

Wawrzyniec Niewodniczański · Wojciech Bartkowiak
Jerzy Leszczynski

Reinvestigation of molecular structure and barrier to internal rotation of pyridinium *N*-phenolate betaine dye

Received: 5 November 2004 / Accepted: 13 April 2005 / Published online: 9 July 2005
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Abstract In the present paper, the results of a systematic theoretical study of the molecular structure of 4-(1-pyridinium-1-yl)phenolate betaine are reported. The ground-state molecular structure and the barrier to internal rotation of the betaine dye molecule were calculated ab initio (with Hartree–Fock theory and the second-order of Möller–Plesset method) and with density functional theory (DFT). In order to estimate the complete basis set limit, the calculations of barriers to internal rotations were performed using correlation-consistent basis sets with a maximal cardinal number of four. It was determined that electron correlation is crucial in order to obtain reliable geometries and rotational barriers of the molecule investigated. For the sake of comparison, the results of calculations using the AM1 Hamiltonian are also presented.

Keywords Betaine dye · Correlation energy · Torsional barrier · Geometrical parameters

Introduction

Betaine dyes are known to be strongly solvatochromic compounds [1, 2]. For example, 2,6-diphenyl-(2,4,6-triphenyl-1-pyridinium)-*N*-phenoxide betaine (Reichardt betaine), exhibits the largest measured shift of the S_0 – S_1 absorption band maximum, of ($-9,730\text{ cm}^{-1}$) on going from diphenyl ether to water [1]. It is well established

that the electronic structure of betaine dyes depends strongly on conformational parameters. In particular, numerous theoretical papers reported the strong dependence of electronic spectra and nonlinear optical properties on the central interplanar angle (ϕ) between aromatic rings (Fig. 1) [3–10]. For example, it has been shown that in the gas phase the two-photon absorption cross section of 4-(1-pyridinium-1-yl)phenolate (pyridinium *N*-phenolate, Fig. 1) is enhanced several times near $\phi = 80^\circ$ in comparison to the planar structure [6]. The molecular structure of the betaine investigated estimated using the semiempirical AM1 Hamiltonian [3, 11] and the HF method [5, 12, 13] has been reported in several papers [3, 5, 11–14]. Moreover, the structures calculated using methods including nondynamic (CASSCF [5]) and dynamic (B3LYP [14]) electron correlation have also been reported. Values of the selected structural parameters reported in the literature are given in Table 1. There are discrepancies between the HF and B3LYP data. The CASSCF results agree well with the results of HF calculations, so Ishida and Rossky suggested that the HF structure is more accurate than the one obtained with B3LYP [5]. On the other hand, in the same article, the authors showed that the minimum of the potential energy surface with respect to the torsional angle ϕ , estimated with and without dynamic electron correlation, varies by about 10° , close to the difference between the HF and B3LYP estimates. Yet another interesting observation was that the size of the basis set has little influence on the molecular geometry [12, 13].

Head-Gordon and Pople in their important paper on internal rotation in conjugated molecules [15] established that the MP2 approach constitutes the simplest method suitable for the inclusion of electron correlation effects. Moreover, Tsuzuki et al. showed that very large basis sets should be used at the MP2 level in order to obtain satisfactory torsional barriers for biphenyl [16]. On the other hand, Fujii and Arulmozhiraja demonstrated that the torsional barrier of biphenyl obtained using density functional theory (DFT) (B3LYP/6-311 + G(2d,2p)) is in good agreement with the experimental values [17].

W. Niewodniczański · W. Bartkowiak
Institute of Physical and Theoretical Chemistry,
Wrocław University of Technology,
Wybrzeże Wyspińskiego 27,
Wrocław, Poland

W. Niewodniczański · W. Bartkowiak (✉) · J. Leszczynski
Computational Center for Molecular Structure and Interactions,
Department of Chemistry,
Jackson State University,
Jackson, MS 39217, USA
E-mail: bartkowiak@kch.kh.pwr.wroc.pl

Finally, in two recent papers, Grein demonstrated that the MP2 method is very sensitive to the basis set selection, much more so than HF and DFT [18, 19].

The aim of the present study is to investigate the influence of the electron correlation contribution and basis set extension on the geometrical parameters of 4-(1-pyridinium-1-yl)phenolate (Fig. 1). We would like to determine the minimal level of theory required for a semi-quantitatively correct estimation of the molecular structure of the molecule investigated. Initially, our choice of computational approaches was based on the existing results of previous theoretical studies of molecular structures, potential energy surfaces, and torsional barrier heights for the biphenyl molecule [16–20]. We believe that the present paper could guide further investigations of larger betaine dye molecules.

Computational details

In order to investigate the ground electronic state geometrical parameters of the molecule studied, ab initio HF and MP2 as well as the semiempirical AM1 method [21] were adopted. Moreover, the DFT approach with the hybrid B3LYP functional [22, 23] was also used. The molecular geometries were fully optimized without symmetry constraints. The rotational barriers height with respect to the central C–N bond, were obtained in: 6-31G(d), 6-311 + G(2d,2p) and cc-PVQZ standard basis sets. Additionally, three of the correlation-consistent basis sets (cc-PV xZ ; $x = D, T, Q$) were used to estimate the complete basis set limit of energy (CBS) at the MP2 level of theory. It should be noted that all energy values were obtained at the 6-31G(d) reference geometry. On such prepared geometries (reoptimized with ϕ angle fixed on values ranging from 0 to 90°) the calculations of the energy barrier heights and the potential surface scan were performed. All ab initio calculations were performed using the GAUSSIAN 98 program package [24]. AM1 results were obtained using the MOPAC 5.0 program [21].

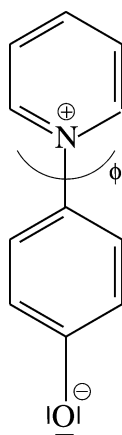


Fig. 1 4-(1-pyridinium-1-yl)phenolate betaine dye

Results and discussion

Geometry

As indicated in the “Introduction” section, the most important structural parameter of the geometry of betaine dyes is most likely the torsional angle ϕ between the central rings. Due to a strong steric repulsion between *ortho*-hydrogen atoms, the structure of this molecule is nonplanar, as reported previously. However, other structural parameters could also influence the properties of the molecules investigated. The calculated values of the most important structural parameters are shown in Table 2. Our results are in good agreement with other theoretical estimates (Table 1). Taking into account electron correlation at MP2 or B3LYP levels of theory leads to significant changes of the structural parameters compared to the HF results. It was found that HF significantly overestimates the values of ϕ . Another interesting observation is that the ϕ angle at the equilibrium geometry obtained at the AM1 level of theory ($\phi = 25.32^\circ$) is closer to the B3LYP and MP2 results than to the HF values. Electron correlation also influences the values of the bond distances, such that the central C–N bond is elongated and the C–O bond is shortened. The AM1 results (1.399 Å for C–N and 1.245 Å for C–O) are again closer to the MP2 and B3LYP results than to HF estimates.

In his papers Grein established that, in the case of the biphenyl molecule, the effect of the basis set extension is different for different methods [18, 19]. Moreover, he suggested that the reason for these discrepancies are diffuse and polarization functions. It is interesting to investigate such changes of the betaine geometry as a result of an increase of basis set size. MP2 and B3LYP calculations with a wide range of basis sets, 6-31G with different sets of polarization and diffuse functions as well as the 6-311 + G(2d,2p), 6-311 + + G(2d,2p) and aug-cc-PVDZ basis sets, were carried out (Table 2). The inclusion of both polarization and diffuse functions leads to an increased value of the torsional angle. However, the addition of polarization functions on the hydrogen atoms can reduce the value of ϕ . Six basis sets (6-31G, 6-31G(d), 6-31(d,p), 6-31G++ , 6-311 + G(2d,2p), 6-311 + + G(2d,2p)) used in Ref. [19] are also used in this study. Therefore, it is interesting to compare these results. In both cases, the MP2 method

Table 1 Chosen geometrical data of the investigated molecule reported in literature

	C–N	ϕ	C–O
AM1 [3, 11]		25	
RHF/3-21G [14]		38.4	
RHF/6-31G(d) [13]	1.424	42	1.219
RHF/DZP [5]	1.429	39.91	1.222
CASSCF [5]	1.424	40.72	1.230
B3LYP/6-31 + G(d,p) [12]	1.406	30.04	1.248

Table 2 Influence of basis set for the selected geometrical parameters of the investigated molecule

	B3LYP			MP2			HF		
	C–N	ϕ	C–O	C–N	ϕ	C–O	C–N	ϕ	C–O
6-31G	1.410	28.83	1.272	1.400	29.48	1.284	1.432	42.24	1.253
6-31G+	1.413	30.17	1.278	1.403	32.36	1.292	1.438	45.31	1.259
6-31G++	1.413	30.32	1.278	1.403	32.27	1.292	1.438	45.51	1.260
6-31G(d)	1.402	29.80	1.242	1.381	29.91	1.248	1.424	41.57	1.219
6-31G(d,p)	1.402	29.38	1.242	1.381	29.21	1.247	1.424	41.51	1.219
6-31+G(d)	1.406	30.76	1.248	1.386	31.46	1.256	1.430	44.30	1.224
6-31+G(d,p)	1.406	30.14	1.248	1.385	30.55	1.256	1.429	43.91	1.224
6-31++G(d,p)	1.406	30.13	1.248	1.385	30.57	1.256	1.430	44.00	1.224
6-311+G(2d,2p)	1.403	29.31	1.241	1.380	27.17	1.240	1.220	42.45	1.430
6-311++G(2d,2p)	1.403	29.20	1.241	1.379	27.03	1.245	1.427	42.55	1.218
aug-cc-PVDZ	1.405	28.72	1.246	1.388	27.74	1.254	1.429	42.32	1.224

reveals stronger basis set dependence than B3LYP, although the influence of the basis set is much smaller for the betaine. The biphenyl torsional angle varies by 5.99° for the MP2 and by 2.77° for the B3LYP calculations. In the case of the betaine, the central angle only varies by 2.77° and 0.71° , respectively. Extension of the basis set also has a small influence on the C–O and C–N bond lengths. Diffuse functions cause an increase of the bond distances, whereas polarization functions shorten them. However, inclusion of extra diffuse and polarization functions on the hydrogen atoms has no impact on the bond lengths. It is worth noting that the differences between the C–N bond length obtained in B3LYP calculations and with MP2 theory increased (from 0.010 to 0.024 Å for 6-31G and 6-311++(2d,2p), respectively) and for the C–O bond became smaller (from 0.012 Å for 6-31G to 0.003 Å for 6-311+(2d,2p) and 0.004 Å for 6-311++(2d,2p)), with increase of the basis set size. HF calculations with the same basis sets were also performed and are listed in Table 2. As mentioned in the “Introduction”, extension of the basis set has no significant impact on the quality of results. Also, addition of polarization and diffuse functions has a very similar influence as for the methods with electron correlation.

The molecular geometry obtained with the 6-31G(d) basis set is in good agreement with the data obtained with the largest basis sets used (6-311++G(2d,2p) and aug-cc-PVDZ) for all levels of theory. The small difference ($\sim 2^\circ$) in the angle ϕ obtained by the MP2 method indicates that the 6-31G(d) basis set is a reasonable compromise between the accuracy of calculations and their computational cost. However, it should be stressed that there are no experimental data with which to compare the quality of the results obtained.

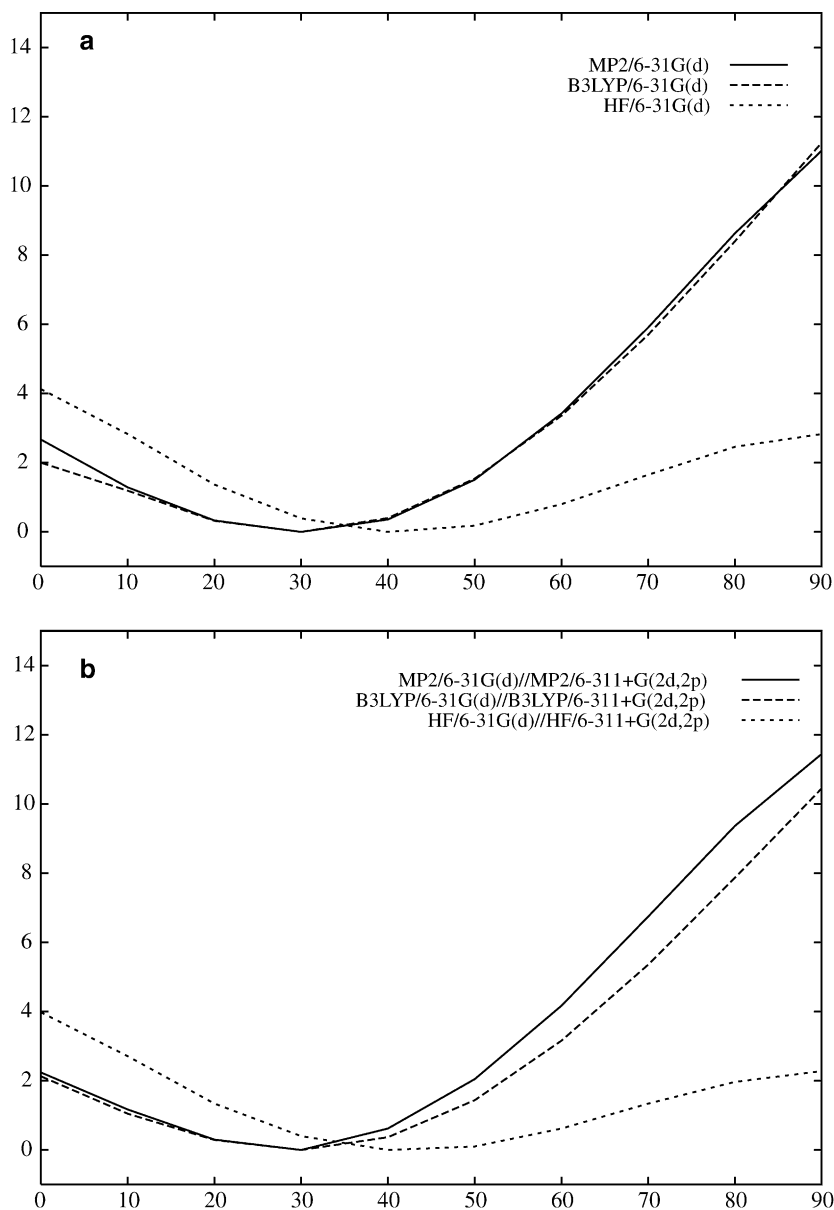
Torsional barriers

In order to determine the internal rotational barrier height, we have carried out a constrained potential energy surface scan for the betaine. In this scan, consecutive geometries were obtained by fixing the values

of the angle ϕ in the range from 0 to 90° while the remaining parameters were allowed to relax. The energy profiles for the central torsional angle (relative to the ϕ angle for the structure with the minimal energy) for an alternative method of the calculation are shown in Fig. 2. The shape of the potential energy curves is strongly sensitive to the level of theory. Especially, large differences in the values of barrier heights between the HF and methods including electron correlation are observed. Moreover, the results shown in Fig. 2 indicate that the potential energy surface is rather flat around the minimum. Therefore, the molecule has a certain degree of freedom of rotation around the C–N bond. Rings can rotate by nearly 20° for the structure obtained for all levels of theory. Our findings support the results of Ishida and Rossky [5] and Fabian et al. [14].

The calculated rotational barrier heights at 0° [$\Delta E_0 = E(\phi=0^\circ) - E(\text{equilibrium})$] and at 90° [$\Delta E_{90} = E(\phi=90^\circ) - E(\text{equilibrium})$] using various levels of theory with different basis sets are shown in Table 3. It is interesting to note that the MP2 and the B3LYP calculations reveal that the internal rotation-barrier height at 90° (ΔE_{90}) is substantially larger than at 0° (ΔE_0). The calculated ratio of the torsional barrier heights ($\Delta E_{90}/\Delta E_0$) obtained at the MP2/cc-PVQZ//6-31G(d) and B3LYP/cc-PVQZ//6-31G(d) levels of theory are equal to 5.46 and 7.12, respectively. This is a very important observation since, in the case of biphenyl, the calculated and experimental torsional barrier ratio $\Delta E_{90}/\Delta E_0$ is close to unity [16, 17]. However, this is not surprising since contrary to biphenyl, betaine dyes are characterized by strongly asymmetric structures [5]. In conclusion, there are large differences of barrier heights between the HF approach and the methods that include electron correlation. As shown in Fig. 3, the value of the angle χ varies by $\sim 15^\circ$ ranging from 166° at the B3LYP and 164° at the MP2 geometries to 180° in the case of the HF structure. Hence, one may conclude that the main reason for this behavior lies in a difference in the geometry. However, energy barriers previously obtained [5] with the MP2 method on the HF geometry are closer ($\Delta E_0 \sim 1.5 \text{ kcal mol}^{-1}$, $\Delta E_{90} \sim 9 \text{ kcal mol}^{-1}$) to the

Fig. 2 Energy profiles for central torsional angle (relative to $\phi(\min(E))$) calculated at the different levels of theory using (a) 6-31G(d) and (b) 6-311+G(2d,2p) basis sets



MP2 results than to the HF ones. Our findings suggest that further investigation of the potential energy surface of the molecules studies should be carried out at least at the B3LYP level of theory.

Since the exponents and contractions in Dunning's correlation-consistent basis sets, cc-PV xZ ($x = D, T,$

$Q, 5, 6$), change systematically to the CBS limit. This prompts an investigation of the systematic convergence of molecular properties to the CBS limit. Lee and Park [25] claimed that the best energy convergence for the MP2 level of theory is obtained from the following extrapolation formula:

Table 3 Calculated internal rotational barrier heights of investigated molecule. Values in kcal mol⁻¹

	6-31G(d)//6-31G(d)		6-311+G(2d,2p) //6-31G(d)		cc-PVQZ//6-31G(d)	
	ΔE_0	ΔE_{90}	ΔE_0	ΔE_{90}	ΔE_0	ΔE_{90}
HF	4.14	2.83	3.98	2.28	3.66	2.66
DFT	2.00	11.25	2.13	10.45	1.53	10.90
MP2	2.67	11.02	2.24	11.45	2.23	12.15

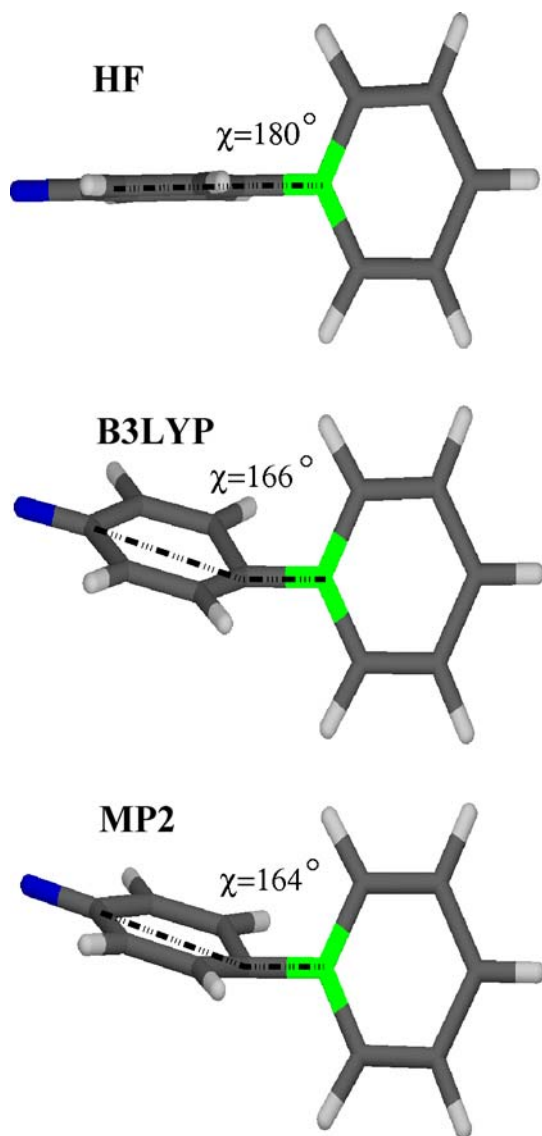


Fig. 3 HF, MP2 and B3LYP geometrical structures of the investigated dye at 90°

$$E(x) = E_{\infty} + \frac{A}{x^3} \quad (1)$$

where x is the cardinal number of the basis set i.e., $x = 2, 3, 4$ for D, T, Q, $E(x)$ is the energy in a given basis set and E is the energy in the CBS limit. In order to assess the quality of the energy barrier obtained, Eq. 1 was adopted with the sequence of three correlation-consistent basis sets (cc-PV xZ , $x = D, T, Q$) at the MP2 level of theory. The extrapolated magnitudes of the energy barriers amount 2.19 kcal mol⁻¹ for 0° and 12.33 kcal mol⁻¹ for 90°. It is interesting that the results obtained with the cc-PVTZ basis set were closest to the CBS limit since the differences are 0.05 and 0.09 kcal mol⁻¹ for ΔE_0 and ΔE_{90} , respectively. However, the results obtained with the cc-PVDZ and cc-PVQZ basis set are also in good agreement. The differences (in kcal mol⁻¹) for ΔE_0 are 0.01 and 0.04, and for ΔE_{90} 0.32 and 0.18 for

cc-PVDZ and PVQZ, respectively. Moreover, the results for barriers derived from the B3LYP calculations, and those resulting from MP2 computations with 6-31G(d) and 6-311 + G(2d,2p) basis sets differ by less than 2 kcal mol⁻¹ compared with the CBS values. In addition to the ab initio and DFT methods, the AM1 Hamiltonian was also used to predict torsional barriers. The values of the barriers (0.95 kcal mol⁻¹ for ΔE_0 and 8.50 kcal mol⁻¹ for ΔE_{90}) are lower from those obtained with the B3LYP and MP2 methods. However, the ratio of the values of barrier heights for the AM1 method (8.94) is much closer to our best estimates than one of for HF. Moreover, the shape of the energy profiles for the central torsional angle is also closer to the one obtained at the MP2 and the B3LYP levels of theory than to the HF curve. However, the value of the important geometrical parameter angle χ is equal to 180°, which is close to the HF estimate. Therefore, the AM1 Hamiltonian can be used in order to obtain a preliminary estimate of the torsional barrier heights.

Recently, Hernandez et al. investigated the influence of rotation on the spectroscopic properties of 2-(1-pyridinium-1-yl)phenolate (Fig. 4) [26]. They chose the MP2/6-31G level of theory in order to obtain internal rotation barriers and the potential energy profiles. This relatively small basis set is often selected in molecular design [27, chap. 2]. Therefore, it is quite interesting to compare the quality of the results obtained at this level of theory with the data reported above. The results of the calculation at the MP2/6-31G level of theory for the betaine investigated are in good agreement with the results obtained with larger basis sets: ΔE_0 equals to 2.17 kcal mol⁻¹ and ΔE_{90} of 10.78 kcal mol⁻¹.

Conclusion

The basis set has only a relatively small influence on the geometrical parameters at the HF level of theory, what is in agreement with previous studies. The same conclusion can be drawn for other often tested levels of theory (B3LYP, MP2). However, there are differences between molecular structures obtained with and without electron correlation. The central torsional angle is larger, the

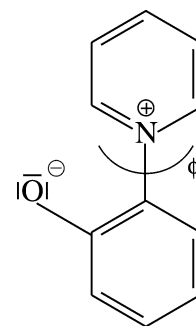


Fig. 4 2-(1-pyridinium-1-yl)phenolate betaine dye

C–N bond is longer and the C–O bond is shorter at the HF level of theory compared to methods that include electron correlation. The energy barrier height and the shape of the potential energy surface are very sensitive to the level of theory. The ratio of the torsional barriers ($\Delta E_{90}/\Delta E_0$) is below one in the case of HF calculations and larger than four at the MP2 and B3LYP levels of theory. The MP2 and B3LYP methods give similar profiles for the potential energy surface. Energy barrier heights obtained using the B3LYP functional and the MP2 method are close to those at the CBS limit. Therefore, the inclusion of dynamic electron correlation is necessary in order to obtain the correct geometry of the betaine investigated. The 6-31G(d) basis sets seems to be a good compromise between accuracy and computational cost. The AM1 Hamiltonian can be used as a first step in the design of new materials based on beta-ines.

Acknowledgments This work was sponsored by the Polish Committee for Science Research (grant no T09A 350297), NSF EP-SCOR grant no. 99-01-0072-08, CREST grant no. HRD-01-25484 and the AHPCRC under the agreement number DAAH04-95-2-00003, contract number DAAH04-95-C-0008, the contents of which do not necessarily reflect the position or policy of the government, and no official endorsement should be inferred. Calculations were carried out using resources at the Wrocław (WCSS) and Mississippi Center for Supercomputing Research (MCSR). The authors would like to thank the Wrocław University of Technology for support.

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