was measured as the distance from the center of the bottom plane to the center of the plane defined by de carbon atoms of the rim (see the example shown in Fig. 3). As another parameter for describing the geometry of the bowl the mean value of the hub-hub-flank dihedral angles (**D**) were calculated as well. Frequency calculations were used for characterizing the transition states and inversion barriers (**ΔEinv**) were computed as the electronic energy difference between the transition state and its corresponding minima.
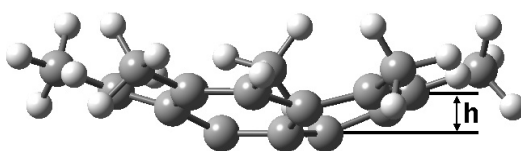

Fig. 3. Definition of the bowl depth using the example of **1-05M** (corannulene with five hydrogen substituted symmetrically by methyl groups).

3. Results and Discussion.

Table 1 presents values of the geometric parameters and the inversion barrier for **1** obtained at different levels of theory. It is observed a minor dependence among the method/basis set used, mainly in the bowl depth that give values similar to the experimental (0.872 Å) measured by X-Ray Diffraction. The more deviated **h** value is the one calculated using aug-cc-pVDZ basis set but even in this case the overestimation represents only 4 % of the experimental value. The inversion barrier values are a little below of the 11.5 kcal/mol reported by Seiders et al.[7] that estimate the height of the inversion barrier by extrapolating the results of dynamic NMR measurements made using corannulene derivatives with two substituents in opposite positions (the same structure of **1-02oX** in Fig. 2). Such extrapolation is based on the following approximation: if the substituents don't interact directly, their influence on the value of the barrier in not significant.

Table 1. Geometric parameters and inversion barrier computed at different levels of theory for corannulene.

	B3LYP/ TZVP	BLYP(RI)/ TZVP	BLYP(RI)/ aVDZ	PBE(RI)/ TZVP
D	152.8	153.0	152.6	152.3
h	0.888	0.887	0.909	0.887
ΔEinv	10.92	10.84	11.03	11.22

D = average hub-hub-spoke dihedral angle (º); **h** = Bowl depth (Å); ΔEinv = Inversion barrier (kcal/mol).

The different levels of calculations were explored more extensively using the family of Br-substituted corannulenes and the results of these calculations are presented in Fig. 4. Again it is observed that the bowl depth is a little overestimated in the calculation with the aug-cc-pVDZ basis set, result that extends regularly from $n = 0$ to $n = 5$. All the levels of calculation show that when the substituents don't interact ($n = 1$, 2o, 4 and 5, following the pattern of Fig. 2) the substitution level has minor effects in the bowl depth. On the contrary, all the levels of theory show that only two substituents in adjacent positions (2a) are enough to decrease the depth of the bowl in a significant amount. When $n \geq 6$ the geometry of **1** forces the substitution in adjacent positions and **h** decreases more rapidly than for $n \leq 5$. That points to the repulsion between the peripheral substituents as the main cause of the shallowing of this family of compounds.
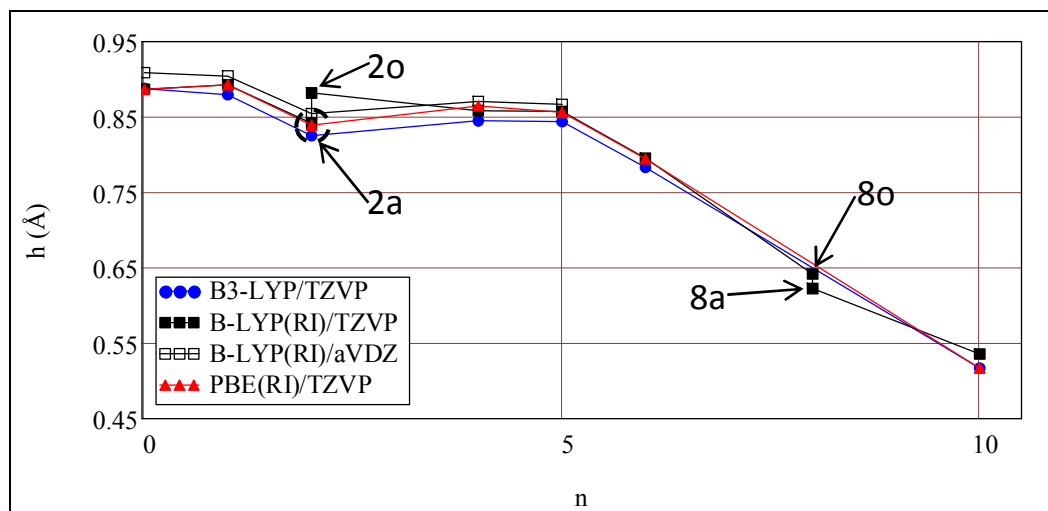

Fig. 4. Bowl depths for the Bromo-derivatives of corannulene ($C_{20}H_{10-n}Br_n$) with different values of **n**, calculated at various levels of theory. The distinction between "a" and "o" structures for $n = 2$ and $n = 8$ is explained in Fig. 2.

During the inversion process, the transformation of the bowl into the transition state structure is accompanied by a certain distancing of the substituents, so the repulsion becomes important only at high substitution levels. In the cases studied here, when $n = 6$ the substituents are grouped in couples, separated from the other couples by one or two hydrogen atom that reduces the peri-repulsion. Following this substitution pattern the geometry of the transition state remains planar for all the cases with $n < 8$. The structure of the transition states corresponding to $n = 8$ deviate from planarity mainly because the Br atoms move out of the plane whether they are separated into two groups of four (**1-08oB**) as if they are all next to each other (**1-08aB**). On the other hand, in the transition state for the inversion of **1-10B** the deformation not only affects the Br but propagates to the carbon atoms network as well (see Fig. 5). This indicates that when the peri-repulsion is important the inversion is achieved deforming progressively the structure of the bowl. In other case the inversion moves all the carbon atoms in the same direction passing across a planar transition state.
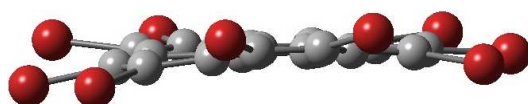

Fig. 5. Side view of the transition state for the inversion of **1-10B**.

The influence of the substitution on the inversion barrier calculated with different DFT methods and the TZVP basis set is presented in Fig. 6. The numerical differences among the calculations levels used are minor and all the results show similar tendencies. For $n = 0$, 1, 2o, 4 and 5, the increasing substitution has a gradual but little effect on the inversion barrier. When two

Br are in opposite positions of the corannulene molecule (**1-02oB**) the inversion barrier diminish in less than the 5 % respect the value presented by **1**. This support the above mentioned approximation used by Seiders and other experimentalist in the estimation of the inversion barrier of corannulene.[7] Nevertheless, care must be taken because the effect is no completely negligible and bigger changes could be observed with other substituents. Comparing with the barrier of **1-02oB** if the two Br atoms are in adjacent positions (**1-02aB**) the inversion barrier decreases in a 20 %. Proportionally, this effect on the energy barrier is two orders of magnitude bigger than the relative change in the bowl depth observed between **1-02aB** and **1-02oB**. The geometry of the transition state is planar for the inversion of both of these molecules, so the big change observed in the inversion barrier should be attributed mainly to the modifications in the bowls. In other words, small structural changes of the ground state translate into pronounced changes in the inversion rates, regularity detected in the dynamics of other systems.
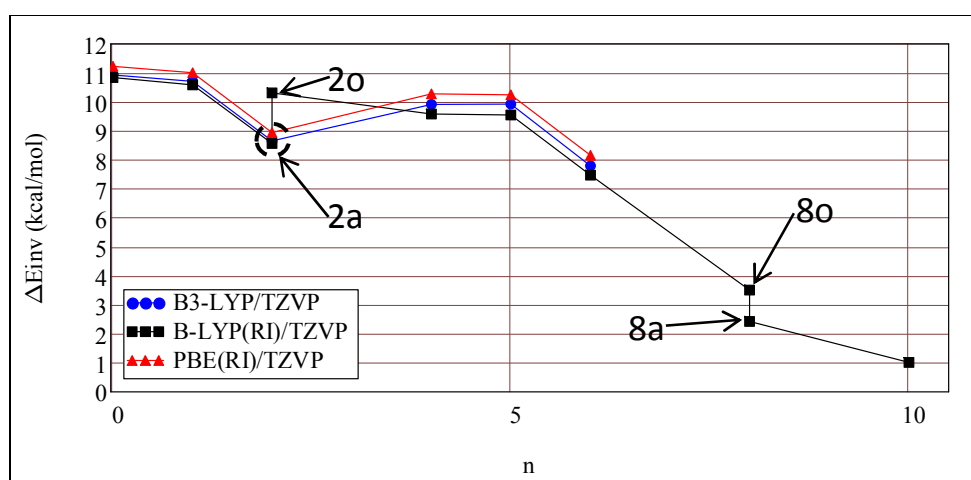

Fig. 6. Inversion barrier for the Bromo-derivatives of corannulene ($C_{20}H_{10-n}Br_n$) with different values of **n**, calculated at various levels of theory (only the results calculated with the TZVP basis set are showed).

For substitution levels beyond symmetrically distributed n = 5 (were the substituents are separated by one hydrogen atoms), the repulsion reflects in proportionally big changes in the inversion barrier. The slope of the tendencies plotted in Fig. 6 increases markedly in the interval 5 < n ≤ 10 compared with the slope observed when n = 0, 1, 2o, 4 and 5. Comparing the two corannulene with eight Br, the higher repulsion present in **1-08aB** causes a lowering of the inversion barrier of almost a 31 % comparing with **1-08o**. The complete substitution (**1-10B**) reduces the barrier in more than the 90 %, relative to the inversion barrier of **1**. Proportionally this effect in the energy barrier is much more intense than the observed in the geometry of **1-10B** which depth is reduced only a 40 %, compared with the bowl depth of **1**. In general is observed that low changes in the geometry of the bowls conduce to comparably high variations in the inversion barrier.

$$\Delta E_{inv} = a \cdot h^4 - b \cdot h^2 \qquad (\textbf{Eq. 1})$$

The correlation between the bowl depth and the inversion barrier is observed systematically in all the family of substituents, as can be seen in Fig. 7. The main tendency is followed by all the substituents studied but some differences between families are appreciable mainly at high substitution levels (the region of the plot corresponding to low inversion barrier and bowl depth). This observation suggests an independent analysis for the different series of substituents. Previous studies indicate that a mixed quartic-quadratic function (Eq. 1) models satisfactorily the structure-energy relationship in a number of systems similar to the molecular bowls studied here. Particularly, this equation has been proved with corannulene derivatives as well as

heterosumanenes[7,8,11] but in all the published studies the data used is composed by molecules with some degree of structural diversity. Variation of bowl depth in the series of corannulene derivatives considered in the present work provides an opportunity to examine the structure and inversion barrier relationship on various series with homogeneous substituents.
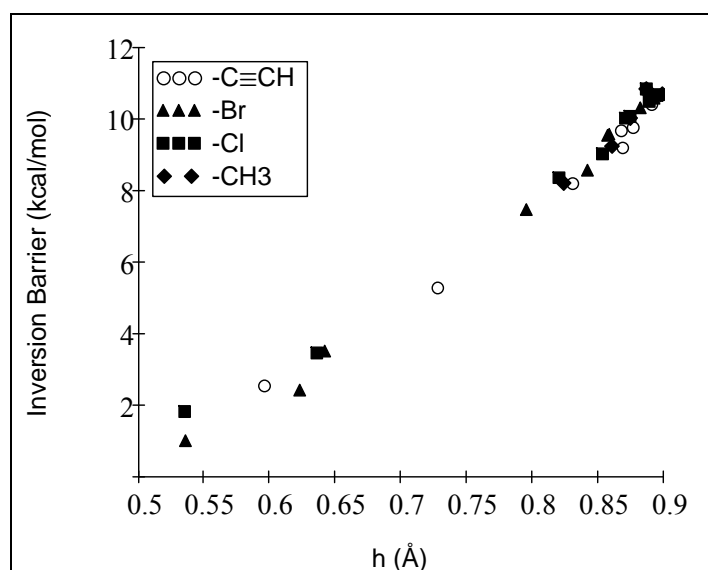

Fig. 7. Relationship of the bowl depth with the inversion barrier calculated at the B-LYP/TZVP level of theory for the substituted corannulenes.

Similar to previous studies, a mixed quartic-quadratic function successfully describes the ΔE_{inv} – h data, as can be seen in Fig. 8 where the result for the Br-substituted corannulene series is showed. As usual in this kind of study, before the analysis the data is normalized to a common value of the transition state energy. The fitting is applied to the original data set for each series with the same substituent but in the plot the points representing the minima are replicated in order to describing the double-well curve for the bowl-to-bowl inversion of any particular molecule.
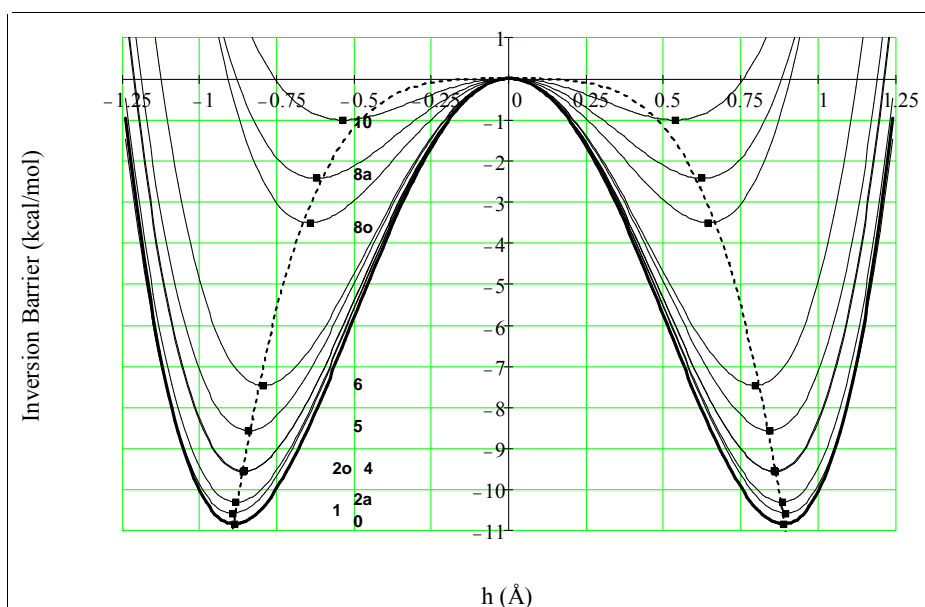

Fig. 8. Structure-energy correlation of the inversión barrier versus bowl depth calculated at the B-LYP/TZVP level of theory for the Bromo-substituted corannulenes. The labels in the graph stands for the substitution pattern (see Fig. 2). The data were normalized to a common value for the transition state energy. Continuous lines are the double well that describes the inversion process and the dotted line is the graph of the quartic-quadratic function fitted to the points.

Even being an empirical equation, Eq. 1 provides a nice description for the dynamic behavior of the bowl inversion process covering the complete interval of substitution of corannulene. Analogous representations, all with good fitting results, are achieved with the data acquired in the studies of the -Cl, -Methyl- and -Acetilene series. The values of the coefficients "a" and "b" resulting in the corresponding fittings are collected in Table 2. There seems to be no direct dependence between the values of the coefficients and the size of the substituents. It is observed that both coefficients vary in dependence of the nature of the substituent that defines the series. This result contradicts the Seiders' conclusion[7] about that in these structure-energy relationships "a" should be constant between derivatives.

Table 2. Values of the coefficients of the equation $\Delta E_{inv} = a \cdot h^4 - b \cdot h^2$ fitted to the inversion barrier – bowl depth data (calculated at the B-LYP/TZVP level of theory) for the different series studied in this work. The rows are in crescent order of the van der Waals radii of the substituents cross section. Np in the last column is the number of points used in each fitting.

Substituents	a	b	Np
$-C\equiv CH$	-13.30	2.65	9
$-Cl$	-12.85	3.31	9
$-Br$	-16.50	0.62	10
$-CH_3$	-11.52	4.22	6

4. Conclusions.

The influence of substitution on the structure and inversion barrier of molecular bowls has been studied theoretically. Corannulenes progressively substituted by different groups conforming homogeneous series were used and as model systems. Equivalent tendencies with only small numerical discrepancies were observed between the results calculated by different DFT methods mainly when combined with the TZVP basis set. The repulsion among the peripheral groups reduces the depth of the corannulene core as well as the value of the energy barrier related to the bowl-to-bowl inversion process. High substitution levels (more than five substituents) are needed for affecting appreciably both, the bowl depth and the inversion barrier. It is observed that when the peri-repulsion is important the inversion is achieved deforming progressively the structure of the bowl. Proportionally, the influence of the substitution is more intense in the inversion barrier than in the bowl depth (small molecular changes are reflected in wide energetic effects). A clear correlation between the bowl depth and the height of the inversion barrier is hold for all the studied series and the dependency follows a quartic-quadratic function. The data of each substitution series were fitted separately using this function with very good results. The values of both of the fitted coefficients depend on the nature of the substituent that defines each series, contradicting the tendency proposed in previous studies where the same equation was applied. The fitting coefficients don't seem to follow a direct relationship with the van der Waals radii of the groups. Systematic study of the differences in bowl depth – inversion barriers among corannulene derivatives can serve as a way to estimate steric or electronic aspects of molecular recognition normally dealt with in biochemistry and supramolecular chemistry.

5. References.

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