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Letter to the Editor

Comments on “Shape-selective diisopropylation of naphthalene in H-mordenite: Myth or reality?”

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ABSTRACT

Recently, the reaction system of isopropylation of naphthalene over USY and H-mordenite zeolites was comprehensively treated experimentally as well as computationally by Buijs et al. [1]. Results from both sources were used to discard shape selectivity as an explanation for the observed product distribution. In this contribution, it is shown that their computational argument cannot be used for this purpose, since after the improvement of their orthogonal projection method, it gives very similar results to those criticised in their paper.

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In a very recent paper, Buijs et al. [1] set out to clear up the chemical events occurring during the isopropylation of naphthalene in USY and H-mordenite. The reaction chosen for experimental and computational scrutiny is an important one, since 2,6-diisopropylnaphthalene can be an important intermediate in the way of producing 2,6-naphthalene dicarboxylic acid. The experimental treatment of this complex reaction system stirred much controversy in recent years, especially because of the ambiguity in the analysis of the reacting mixture [2]. A continuous improvement in the analytical method changed or at least modified the interpretation of the experimental findings [3]. In the paper, being commented the analytical technique was superb; thus, no one has any reason to doubt the validity of the experimental results obtained. Furthermore, the whole experimental work, not just the analytical part, is quite comprehensive and very convincing. Obviously, the results provide more than adequate ammunition for meaningful and detailed rationalisation of the entire reaction system.

However, the computational part of the paper is a somewhat different matter. The authors have chosen the B3LYP/6-31G* method for the full geometry optimisation of the possible diisopropylnaphthalene (DIPN) isomers and calculated the isomer composition at thermodynamic equilibrium at 200 °C. They have related these results to their experimental findings and to the calculated composition based on fully optimised geometric data computed at MP2(full)/6-31G* level at 25 °C published in one of our earlier papers [4]. They claimed that contrary to our results (we have stated that 2,6-DIPN is smaller than 2,7-DIPN; thus, it fits better to the main channel of H-Mordenite), the dimensions of 2,6-DIPN were equal to those of 2,7-DIPN. Since a complete set of geometric data on the isomers is not published in the commented work (only those of 2,6-DIPN and, of course, those of 2,7-DIPN being equal with those of 2,6-DIPN are communicated), after the appearance of the manuscript in the ScienceDirect database, we have asked the authors about the geometries of the isomers and the method of obtaining molecular dimensions. They were kind enough to provide with the geometries as well as the way of obtaining the dimensions. The latter was as follows: after geometry optimisation (and checking whether it was a minimum or not), the molecule was orthogonally projected, and dimensions and the cross-section dimensions were measured with a ruler. The geometries received from the authors allowed us to cross-check our results. We have found that applying our method [4] for determining molecular dimensions for the most stable conformers (3D grids consisting of 400 × 400 × 400 points were taken around each molecule, the electron density was calculated, and for each conformer, a sequence of molecular shapes and dimensions was generated using a set of cut-off values {0.0005, 0.001, 0.002, 0.003, 0.004, 0.005}), but using the B3LYP/6-31G* method for electron density calculations, gave nearly identical results to our previously published data (compare MP2^a and B3LYP^b data in Table 1).

The minor differences experienced for 1,2 and 1,4 isomers may be accounted for easily. For these molecules, the most stable con-

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Table 1
Molecular dimensions (*x*, *y*, *z*, in angstroms) of the most stable conformers of the DIPN isomers at various levels of theory.

Isomer	MP2[a]			B3LYP[b]			B3LYP[c]		
	x	*y*	*z*	*x*	*y*	*z*	*x*	*y*	*z*
1.4	6.22	9.46	12.05	6.48	9.63	12.19	6.52	9.60	12.17
1.5	6.45	8.78	12.44	6.50	8.79	12.47	6.51	8.86	12.45
1.8	6.59	9.99	10.16	6.64	9.99	10.19	6.66	10.00	10.19
1.2	6.95	8.72	11.69	6.88	9.47	11.33	6.88	9.36	12.01
1.3	6.89	10.51	10.59	6.96	10.56	10.65	6.99	10.00	11.80
1.6	6.81	8.10	13.17	6.80	8.11	13.22	6.88	8.10	13.22
1.7	6.87	8.96	11.84	6.86	8.99	11.88	6.92	9.06	11.87
2.3	6.76	9.86	11.25	6.78	9.89	11.29	6.80	9.75	11.89
2.6	6.61	6.61	14.23	6.60	6.60	14.30	6.60	6.63	14.34
2.7	6.62	7.26	13.76	6.63	7.29	13.81	6.68	7.32	13.81

[a] Original method at the MP2/6-31G* level of theory.
[b] Original method at the B3LYP/6-31G* level of theory.
[c] Orthogonal projection method of Buijs et al. [1] at the B3LYP/6-31G* level of theory.

Table 2
Molecular dimensions (in angstroms) at various cut-off values.

ρ_0/au	2,6-DIPN	2,7-DIPN
0.0005	6.94, 6.94, 14.56	6.95, 7.59, 14.09
0.001	6.61, 6.61, 14.23	6.62, 7.26, 13.76
0.002	6.28, 6.28, 13.91	6.28, 6.93, 13.43
0.003	6.09, 6.09, 13.72	6.09, 6.74, 13.24
0.004	5.96, 5.96, 13.59	5.96, 6.60, 13.11
0.005	5.85, 5.85, 13.49	5.85, 6.50, 13.01

formers at the MP2 level are not the most stable at the B3LYP level. Generally speaking, the MP2 level molecular shapes are somewhat more compact than those computed at the B3LYP level. These molecular shapes come closer to the actual ones than the B3LYP method, which is known to strongly underestimate the long-range non-bonding interactions in alkanes and aromatics [5].

Nevertheless, the B3LYP calculations combined with our previously published method described above (in the followings, it will be called the "grid method") should give nearly identical results to the orthogonal projection method, but in the hands of the authors of the commented paper, it did not. Let us show here that when an improved orthogonal projection is applied, the molecular dimensions, especially the cross-sections, become very similar to those obtained by the "grid method" irrespective whether MP2 or B3LYP calculations are performed.

The improvement is the following. The B3LYP molecular shapes obtained with cut-off value of 0.001. au using the geometries supplied to us by the authors of the commented paper were rotated around the *x*, *y*, *z* axis by 0.2 rad, and each structure was projected orthogonally onto the *x*, *y* plane. This means 27,000 orientations for each molecule. Out of these projections, the one with the smallest cross-section was chosen. The obtained data are displayed in Table 1 under the heading B3LYP^c. It is to be seen that they are practically the same as those listed under the heading B3LYP^b. This means that the "grid method" and the improved orthogonal projection method do give very similar results, just as it should be.

One more point should be emphasised. Depending on the chosen cut-off value, the sizes vary. For instance, if we choose $\rho = 0.002$ as the cut-off value, the absolute sizes will be smaller. This is the most often used value in the literature (we could have used it in our original paper as well instead of 0.001). When it is applied (Table 2), every isomer can enter the main channel of H-Mordenite; thus, the problem mentioned in the sixth paragraph of the Discussion section of the commented paper disappears and the argumentation used there loses its validity.

Nevertheless, irrespective to cut-off values used, the relative size differences remain, i.e. the cross-section of 2,6-DIPN is smaller than that of 2,7-DIPN and those of the other DIPN isomers.

In this comment, we have shown that the computational part of the commented paper gives very similar results to our previously published and criticised data, if an improved orthogonal projection method described here is used. Therefore, choosing a proper cut-off value invalidates the computational argument used against the possibility of shape selectivity. The authors still may have enough arguments based on the experimental results, but computational data certainly cannot be used for this purpose.

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