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Basis set effects on the structure of isomeric nitroanilines: the role of basis set expansion, additional diffuse and polarization functions within the frame of DFT and MP2 approaches

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Influence of the basis set on the geometrical parameters and structural aromaticity indices of isomeric nitroanilines was studied in the framework of MP2 and DFT methods (M06-2X functional). Series of cc-pV(N)Z and def2-(N)ZVP basis sets of double-ζ, triple-ζ, and quadruple-ζ quality augmented with additional diffuse and/or polarization functions were investigated. It was found that using the basis sets of double-ζ quality can be the source of the significant error in MP2 calculations. Important role of additional diffuse functions and negligible influence of additional polarization functions was shown.
Keywords: structural aromaticity indices, isomeric nitroanilines, MP2 calculation.

Влияние базисного набора на геометрические параметры и структурные индексы ароматичности изомерных нитроанилинов рассмотрено в рамках методов MP2 и DFT (функционал M06-2X). Серия дважды, трижды и четырежды валентно расщепленных базисов cc-pV(N)Z и def2-(N)ZVP, дополненных диффузными и/или поляризационными функциями, изучена в работе. Обнаружено, что использование дважды валентно расщепленных базисных наборов может быть источником существенных ошибок в расчетах методом MP2. Показана важная роль диффузных функций и пренебрежимо малая — поляризационных.

Вплив базисного набору на структуру ізомерних нітроанілінів: роль розширення базиса, додаткових дифузних і поляризаційних функцій у рамках теоретичних методів MP2 і DFT. *І.В.Омельченко, О.В.Шишкін*.

Вплив базисного набору на геометричні параметри і структурні індекси ароматичності ізомерних нітроанілінів розглянуто у рамках методів MP2 і DFT (функціонал M06-2X). Серію двічі, тричі і чотири рази валентно розщеплених базисів cc-pV(N)Z і def2-(N)ZVP, доповнених дифузними та/або поляризаційними функціями, вивчено у роботі. Знайдено, що використання двічі валентно розщеплених базисних наборів може бути джерелом суттвих помилок при розрахунках методом MP2. Показано важливу роль дифузних функцій та нехтувано малу — поляризаційних.

1. Introduction

Accurate prediction of the molecular structure is one of the most important goals of quantum chemistry [1]. The calculation method and the basis set are the two decisive factors for obtaining precise results [1, 2]. Though investigation of the structure of small molecules had been a challenge in early years of computational chemistry

[3–5], it became a routine task in last decade, with the rapid increasing of computers power and development of new theoretical methods [6]. However, calculation of the molecular properties still requires the very accurate choice of the basis set: one of the typical examples is the hyperpolarizability of the push-pull molecules [7], particularly para-nitroaniline [8, 9]. It is known that value of hyperpolarizability strongly depends on the basis and method [9, 10].

However, in the numerous studies of hyperpolarizability of para-nitroaniline, there are no consistent approach to the source of molecular geometry for this calculations. It can be fixed at the geometry obtained from the crystal [11], obtained by semi-empirical calculations [12–14], at Hartree-Fock and CPHF levels of theory with different basis sets [15, 16], and a combination of these forms [17]. Though it was known that amino group in anilines can be non-planar [18], the idea of strictly planar amino group and fixed geometry of para-nitroaniline was popular until the beginning of 2000th [19–21], of even was meant on default [22]. In last decade, the DFT methods became the "gold standard" for obtaining the structure of small organic molecules, including nitroaniline [7, 23–25]; however, MP2 theory [9] and molecular dynamics methods [26, 27] are also used. Most of the authors choose more than one basis set for calculations, but the choice is usually arbitrary [9]. One can face the same problems with calculations of the geometries of other nitroanilines with the view of molecular properties [28, 29]. Generally, authors neglect of the accurate structure of the molecule when calculating its properties, though it was shown that the geometrical parameters affect it strongly [30]. At the time, different methods give very different results: it is applies not only to the issue of amino group planarity that was mentioned above, but also to the question of the degree of push-pull polarization in the ground state of para-nitroaniline that can vary in a wide range and differ significantly from the crystal geometry [26, 31, 32].

It is known that basis set size (and presence of diffuse functions) can strongly affect molecular conformation [33, 34]. Presence of diffuse functions can therefore be essential for planar molecules. The degree of the intramolecular polarization is great in the case of donor-acceptor nitroaniline system so presence of the polarization function can also influence on its geometrical parameters. In the present paper, authors try to clarify what quality of basis set is essential and sufficient for accurate quantum chemical modeling of the geometrical parameters of isomeric nitroanilines. We were focused first of all on practically helpful results and therefore used widely implemented Dunning and Ahlrichs basis sets and commonly used MP2 and DFT (M06-2X functional) methods.

2. Methods of calculation

The structures of all molecules and molecular complexes under consideration have been optimized using the Moller-Plesset second order perturbation theory [35] and using the M06-2X method [36] with the series of Dunning-Huzinaga [37] and Ahlrichs [38] basis sets of double-ζ, triple-ζ, and quadruple-ζ quality augmented with additional diffuse (aug-prefix for Dunning sets and -d suffix for Ahlrichs sets) or polarization (core polarized pCVTZ Dunning set and -p suffix for Ahlrichs sets) functions. Para-nitroaniline (pNA) was studied with extended number of basis sets. Character of stationary point on potential energy surface was checked by calculations of Hessian at the same level of theory. No negative eigenvalues of Hessian were found for the studied species. Aromaticity was estimated with structural Bird's I_6 [39] and HOMA [40] indices calculated according to the formulas (1) and (2). Bond orders for Bird's index calculation were obtained from experimental bond lengths using the Gordy equation [41] with empirical constants. All calculation were performed using Gaussian'09 program package [42]; both built-in and external basis sets (taken from EMSL library [43, 44]) were used. Heightened integration grid accuracy for two-electron integrals were used in all DFT calculations.

$$I_6 = 100 \cdot \left\{1 - \frac{1}{V_{local}}\left[\frac{100}{\overline{N}}\sqrt{\sum_{i=1}^{6}\frac{(N_i - \overline{N})^2}{6}}\right]\right\}, \quad (1)$$

where N_i is i^{th} bond order, $\overline{N}$ is the mean order of endocyclic bond, V_{local} is the I_6 value for ideally bond localized structure with alternating bond orders equal to 1 and 2.

$$HOMA = 100 \cdot \left\{1 - \frac{\alpha}{n}\sum_{i=1}^{n}(R_{opt} - R_i)^2\right\}, \quad (2)$$

where R_i is i^{th} bond lengths, R_{opt} is optimal aromatic bond length and α is an scale pa-

Table 1. Values of selected bond lengths (Å) and amino group pyramidality ($\sum(NH_2)$, °) for isomeric nitroanilines in different basis sets within MP2 and M06-2X approaches

Isomer	Basis set	MP2			M06-2X		
		$C–NH_2$, Å	$C–NO_2$, Å	$\sum(NH_2)$, °	$C–NH_2$, Å	$C–NO_2$, Å	$\sum(NH_2)$, °
*o*NA	cc-pVDZ	1.387	1.473	341.3	1.353	1.457	360.0
	aug-cc-pVDZ	1.381	1.465	350.2	1.356	1.454	360.0
	cc-pVTZ	1.373	1.459	347.7	1.353	1.455	360.0
	aug-cc-pVTZ	1.370	1.456	351.5	1.352	1.453	360.0
	aug-cc-pCVTZ	1.369	1.455	351.4	1.352	1.453	359.1
	cc-pVQZ	1.367	1.455	350.7	1.351	1.453	360.0
	def2-TZVP	1.369	1.457	348.7	1.352	1.454	360.0
	def2-TZVPD	1.372	1.458	351.4	1.352	1.453	360.0
	def2-QZVP	1.367	1.454	351.6	1.352	1.453	360.0
*m*NA	cc-pVDZ	1.400	1.475	335.8	1.388	1.480	341.2
	aug-cc-pVDZ	1.401	1.477	341.1	1.390	1.479	344.5
	cc-pVTZ	1.390	1.469	340.5	1.386	1.479	345.3
	aug-cc-pVTZ	1.390	1.468	342.4	1.386	1.479	345.4
	aug-cc-pCVTZ	1.390	1.468	342.5	1.386	1.479	344.3
	cc-pVQZ	1.387	1.467	342.2	1.385	1.478	345.0
	def2-TZVP	1.389	1.470	342.2	1.385	1.479	345.7
	def2-TZVPD	1.388	1.470	343.4	1.385	1.479	345.5
	def2-QZVP	1.387	1.467	343.1	1.385	1.478	345.3
*p*NA	cc-pVDZ	1.400	1.481	336.2	1.379	1.464	345.4
	aug-cc-pVDZ	1.400	1.470	342.0	1.379	1.462	349.3
	cc-pVTZ	1.389	1.462	341.3	1.375	1.462	349.8
	aug-cc-pVTZ	1.389	1.460	343.4	1.375	1.461	349.9
	aug-cc-pCVTZ	1.388	1.460	343.4	1.375	1.461	348.6
	cc-pVQZ	1.386	1.459	343.2	1.375	1.461	349.3
	def2-TZVP	1.387	1.462	343.1	1.374	1.461	350.2
	def2-TZVPP	1.388	1.462	342.3	1.375	1.461	349.7
	def2-TZVPD	1.387	1.462	344.2	1.375	1.461	350.0
	def2-QZVP	1.385	1.459	344.0	1.374	1.461	349.8
	def2-QZVPP	1.388	1.462	342.3	1.374	1.461	349.8
	def2-QZVPD	1.385	1.459	344.4	1.374	1.461	350.0

rameter, α and R_{opt} are empirical parameters taken from fitting with experimental data [40].

3. Results and discussion

Geometrical parameters of substituents. The most significant individual geometrical parameters in ortho-(*o*NA), meta-(*m*NA) and para-(*p*NA) nitroanilines are the lengths of $C–NH_2$ and $C–NO_2$ bonds and the pyramidality of amino group (calculated as the sum of bond angles centered on the amino nitrogen, $\sum(NH_2)$). They reflect the degree of π-system polarization and conjugation between the π-systems of substituent with aromatic ring. The corresponding calculated values for different basis sets are given in Table 1 (MP2 and M06-2X methods).

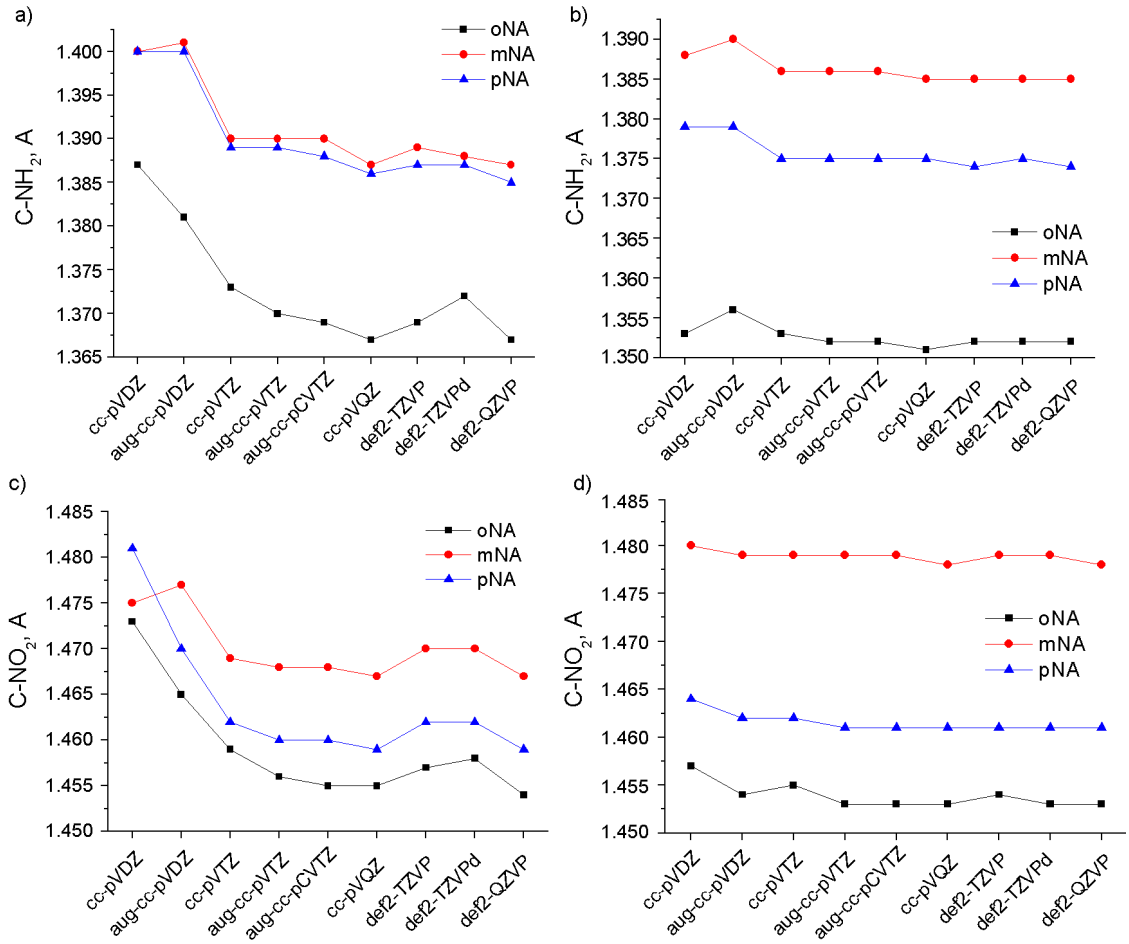

Fig. 1. Values of the C–NH_2 (a,b) and C–NO_2 (c,d) bond length depending of the basis set: MP2 (a,c) and M06-2X (b,d) data.

One can see that changes of the geometrical parameters upon the extension of the basis set are essential. The C–NH_2 bond range reaches 0.013–0.020 Å for different isomers in MP2 calculations but is much smaller in M06-2X (0.005 Å). The C–NO_2 bond is also sensitive to basis set effect (range of its variation is 0.010–0.022 in MP2 and 0.002–0.004 in M06-2X). Changes of pyramidality of the amino group is about 6–10° in MP2 and 0–4° in M06-2X. There is no significant difference between absolute values obtained in Dunning and Ahlrichs basis sets. The double-ζ basis sets are the source of the greatest differences in the bond lengths and pyramidalities in MP2 calculations: taking into account only triple-ζ and quadruple-ζ sets, one can note that the variation range is of the same magnitude as in the framework of the M06-2X methods (0.02–0.06 Å for bond lengths and 3° for pyramidality of the amino group).

Figures 1–3 present visualization of changes of listed geometrical parameters upon the extension of the basis set. There are some marked regularities in these changes:

(a) although absolute changes of values in M06-2X calculations are smaller, the double-ζ basis sets make an essential error as compare to higher level calculations with triple- and quadruple-ζ sets in both methods. Moreover, the nonlinearity of the changes can be noted: while in some cases (i.e. C–NH_2 bond lengths in *o*NA, MP2 data, see Fig. 1a) the value smoothly approaches to the extrapolation limit upon the addition of diffuse function to the cc-pVDZ basis set, in other cases (i.e. C–NH_2 bond lengths in *o*NA, M06-2X data, see Fig. 1b) it corresponds to extra peaks with high nonlinearity of changes;

(b) MP2 and DFT methods demonstrate different behavior upon the basis set expan-

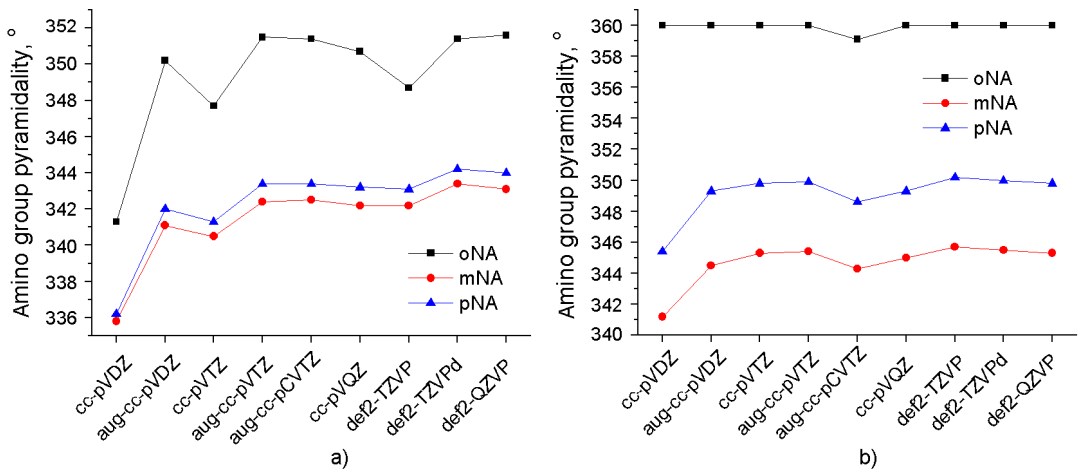

Fig. 2. Values of the amino group pyramidality depending of the basis set: MP2 (a) and M06-2X (b) data.

sion and adding a diffuse and polarization functions;

(c) Dunning/Huzinaga basis sets demonstrate good- and in most cases smooth - convergence to the extrapolation limit (complete basis set limit, CBS) in MP2 calculations in the following order: cc-pVDZ — aug-cc-pVDZ — cc-pVTZ — aug-cc-pVTZ — cc-pVQZ. In M06-2X method, aug-cc-pVDZ basis set should be excluded from this order for getting a smooth dependence. Convergence of the Ahlrichs type basis sets is bad in MP2 and satisfactory in M06-2X.

(d) Adding an extra core polarization to aug-cc-pVTZ set (aug-cc-pCVTZ) almost do not change the geometrical structure in comparison to the original basis, and in individual cases increases the error (i.e. amino group planarity changes in M06-2X calculations, see the negative peak on the Fig. 2b). Adding a diffuse function to cc-pV(N)Z basis always improve the results in MP2 calculation and in most cases improve it in M06-2X. At the time, adding a diffuse function to def2-(N)ZVP can make the accuracy worse in MP2 calculations (see Fig. 1a,c) and almost do not affect it in M06-2X approach (Fig. 1b,d and Fig. 2b,d);

On the example on *p*NA molecule, the role of polarization functions in Ahlrichs basis sets was investigated. Adding them to the def2-TZVP and def2-QZVP sets do not improve the results as compare to extrapolation limit but can increase the error in both DFT and MP2 approaches (see Table 1, Fig. 3). Presence of diffuse functions is crucial for the amino group geometry: it sharply increases group pyramidality with the change from cc-pVDZ to aug-cc-pVDZ basis, and the pyramidality in aug-cc-pVDZ/MP2 calculations is even higher than

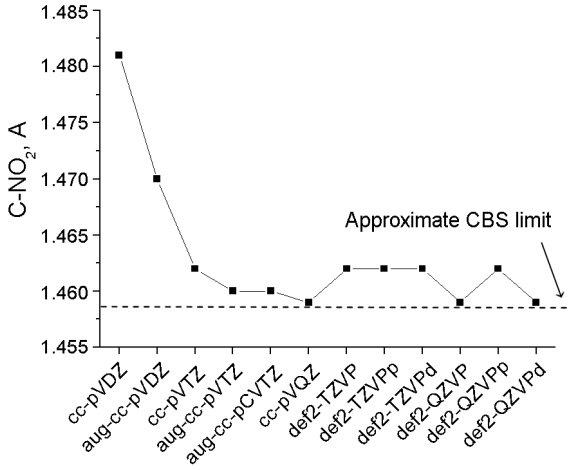

Fig. 3. Values of the C–NO_2 bond length in *p*NA depending of the basis set: MP2 data.

in cc-pVTZ/MP2. In the framework of M06-2X method, the role of diffuse function is not as decisive as the role of the basis set total size (see Fig. 2b).

Thus, cc-pV(N)Z family basis set can be extended either by augment of diffuse functions (i.e. moving from cc-pVTZ to aug-cc-pVTZ) or by increasing of the (N) number (from cc-pVDZ to cc-pVQZ) and both ways will reduce the absolute basis set error (excluding the case of aug-cc-pVDZ/DFT), while for the def2-(N)ZVP family, moving from (N) to (N+1) basis is the only way of its correct expansion.

Generally, difference between two types of basis sets decreases with the increasing of the set size: a quadruple-ζ quality sets cc-pVQZ and def2-QZVP show almost the same — and the smallest — absolute errors.

Aromaticity indices. Structural indices of aromaticity can be used as an integral indicator of the structural changes in the ben-

Table 2. Values of structural aromaticity indices I_6 and HOMA (%) for isomeric nitroanilines in different basis sets within MP2 and M06-2X approaches

Isomer	basis set	MP2		M06-2X	
		I_6, %	HOMA, %	I_6, %	HOMA, %
*o*NA	cc-pVDZ	90.59	87.83	84.41	89.81
	aug-cc-pVDZ	89.41	84.80	84.35	89.77
	cc-pVTZ	89.73	95.58	84.21	92.57
	aug-cc-pVTZ	89.05	94.87	84.04	92.41
	aug-cc-pCVTZ	89.09	95.12	84.05	92.40
	cc-pVQZ	89.05	95.82	84.19	92.65
	def2-TZVP	89.69	95.56	84.10	92.40
	def2-TZVPD	89.05	94.94	84.07	92.36
	def2-QZVP	89.05	95.81	84.07	92.53
*m*NA	cc-pVDZ	94.48	91.57	93.22	97.71
	aug-cc-pVDZ	95.15	90.10	93.91	97.95
	cc-pVTZ	94.73	98.60	93.50	98.82
	aug-cc-pVTZ	94.96	98.54	93.72	98.90
	aug-cc-pCVTZ	94.97	98.68	93.73	98.90
	cc-pVQZ	94.88	99.05	93.69	98.87
	def2-TZVP	94.81	98.61	93.54	98.84
	def2-TZVPD	94.94	98.56	93.65	98.88
	def2-QZVP	94.87	99.05	93.65	98.86
*p*NA	cc-pVDZ	93.88	92.22	90.66	96.35
	aug-cc-pVDZ	94.36	90.86	90.98	96.45
	cc-pVTZ	93.90	98.56	90.69	97.59
	aug-cc-pVTZ	94.08	98.51	90.84	97.67
	aug-cc-pCVTZ	94.09	98.62	90.86	97.68
	cc-pVQZ	94.03	98.87	90.73	97.61
	def2-TZVP	93.89	98.54	90.69	97.59
	def2-TZVPP	93.97	98.56	90.76	97.62
	def2-TZVPD	93.99	98.50	90.81	97.65
	def2-QZVP	93.95	98.88	90.83	97.67
	def2-QZVPP	93.95	98.88	90.83	97.67
	def2-QZVPD	93.95	98.87	90.82	97.66

zene ring. In the Table 2, I_6 and HOMA indices for isomeric nitroanilines in different basis sets are given (MP2 and M06-2X data). Visualization is given on the Fig. 4.

Aromaticity index HOMA show generally the same dependences as in the changes of geometrical parameters of substituents: it changes in the range up to 8 % in MP2 approach and up to 3 % in M06-2X. However, the I_6 index demonstrates surprising insensibility to the basis set quality in both methods (changes up to 1.5 %). Taking into account that I_6 index reflects degree of the bond lengths alternation, while HOMA index accounts also the symmetrical changes of the aromatic ring geometry [40], one can say that the alternation does not depend on the basis set, but the mean endocyclic bond length does.

Detailed analysis shows that adding a diffuse function to the cc-pVDZ basis set in MP2 calculation causes the opposite effects

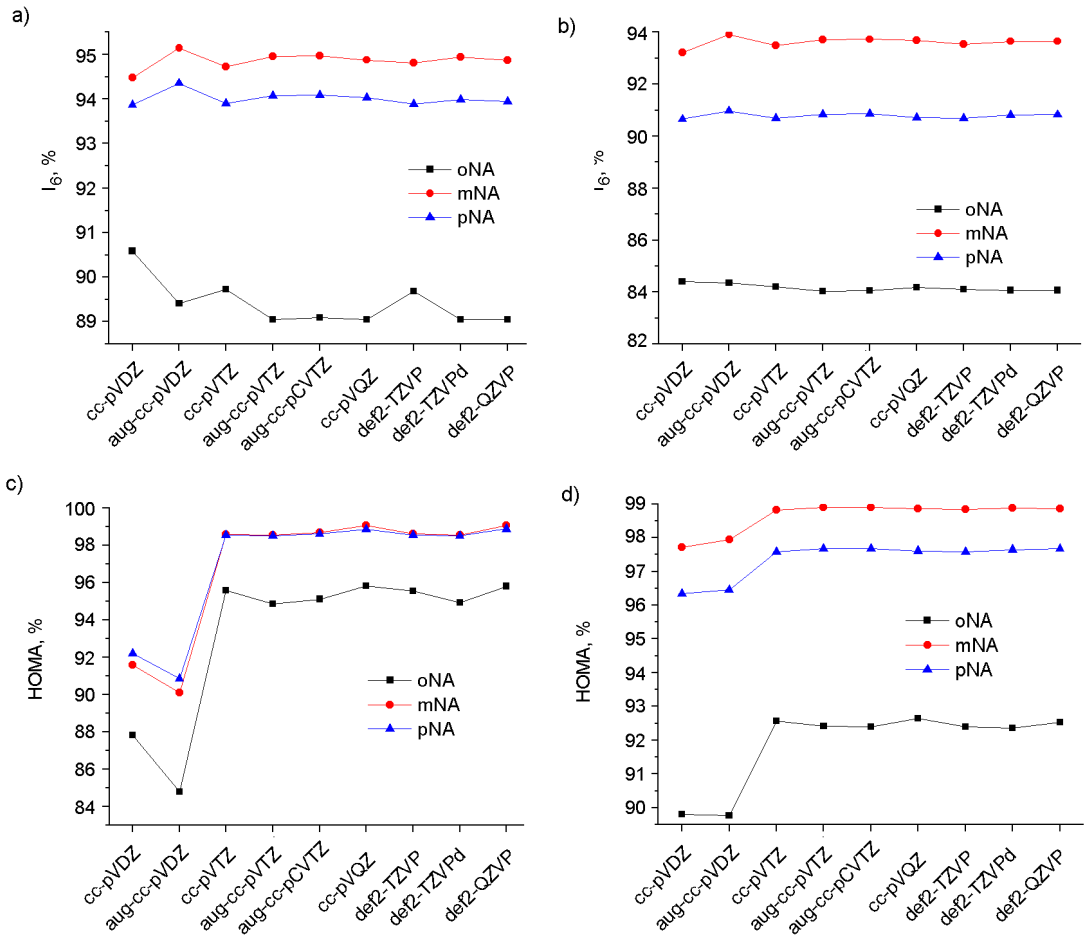

Fig. 4. I_6 (a,b) and HOMA (c,d) aromaticity indices change depending of the basis set: MP2 (a,c) and M06-2X (b,d) data.

in different isomers: in *o*NA, it leads to the increase of aromaticity, while in *p*NA and *m*NA, the aromaticity decreases (see Fig. 4a). In basis sets of higher quality, the effect do not observed. The HOMA index changes similar to the change of the planarity of amino group of the molecules: basis sets of double-ζ quality reveal a great absolute error in both MP2 and M06-2X methods, while all other sets give more or less the same results (excluding possibly the small negative def2-TZVPd peaks, see Fig. 4c).

4. Conclusions

The choice of the basis set is essential for correct modeling of the geometrical structure of nitroanilines with both MP2 and DFT quantum chemical methods. Generally, calculations using the MP2 method require bigger basis set: changes of geometrical parameters upon the basis set extension are much greater than in M06-2X method. At least triple-ζ quality basis should be used in the case. For M06-2X calculations, double-ζ basis give satisfactory results close to the higher quality sets. However, difference between Dunning cc-pVDZ and aug-cc-pVDZ is unpredictable in both methods: adding a diffuse function can either increase the error or decrease it. In all sets of triple-ζ and quadruple-ζ quality, adding the diffuse functions to Dunning sets decrease the error, but can increase it for Ahlrichs sets: it is the most essential when calculating accurate amino group pyramidality. Using an additional polarization function is not recommended: it does not improve the results in all cases. Difference between Dunning and Ahlrichs basis sets of approaches to zero when using the triple-ζ sets in DFT calculations and quadruple-ζ in MP2.

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